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Volume 56



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Advances in **QUANTUM CHEMISTRY**

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PREFACE

Advances in Quantum Chemistry publishes articles and invited reviews by leading international researchers in quantum chemistry and neighboring interdisciplinary fields. Quantum chemistry is a subject concerned with the quantum mechanical description and dynamics of atoms, molecules, and condensed matter, with important contributions to human activities like advanced computer and data communications, atmospheric science, not to mention recent developments in genomic information and diagnostics in medicine. Volume 56 invites our reader to six chapters of recent advances of quantum theoretical methods and applications. There are theoretical applications to photophysical and photochemical processes where the calculations indicate the importance of relativistic effects on the photodissociations of heavy atomic molecules (Liu-Fang). Another theoretically interesting report (Nooijen) discusses variations on the Hohenberg–Kohn construction of in principle exact density functionals and the foundations and physical implications of density functional theory. The chapter by Nalewajski discusses “Communication Theory of Chemical Bonds,” which concerns the use of information theoretic concepts to deal with several classical issues in electronic structure such as single versus multiple bonds, hybridization, and the like.

In a fundamental theoretical paper, Tapia discusses the contradiction between the standard Born–Oppenheimer approach and generalized diabatic models carrying the logics of the exact operator time evolution. In the end, we offer two chapters linked to important application to diagnostics in oncology and in medical developments related to hadron radiotherapy in medicine (Belkic). The Fast Padé Transform for Magnetic Resonance Spectroscopy is demonstrated, in the first review, to perform full validation of exact noise separation, which is of critical relevance in clinical oncology. The second contribution concerns the full treatment of inelastic collisions between bare nuclei and hydrogen-like atoms of fundamental importance to particle transport physics in general and heavy ions in medicine in particular. Finally, we want to thank all authors for their help and willingness to share their unique insights of quantum chemistry at the state-of-the-art.

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CHAPTER 1

Multireference and Spin–Orbit Calculations on Photodissociations of Hydrocarbon Halides

Ya-Jun Liu* and Wei-Hai Fang*

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1. INTRODUCTION

Mechanistic photodissociation of a polyatomic molecule has long been regarded as an intellectually challenging area of chemical physics [1]. It draws long-standing interest of both experimental and theoretical chemists mainly by three reasons. First, the practical importance for the environment and atmosphere [2–6] and biological systems [7]. Second, their functions in organic synthesis [8–11] and others [12,13]. Third, pure academic point of view for understanding the fundamental photochemical reaction mechanisms following laser excitation. A detailed understanding of the initial dynamics is a condition for the possibility of actively intervening with and ultimately controlling the outcome of a chemical reaction. Recent advances in femtosecond laser techniques make the deep and detailed understanding of photodissociation dynamics possible [14–16]. In concert with the experimental research, theoretical study on photochemistry also has made a great leap due to the development of computer and computational methodologies [17–22]. Photochemical and photophysical processes are complicated, besides radiation transition, excited-state vibrational relaxation (VR), internal conversion (IC), intersystem crossing (ISC), and direct reactions along excited- or ground-state pathways are generally included. Theoretically, the VR, IC, and ISC processes can be treated by quantum mechanics through solving Schrödinger equation for nuclear motion on the multiple potential energy surfaces (PESs). Actually, this is only available to very small molecules. High-quality calculated potential energy curves (PECs) can provide much useful information for a detailed understanding of the dissociation dynamics following excitation at a specific wavelength. However, accurate PESs are hard or even impossible to obtain from first principles for polyatomic molecules. Nowadays, state-of-the-art *ab initio* methods, complete active space self-consistent field (CASSCF), CASSCF with second-order perturbation (CASPT2), and multistate CASPT2 (MS-CASPT2), are powerful tools to build accurate PECs [23–25]. The accurate PECs are necessary for considering conical intersection, which plays an important role in nonadiabatic dynamics of photodissociation [26–32]. We have done a series of theoretical studies on photodissociations of hydrocarbon halides [33–41]. Below is a rough summary on their photodissociation mechanisms.

The photodissociation channels of aryl halides could be categorized into four types. (i) Direct dissociation along a repulsive PES when the photon creates a single quantum state in the upper electronic state; (ii) electronic predissociation (Herzberg type I predissociation): the molecule undergoes a radiationless transition from the binding to the repulsive state and subsequently decays; (iii) vibrational predissociation (Herzberg type II predissociation): the photon creates a quasi-bound state in the potential well which decays by tunneling or by internal energy redistribution; (iv) hot molecular decay: the photon creates a bound level in the upper electronic state which

subsequently decays as a result of radiationless transition to the ground state. Besides the practical importance in atmospheric chemistry and synthesis of many commercial carbohydrate halide derivatives [42–48], organohalide compounds especially halomethanes serve as examples for understanding different photodissociation mechanisms, since they are relatively small and easy to be considered by high-level calculations including spin–orbit and relativistic effects [38,40,41].

The theoretical study on the photodissociations of all kinds of hydrocarbon halides is quite a big topic. The photodissociations on aliphatic and aryl halides are representative and distinctive. This chapter will focus on mechanistic photodissociations of aliphatic and aryl halides by state-of-the-art ab initio calculations. The mainly targeted aryl halides are monohalobenzenes including chlorobenzene (ClBz), bromobenzene (BrBz), and iodobenzene (IBz); dibromobenzene including *o*-, *m*-, and *p*-dibromobenzene (*o*-, *m*-, and *p*-diBrBz); 1,3,5-tribromobenzene (1,3,5-triBrBz); and chlorotoluene including *o*-, *m*-, and *p*-chlorotoluene (*o*-, *m*-, and *p*-ClT). The mainly targeted aliphatic halides are bromiodomethane (CH₂BrI), dichloromethane (CH₂Cl₂), and diiodomethane (CH₂I₂). The below effects on the photodissociation channels and mechanisms of hydrocarbon halides will be discussed in detail. The heavy atomic effect, substituent effect, employed photon energy effect, methyl rotation effect, and relativistic effect.

2. COMPUTATIONAL METHODS

For the aryl halides (FBz, ClBz, BrBz, IBz, *o*-, *m*-, and *p*-diBrBz, 1,3,5-triBrBz, and *o*-, *m*-, and *p*-ClT), the geometries of the ground state, as well as some excited states, were optimized using the CASSCF method [49]. The MS-CASPT2 method [50,51] was used to calculate the vertical excitation energies (T_v) of the low-lying singlet and triplet states. Ground- and excited-state PECs along the halogen–carbon bond distances of the aryl halides were calculated using the MS-CASPT2 method. The phenyl geometries of the excited states were kept equal to the respective relaxed CASSCF optimized ground-state geometry. All these PECs were drawn adiabatically, and part of them was also drawn diabatically. The selection of active electrons and active orbitals is 12-in-10 for FBz, ClBz, BrBz, and IBz; 14-in-12 for *o*-, *m*-, and *p*-diBrBz; and 16-in-13 for 1,3,5-triBrBz. For all the monobromobenzenes, dibromobenzenes, and 1,3,5-tribromobenzene, the cc-pVDZ basis set [52] was used for C and H, and the relativistic ab initio model potential (AIMP) and effective core potential (ECP) of Barandiaran and Seijo [53] was used for I with 17 valence electrons and Br, Cl, and F with 7 valence electrons. For *o*-, *m*-, and *p*-ClT, the T_v and oscillator strengths (f) of the spin-coupled states were also evaluated by the MS-CASPT2 with spin–orbit interaction through complete active space state (MS-CASPT2/

CASSI-SO) approach [54] in conjunction with atomic mean-field integral (AMFI) approximation [55]. The selected active space comprises 12 electrons in 10 orbitals. The relativistic basis sets of the atomic natural orbital type, ANO-RCC [56], were used with a double zeta- type contraction (denoted as ANO-VDZP henceforth).

For halomethanes, CH_2BrI , CH_2Cl_2 , and CH_2I_2 , the geometries and harmonic vibrational frequencies of the ground states, transition states (TSs), and excited states were calculated using both the CASSCF and the CASPT2 [57,58] methods. The T_v and f values of the spin-free states were calculated using the MS-CASPT2 method. The spin-coupled states were computed by the MS-CASPT2/CASSISO approach in conjunction with the AMFI approximation. The scalar relativistic effect was considered by the so-called second-order Douglas-Kroll-Hess (DKH2) type of transformation [59,60]. The selection of active electrons and active orbitals for CH_2Cl_2 , CH_2I_2 , CH_2BrI , and related isomers are 12-in-10, 16-in-12, 16-in-12, and so on, respectively. For the optimizations, an ANO-VDZP basis set was used. Single-point energies were recalculated by MS-CASPT2 (for spin-free states) or MS-CASPT2//RASSI-SO (for spin-coupled states) methods with a triplet zeta-type contraction of ANO-RCC basis set (referred as ANO-VTZP henceforth).

All calculations of halomethanes and chlorotoluenes were performed using the MOLCAS 6.2 [61] quantum chemistry software. Others were performed using the MOLCAS 5.4 [62].

3. PHOTODISSOCIATION OF ARYL HALIDES

3.1. Monohalobenzenes and heavy atomic effect

There are rich experimental reports on the photodissociation of IBz [63–75], BrBz [75–78], and ClBz [64,75,76,79–81]. Density functional theory [82] and spin-orbit (SO)-MCQDPT [83–85] calculations have been used to study the photodissociations of IBz. Hartree-Fock [77] and CASSCF [78] calculations were performed for the photodissociation of BrBz. The studies revealed two reaction mechanisms of IBz: a direct dissociation caused by excitation to an antibonding (n,σ^*) state and an indirect dissociation caused by a transition to a (π,π^*) state of the phenyl ring that is predissociated by the (n,σ^*) state. However, there is only one photodissociation mechanism for BrBz and ClBz: an indirect dissociation via ISC between a (π,π^*) and a (n,σ^*) state. High-level calculation is still needed for clearly interpreting the fast photodissociation processes of IBz, BrBz, and ClBz observed by experiments and making reliable comparisons between the different molecules. For example, it may be possible to clarify to what extent observed differences in photodissociation rates are caused by subtle differences in the predissociation barriers of the excited states and how the heavy atomic effect affect the dissociation channels.

The PECs of the lowest singlet and triplet states of C_6H_5-X (X is Cl, Br, or I) were calculated by the MS-CASPT2//CASSCF method as described in Section 2. As far as possible, these curves are drawn diabatically so that they follow a particular electronic configuration through avoided crossings between two states of the same symmetry. Here we only focus on those possible states related to the experimentally observed photodissociation channels at 266 nm. Their PECs were included in one figure (Figure 1.1) for comparison. For details of the adiabatic and diabatic PECs, see Ref. [34].

All experimental investigations of the photodissociation of BrBz at 266 nm have indicated decay via a single fast photodissociation channel [75,77,78]. Kadi et al. [75] measured its time constant to be 28 ps. According to our calculations, the only singlet excited state that 266 nm could reach is the bound S_1-B_2 state, which is reached by a (π, π^*) transition. The S_1-B_2 state

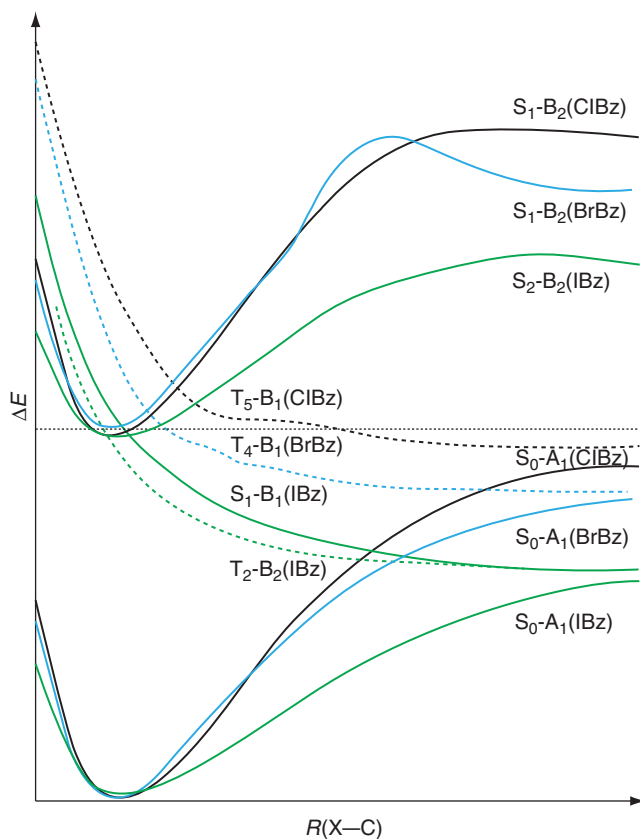


Figure 1.1 Schematic MS-CASPT2 diabatic PECs along the X—C bond distance of ClBz, BrBz, and IBz, illustrating their fast photodissociation channels at 266 nm.

crosses a repulsive triplet state T_4-B_1 , which is reached by a (n,σ^*) transition. The T_v value is about 4.91 eV at the crossing point, which is near the 266 nm (4.66 eV) used in the experiments [75,77,78]. As errors in CASPT2-computed excitation energies are typically less than 0.3 eV [86], we assign the dissociation with 28 ps lifetime to a Herzberg's type I predissociation, with strong coupling between the bound S_1-B_2 state and the repulsive T_4-B_1 state leading to dissociation, as shown in Figure 1.1.

According to Figure 1.1, the photodissociation situation of ClBz is similar to that of BrBz. The bound S_1-B_2 state, of (π,π^*) origin, crosses a repulsive T_5-B_1 state, of (n,σ^*) origin. But the T_v value at the crossing point is 0.49 eV higher than the 266 nm excitation energy used in the experiments [75,79]. This difference exceeds the anticipated CASPT2 calculation errors. In fact, the crossed molecular beam technique did not detect such a fast photodissociation at 266 nm. The photodissociation studies using femtosecond pump-probe spectroscopy upon excitation at 266 nm detected a slow dissociation for ClBz with 1 ns time constant [75]. This slow photodissociation is not caused by a Herzberg's type I predissociation, with coupling between the bound S_1-B_2 state and the repulsive T_5-B_1 state. The photodissociation mechanism of ClBz at different wavelength will be discussed in Section 3.3.

The photodissociation of IBz is different from that of BrBz and ClBz. The experimental investigations [65,68,75,82] at 266 nm detected two photodissociation channels for IBz. The femtosecond pump-probe spectroscopy gave the two time constants of 700 and 350 fs [75]. El-Sayed and coworkers [65,67,71] as well as Zewail and coworkers [87] proposed that the faster dissociation is due to a direct dissociation of the repulsive triplet (n,σ^*) state, and the slower dissociation is due to a spin-orbit-induced crossing from the triplet (π,π^*) state to the repulsive singlet (n,σ^*) state. Previous calculations using density functional theory (DFT) and (SO)-MCQDPT methods [82,84] supported this explanation. According to the present calculations, the first triplet excited state of IBz is not a repulsive state. However, the first singlet excited state, S_1-B_1 , is a repulsive (n,σ^*) state with 4.5 eV T_v , which is 0.16 eV lower than 266 nm. So, the fast dissociation, 350 fs, was assigned to a direct dissociation of S_1-B_1 . The first bound singlet excited state of IBz is a S_2-B_2 state with a T_v of 4.60 eV. From Figure 1.1, the lowest repulsive triplet excited state that the bound (π,π^*) S_2-B_2 state crosses is T_2-B_2 . The T_v value of the crossing point is 4.33 eV. This energy is lower than the 266 nm excitation used in the experiments. So, we assign the other fast photodissociation, 700 fs, to a Herzberg type I predissociation, with the strong couplings between the bound S_2-B_2 state and the repulsive T_2-B_2 state leading to dissociation. As shown in Figure 1.1, the crossing point between the S_2-B_2 and the T_2-B_2 states is very low in energy and close to the minimum of this S_2-B_2 state.

To conclude, ClBz, BrBz, and IBz all have Herzberg's type I predissociations with a (π,π^*) bound singlet state crossing a repulsive (n,σ^*) triplet state. For ClBz, the spin-orbit coupling occurs between the S_1-B_2 state and the

T_5 - B_1 state. For BrBz, it occurs between the S_1 - B_2 state and the T_4 - B_1 state. However, for IBz, the spin–orbit coupling instead takes place between the S_2 - B_2 state and the T_2 - B_2 state. The relative energies of the crossing points (connected to the predissociation barriers) to the experimentally employed 266 nm wave-length photon are 0.49 eV for ClBz, 0.25 eV for BrBz, and -0.33 eV for IBz. This clearly shows that the spin–orbit coupling is becoming stronger from ClBz to BrBz to IBz for heavy atomic effect. The presence of an atom of high atomic number enhances the rate of a spin-forbidden process, which results in a spin–orbit coupling enhancement. For IBz, it even opens another direct photodissociation channel via S_1 - B_1 state.

3.2. Bromobenzene, dibromobenzene, and 1,3,5-tribromobenzene and bromine substituent effect

The PECs of some lowest singlet and triplet states of BrBz; *o*-, *m*-, and *p*-diBrBz; and 1,3,5-triBrBz were calculated by the MS-CASPT2//CASSCF method. Please see Ref. [33] for detailed adiabatic and diabatic PECs. These four molecules have photodissociation mechanism in similarities and differences. In order to compare their photodissociation mechanism, a schematic figure of PECs, Figure 1.2, was employed. The experimentally [75,88] employed 266 nm

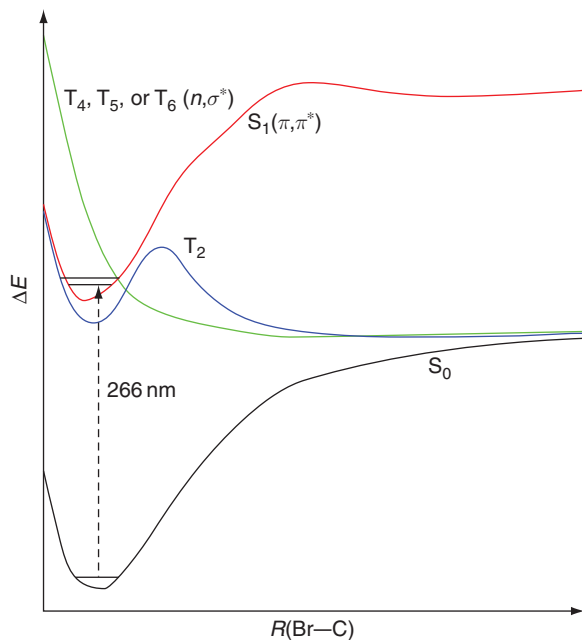


Figure 1.2 Schematic diabatic PECs along the Br–C bond distance of BrBz, *o*-, *m*-, and *p*-diBrBr, and 1,3,5-triBrBz, illustrating their photodissociation channels at 266 nm.

wave-length photon can reach the S_1 state of all the four molecules. All these S_1 states are (π, π^*) bound ones and cannot dissociate themselves. For each molecule, the (π, π^*) bound S_1 state crosses with the PEC of a repulsive (n, σ^*) triplet state and results in a Herzberg's type I predissociation, as shown in Figure 1.2. The repulsive (n, σ^*) triplet state is T_4-B_1 for BrBz, T_6-A'' for *o*-diBrBz, T_4-A' for *m*-diBrBz, T_5-B_1 for *p*-diBrBz, and T_5-B_1 for 1,3,5-triBrBz. The position of the crossing point is getting lower from BrBz to *p*-diBrBz to *m*-diBrBz to *o*-diBrBz and to 1,3,5-triBrBz (see Ref. [33] for details), which roughly reflect their dissociation rate, 36, 18.2, 13.3, 7.5, and 1 ps, respectively. The rate of this process increased with the number of bromine atoms on the ring and also with decreasing distance between the bromine atoms, as expected for a process mediated by spin-orbit interaction. Another important state is T_2 in Figure 1.2, which is a quasi-bound state for all the four molecules. The saddle point of the T_2 state is unreachable by 266 nm photon for BrBz, *p*-diBrBz, and 1,3,5-triBrBz. *o*- and *m*-diBrBz have lower barrier for the T_2 state, and their saddle points are lower than the corresponding crossing point of the above Herzberg's type I predissociation. So the experimentally employed 266 nm photon can easily reach the saddle point of the *o*- and *m*-diBrBz T_2 state. This results in the other faster dissociation channels for *o*- and *m*-diBrBz via Herzberg's type II predissociation. Moreover, as the potential barrier is lower in *o*-diBrBz than in *m*-diBrBz, this mechanism agrees with the observation that the second dissociation rate of *o*-diBrBz is smaller [88]. As discussed above, the additional bromine atoms increased the dissociation rates through the increasing spin-orbit interaction, and the different substituent position also caused the difference in the dissociation of dibromobenzenes.

3.3. Photon energy effect on the dissociation channels: chlorobenzene dissociation at 193, 248, and 266 nm

Experimentally, the photodissociation dynamics of ClBz has been studied at 266 [75,79], 248 [80], and 193 nm [64,80,89]. It was concluded that the photodissociation of the C—Cl bond in ClBz at 193 nm takes place through three different dissociation channels with probabilities of similar magnitudes. The first channel was assigned to a direct dissociation or very fast predissociation, the second channel is via vibrationally excited triplet levels, and the third dissociation channel is via highly excited vibrational levels of the ground electronic state (hot molecules). The photodissociation of ClBz at 248 nm was proposed to occur dominantly via the second and third of the above-mentioned channels. The photodissociation at 266 nm has been given alternative explanations. On the one hand, it was proposed to be due to a hot molecule mechanism by Wang et al. [79] On the other hand, Kadi et al. [75] assigned it to the decay of an initially excited (π, π^*) state to a repulsive triplet (n, σ^*) state due to spin-orbit coupling, and they observed its time constant to be 1 ns [75].

The MS-CASPT2 PECs of 12 singlet and 12 triplet states of ClBz was calculated. The shortest excitation wavelength employed in the experiments was 193 nm, and we therefore focus mainly on the excited singlet states with T_v under or near 193 nm and the repulsive triplet states that are likely to interact with these singlet states. These are the S_0-A_1 , S_1-B_2 , S_2-A_1 , S_3-B_2 , S_4-B_1 , and T_5-B_1 states (see Ref. [36] for details). There is one avoided crossing between S_1-B_2 and S_3-B_2 . We extracted the PECs of these states from the diabatic PECs of the 12 singlet and 12 triplet states and included them in Figure 1.3. From Figure 1.3 and the transition characteristics, S_1 , S_2 , and S_3

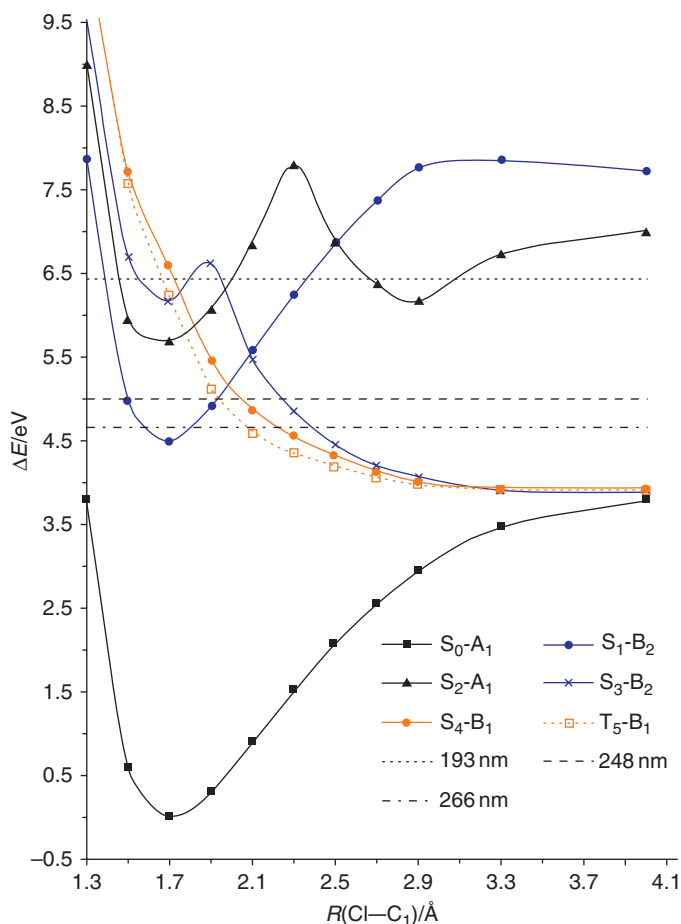


Figure 1.3 The MSCASPT2 diabatic potential energy curves along the Cl–C bond distance of one triplet and five singlet states of ClBz. The horizontal dashed lines indicate the 193-, 248-, and 266-nm excitation energy used in previous experiments.

are bound (π, π^*) states, whereas S_4 and T_5 are repulsive (n, σ^*) states. S_4 - B_1 , with 6.59 eV T_v , is the highest singlet excited state that the photon of 193-nm wavelength could reach. It is a repulsive state that will dissociate directly on a very short time scale. This direct dissociation should contribute to the fastest of the three channels observed in Ref. [80]. As shown in Figure 1.3, S_3 - B_2 is a quasi-bound state with a barrier that blocks immediate dissociation. The energy gap between its saddle point and the minimum of the ground state is about 6.6 eV. It is possible that molecules excited by 193 nm photons can overcome the predissociation barrier if the MS-CASPT2 error of 0.3 eV is taken into account. If so, its lifetime will depend on the tunneling rate. This process would proceed via Herzberg's type II predissociation. This fast predissociation could then also contribute to the fastest dissociation channel as proposed in Ref. [80]. From Figure 1.3, the PEC of S_3 - B_2 crosses the repulsive (n, σ^*) T_5 - B_1 state. The Cl—Cl bond distance at the crossing point is about 1.82 Å. It is also about 0.2 eV lower than 193 nm. So, we assign the second experimentally observed channel as the ISC from the bound (π, π^*) S_3 - B_2 state to the repulsive (n, σ^*) T_5 - B_1 state. The complex will ultimately decay with a rate that depends on the coupling between the two electronic states. This is a Herzberg's type I predissociation. The third photodissociation channel is slower than the first two channels and was suggested to take place via IC to highly excited vibrational levels of the ground state [80]. From Figure 1.3, it appears likely that the S_3 - B_2 state first undergoes IC to the S_1 - B_2 state. The lowest vibrational state of S_1 is much closer in energy to the dissociation limit of S_0 , and thereby makes IC from S_1 to S_0^* more likely. This mechanism is compatible with the third observed photodissociation channel with lower rate.

The highest singlet excited state the photon with 248-nm [80] wavelength can reach is S_1 - B_2 , whose T_v is 4.50 eV. S_1 is a bound (π, π^*) state, which cannot dissociate by itself. However, the S_1 - B_2 state can undergo an ISC to the repulsive (n, σ^*) T_5 - B_1 state. The Cl—C calculated bond distance at the crossing point is about 2.02 Å. The energy gap between this point and the minimum of the ground state is about 5.0 eV. The complex will ultimately decay due to spin-orbit coupling between the two electronic states. So, the first channel of photodissociation of ClBz at 248 nm is the ISC from S_1 - B_2 to T_5 - B_1 , and it is a Herzberg's type I predissociation. From Figure 1.3, the PEC of S_1 - B_2 also undergoes an IC with the repulsive (n, σ^*) S_4 - B_1 state. The Cl—C bond distance at the crossing point is about 2.06 Å. The energy gap between this point and the minimum of the ground state is about 5.15 eV. If the 248-nm wavelength photon used in the experiment overcomes this energy barrier, then the complex will ultimately decay by IC. So, the first channel of photodissociation of ClBz at 248 nm is also possibly via the IC from S_1 - B_2 to S_4 - B_1 . The second slower photodissociation channel observed experimentally is again possibly dissociation via the highly vibrational levels of the ground state, S_0^* . As discussed above, S_0^* could be produced by IC from the S_1 state. The 266-nm wavelength photon can also reach the S_1 - B_2 state. As

with the 248-nm excitation, this state cannot dissociate by itself. The PEC of S_1 -B₂ crosses to the PECs of T₅-B₁ and S₄-B₁ states. The photoexcitation energies required to reach these two crossing points are about 5.0 and 5.25 eV, respectively. The 266-nm wavelength photon is unlikely to reach either of the two points, even considering an estimated error of 0.3 eV, just as we discussed in Section 3.1. If the predissociation channels are out of reach, the only remaining photodissociation channel at 266 nm is again via the highly vibrational levels of the ground state, S_0^* , produced by the IC from the S_1 state.

3.4. Chlorobenzene, chlorotoluene, and methyl substituent and rotation effects

Following the studies on the photodissociation of ClBz, a number of investigations [90–94] have been performed to the photodissociations of *o*-, *m*-, and *p*-ClT for exploring the methyl substituent effect. The direct effect of the methyl substituent is to decrease symmetry and increase degree of freedom. From the theoretical viewpoint, a decrease in symmetry conduces to a decrease in forbiddenness, and absorption is thus more intense in ClT than in ClBz. The fluorescence quantum yield of ClBz is very low [95], while the band origins of *o*-, *m*-, and *p*-ClT had been identified to be 36 863, 36 602, and 36 281 cm^{−1}, respectively [96]. Besides, Timbers et al. [97] suggested that the methyl rotor acts as an accelerating group for intramolecular vibrational energy redistribution (IVR). The introduction of the methyl group to ClBz may lead to a different photochemical dynamics. For instance, the lifetime of excited *p*-ClT upon excitation at 266 nm have been determined to be 150 ± 4 ps [98], which is shorter than that of ClBz (600 ps) [99]. Upon excitation at 193 nm, experimental results show that *p*-ClT has three dissociation channels [92] similar to those of ClBz as discussed in Section 3.3 but with different probabilities. As can be seen, the methyl substituent on ClBz remarkably induces dissociation through triplet states. Nascent Cl atoms from photolysis of *p*-ClT have been detected splitting into two spin-state species, Cl*(²P_{1/2}) and Cl(²P_{3/2}). The Cl*/Cl ratio at 212.6 nm photolysis was determined to be of the order of 0.1 by Satyapal et al. [93].

In order to deeply discuss the methyl rotation and substituent effects on the dissociation dynamics and interpret the experimentally observed spin-state products as well, the MS-CASPT2 and MS-CASPT2/CASSI-SO PECs were calculated as described in Section 2 on the *o*-, *m*-, and *p*-ClT. According to their MS-CASPT2 scanned PECs of *o*-, *m*-, and *p*-ClT along the C–Cl bond (see Ref. [35] for details), the five excited states of S_1 -A', S_3 -A'', T_1 -A', T_2 -A', and T_4 -A'' for *o*- and *m*-ClT, and S_1 -A', S_2 -A', T_1 -A', T_2 -A'', and T_3 -A' for *p*-ClT join asymptotically to the ground state at larger values of the C–Cl bond distances. To detect the energy splitting between the two J states of

$\text{Cl}^*(^2P_{1/2})$ and $\text{Cl}(^2P_{3/2})$, the PECs of the spin-coupled states were computed by the MS-CASPT2/CASSI-SO approach along the dissociation coordinates from 3.45 to 4.0 Å in steps of 0.2 Å. The PECs of the 12 spin-coupled states were obtained from the splitting of the six spin-free states joining to the ground state as mentioned above. The 12 spin-coupled states of all the CITs split into two groups. The group with lower energy is identified to be $\text{CH}_3\text{C}_6\text{H}_4\cdot + \text{Cl}(^2P_{3/2})$, and the upper group is assigned to $\text{CH}_3\text{C}_6\text{H}_4\cdot + \text{Cl}^*(^2P_{1/2})$. For convenient comparison, a schematic figure, Figure 1.4, was used here.

Upon photoexcitation at 193 nm (6.42 eV), *o*-CIT molecules will mainly populate in the second (π, π^*) state $S_2\text{-A}'$ ($T_v = 6.24$ eV). The $S_2\text{-A}'$ state is of the most intensive transition with f of $5.2\text{E-}02$. As shown in Figure 1.4, $S_2\text{-A}'$ is a bound state, but it crosses with $S_3\text{-A}''$, a repulsive (n, σ^*) state. The $S_2\text{-A}'/S_3\text{-A}''$ crossing point has been located near the FC region with Cl—C distance of 1.710 Å. The energy gap between this point and the minimum of the ground state is determined to be 6.24 eV by the CASPT2 calculation, which is lower than the 193-nm photon energy. This indicates that IC is easily to take place via the $S_2\text{-A}'/S_3\text{-A}''$ crossing point and subsequently leads to a fast dissociation. This Herzberg's type I predissociation should contribute to the fastest of the three experimentally observed channels

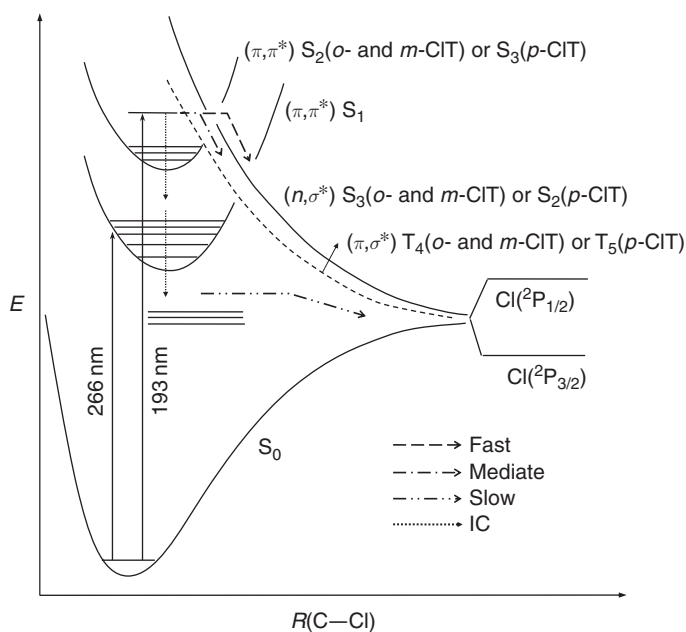


Figure 1.4 Schematic profile of the PESs for the CITs dissociate in 193, and 266 nm, illustrating the mechanisms of the fast, mediate, and slow fragmentation pathways.

[92,100]. The second (π, π^*) state $S_2\text{-A}'$ also crosses to the repulsive (π, σ^*) $T_4\text{-A}''$ state at nearly the same position of the $S_2\text{-A}'/S_3\text{-A}''$ crossing point, which was roughly described in Figure 1.4. The CASPT2 calculated energy gap between $S_2\text{-A}'/T_4\text{-A}''$ and the minimum of the ground state is about 6.19 eV. Under this condition, the ISC of $S_2\text{-A}'/T_4\text{-A}''$ is also accessible in energy at 193-nm photolysis. We assign the second experimentally observed channel [92,100] to the predissociation via the ISC from the bound (π, π^*) $S_2\text{-A}'$ state to the repulsive (π, σ^*) $T_4\text{-A}''$ state. The complex will ultimately decay with a rate that depends on the coupling between the two electronic states. The third photodissociation channel is slowest, which generally takes place via hot molecule mechanism. It has been found experimentally that the primarily excited S_2 state of benzene decays fast by IC to the S_1 and S_0 states [101]. Likewise, as shown in Figure 1.4, the initially excited *o*-CIT molecule in the $S_2\text{-A}'$ state can internally convert to the $S_1\text{-A}'$ state and subsequently to the $S_0^*\text{-A}'$ state. The dissociation energy of Cl–C bond is experimentally determined to be 4.2 eV [92], and the band origin of the first excited state of *o*-CIT is 4.57 eV [96]. Therefore, the S_0^* formed by IC from the upper (π, π^*) state possesses enough energy to overcome the dissociation energy limit.

Upon photoexcitation at 266 nm, *o*-CIT molecule possessing internal energy of 4.66 eV will mainly populate in the $S_1\text{-A}'$ state. The calculated f values suggest that the transition to $S_1\text{-A}'$ is not as intensive as to $S_2\text{-A}'$. $S_1\text{-A}'$ is a bound (π, π^*) state, and it cannot dissociate by itself. The PEC of $S_1\text{-A}'$ crosses the PECs of $S_3\text{-A}''$ and $T_4\text{-A}''$ repulsive states. The Cl–C distance is determined to be 2.099 and 2.046 Å at the $S_1\text{-A}'/S_3\text{-A}''$ and $S_1\text{-A}'/T_4\text{-A}''$ crossing points, respectively. The CASPT2 calculated energies of the crossing points $S_1\text{-A}'/S_3\text{-A}''$ and $S_1\text{-A}'/T_4\text{-A}''$ are 5.67 and 5.49 eV higher than the minimum of the ground state, respectively. This means that *o*-CIT molecule is not able to reach these crossing points at 266 nm. Therefore, the most possible mechanism at 266 nm is the *o*-CIT molecule dissociation via the hot molecule mechanism after IC from the origin $S_1\text{-A}'$ state, as shown in Figure 1.4. Experiments observed that the photodissociation following long-wavelength excitation is slow [94,98].

The diabatic PECs of *m*- and *p*-CIT are similar to those of *o*-CIT, and the assignments of the observed photodissociation channels are also similar. We summarized the photodissociation mechanism of *o*-, *m*-, and *p*-CIT in Figure 1.4. At 193 nm, the photon initially excites to the second (π, π^*) singlet state (S_2 for *o*- and *m*-CIT, and S_3 for *p*-CIT), and the experimentally observed fast, mediate, and slow channels were assigned to (i) the fast dissociation of a repulsive (n, σ^*) singlet state (S_3 for *o*- and *m*-CIT, and S_2 for *p*-CIT) after the IC from the photon initially excited state, (ii) dissociation of a repulsive (π, σ^*) triplet (T_4 for *o*- and *m*-CIT, and $T_5\text{-A}'$ for *p*-CIT) after the ISC from the photon initially excited state, and (iii) dissociation via vibrationally excited ground state S_0^* , respectively. In the case of the photolysis of

CITs at 266 nm, the above channel (iii) is the only accessible one. The *o*-, *m*-, and *p*-CIT molecules dissociate via hot molecule mechanism after the IC from the originally excited (π, π^*) bound S_1 state. The MS-CASPT2/CASSI-SO calculations clearly assigned the experimentally observed spin-coupled products $\text{Cl}^*(^2P_{1/2})$ and $\text{Cl}(^2P_{3/2})$ and roughly indicated that photolysis of CITs at 193 and 266 nm mainly generate $\text{Cl}(^2P_{3/2})$.

Upon excitation at 193 nm, experimental results by Ichimura et al. [92] and Lin et al. [100] show that the three channels have different dissociation probabilities for CITs and ClBz. Compared with ClBz, the quantum yield of the mediate channel is much increased while the slow one is decreased for CIT. This trend is more distinct for *p*-CIT. This indicates that the mediate channel is enhanced by the methyl group substituent. The methyl internal rotation in the S_1 states of fluoretoluene [97] and *o*-, *m*-, and *p*-methylanisole [102] has been experimentally investigated. The general conclusion is that methyl as a rotor can accelerate the IVR rate due to the large increased density of coupled states by introducing the internal rotation–vibration interaction. For our case, the methyl group enhances the ISC between the 193-nm photon initially populated bound single state (S_2 for *o*- and *m*-CIT, and S_3 for *p*-CIT) and the repulsive triplet state (T_4 for *o*- and *m*-CIT, and T_5 for *p*-CIT). The methyl of *p*-CIT is almost a free rotor by the present calculations and experiment [103]. So, the methyl rotation of *p*-CIT may provide higher level density of coupled states and increase the ISC rate. It may be the reason that the increasing quantum yield of the mediate channel is most distinct for *p*-CIT among the three CITs.

4. PHOTODISSOCIATION PROCESSES OF HALOMETHANE

Small polyhalomethanes are good examples for understanding the fundamental reaction mechanism of photochemistry upon laser excitation. High-level calculations can be used on them. We have calculated the properties of excited states, assigned the photodissociation channels, and scanned the isomerization process of CH_2Cl_2 [40], CH_2BrI [38], and CH_2I_2 [41] by CASSCF, CASPT2, and MS-CASPT2//CASSI-SO methods.

4.1. Bromiodomethane (CH_2BrI)

CH_2BrI with two different carbon–halogen bonds is an excellent model for investigating selective bond dissociations upon electronic excitation. Earlier molecular beam studies in the gas phase have shown that CH_2BrI exhibits two absorption bands, A and B, centered at 266 and 211 nm, respectively [104,105]. Man et al. subsequently measured some time-resolved resonance Raman spectra (TRRS) in the A- and B-band absorptions of CH_2BrI in cyclohexane solution [106]. Tarnovsky et al. studied the A-band

photodissociation in acetonitrile solution by femtosecond pump-probe spectroscopy [107]. All these experiments assigned the A band to a $n(\text{I}) \rightarrow \sigma^*(\text{C—I})$ transition and the B band to a $n(\text{Br}) \rightarrow \sigma^*(\text{C—Br})$ transition. The experimental assignments have been confirmed by theoretical investigations on the photoexcitation, isomerization reaction, and bond-selective photochemistry of CH_2BrI [108–110] by DFT B3LYP, CASSCF, and configuration interaction singles (CIS) methods. More advanced calculations, however, are needed for a quantitative explanation of the experimental observations. Scalar relativistic effects have to be included, which is a necessity for heavy atoms like Br and I, and spin–orbit coupling effects, previously not considered, have to be taken into account. This is crucial if experimentally observed spin-forbidden transitions are to be identified. The DFT approach is known to have problems with excited states of the charge-transfer and double-excitation types [111].

The PECs of 21 spin-coupled states were calculated by MS-CASPT2(/CASSI-SO)//CASSCF method for CH_2BrI with the C—I and C—Br bonds as the dissociation coordinates, respectively, as shown in Figure 1.5a and b. In Figure 1.5a, the lowest group of the photodissociation is identified as $\text{CH}_2\text{Br} + \text{I}^2\text{P}_{3/2}$. The second group is identified as $\text{CH}_2\text{Br} + \text{I}^2\text{P}_{1/2}$. When the Br—C bond is ruptured as shown in Figure 1.5b, the ground dissociation products are $\text{CH}_2\text{I} + \text{Br}^2\text{P}_{3/2}$, and the second group of dissociation products is identified as $\text{CH}_2\text{I} + \text{Br}^2\text{P}_{1/2}$. For detailed discussion see Ref. [38].

According to the present calculations, the $2^1\text{A}'$ and $1^1\text{A}''$ states are responsible for the A band at 266 nm. The dominant configuration of the $2^1\text{A}'$ state is a $n_o(\text{I}) \rightarrow \sigma^*_{\text{C—I}} + \sigma^*_{\text{C—Br}}$ excitation. The $1^1\text{A}''$ state has three dominant configurations: 40.1% $n_\pi(\text{I}) \rightarrow \sigma^*_{\text{C—I}} + \sigma^*_{\text{C—Br}}$, 21.9% $n_\pi(\text{Br}) \rightarrow \sigma^*_{\text{C—I}} + \sigma^*_{\text{C—Br}}$, and 14.5% $n_\pi(\text{I}) \rightarrow \sigma^*_{\text{C—H}}$ (symmetric). From the character of these states, it is mainly expected to lead to dissociation of the C—I bond. The PECs of the spin-coupled states in Figure 1.5a give a clearer explanation of the experimental observations [104,105]. States 8 and 9 are assigned to the A-band transitions. State 8 is composed of 65.1% of a $1^1\text{A}''$ state, 28.7% of a $2^3\text{A}'$ state, and 5.1% of a $1^3\text{A}'$ state. State 9 is composed of 57.3% of a $2^1\text{A}'$ state, 21.2% of a $2^3\text{A}'$ state, 15.5% of a $1^3\text{A}''$ state, and 3.6% of a $1^3\text{A}'$ state. As shown in Figure 1.5a, both states 8 and 9 are repulsive along the C—I bond coordinate and dissociate into the ground products. As shown in Figure 1.5b, state 8 is also a repulsive state along the C—Br bond coordinate, which dissociates to $\text{CH}_2\text{I} + \text{Br}^2\text{P}_{3/2}$. Since the PEC of state 8 is much steeper in the direction of C—I bond breakage as compared to C—Br bond breakage, C—I bond cleavage is favored. State 9, however, is a quasi-bound state with a shallow local minimum with respect to the C—Br bond coordinate. Hence, The spin-coupled states 8 and 9 are assigned to the observations in the A-band, with the main photodissociation products identified as $\text{CH}_2\text{Br} + \text{I}^2\text{P}_{3/2}$ and the recombination product as iso- CH_2BrI .

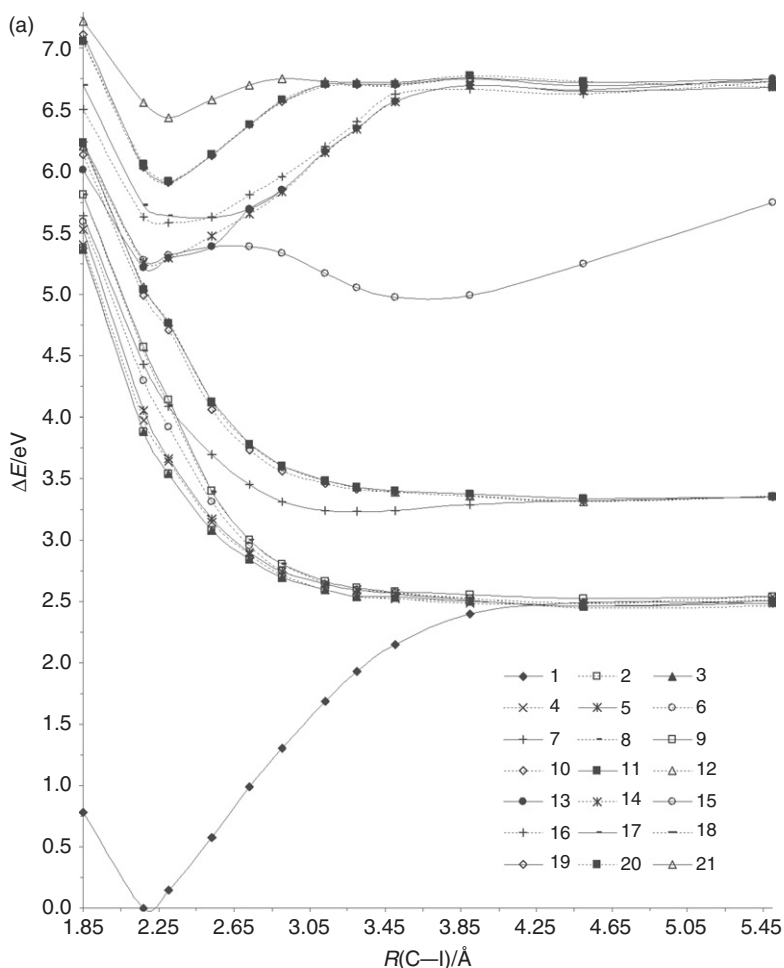


Figure 1.5 (a) The spin-orbit-coupled MS-CASPT2(/CASSI-SO)//CASSCF PECs with respect to the C—I bond coordinate of CH_2BrI . (b) The spin-orbit-coupled MS-CASPT2(/CASSI-SO)//CASSCF PECs with respect to the C—Br bond coordinate of CH_2BrI . (c) Schematic diagram depicting the reaction of iso- $\text{CH}_2\text{Br—I}$ to iso- $\text{CH}_2\text{I—Br}$.

The computed spin-free $2^1\text{A}''$ and $3^1\text{A}'$ state are assigned to the experimentally observed B band (211 nm) [104,105]. The $2^1\text{A}''$ state is 34.8% an excitation $n_\pi(\text{Br}) \rightarrow \sigma^*_{\text{C—I}} + \sigma^*_{\text{C—Br}}$, 17.3% $n_\pi(\text{Br}) \rightarrow \sigma^*_{\text{C—H}}$ (symmetric), and 18.6% $n_\pi(\text{I}) \rightarrow \sigma^*_{\text{C—I}} + \sigma^*_{\text{C—Br}}$. The characteristic of the $3^1\text{A}'$ state is 58.1% an excitation $n_\pi(\text{Br}) \rightarrow \sigma^*_{\text{C—I}} + \sigma^*_{\text{C—Br}}$ and 16.0% an excitation $n_\pi(\text{I}) \rightarrow \sigma^*_{\text{C—H}}$. Thus, the $2^1\text{A}''$ and $3^1\text{A}'$ states of CH_2BrI mainly lead to cleavage of the C—Br bond. However, some C—I cleavage is also expected. The spin-coupled

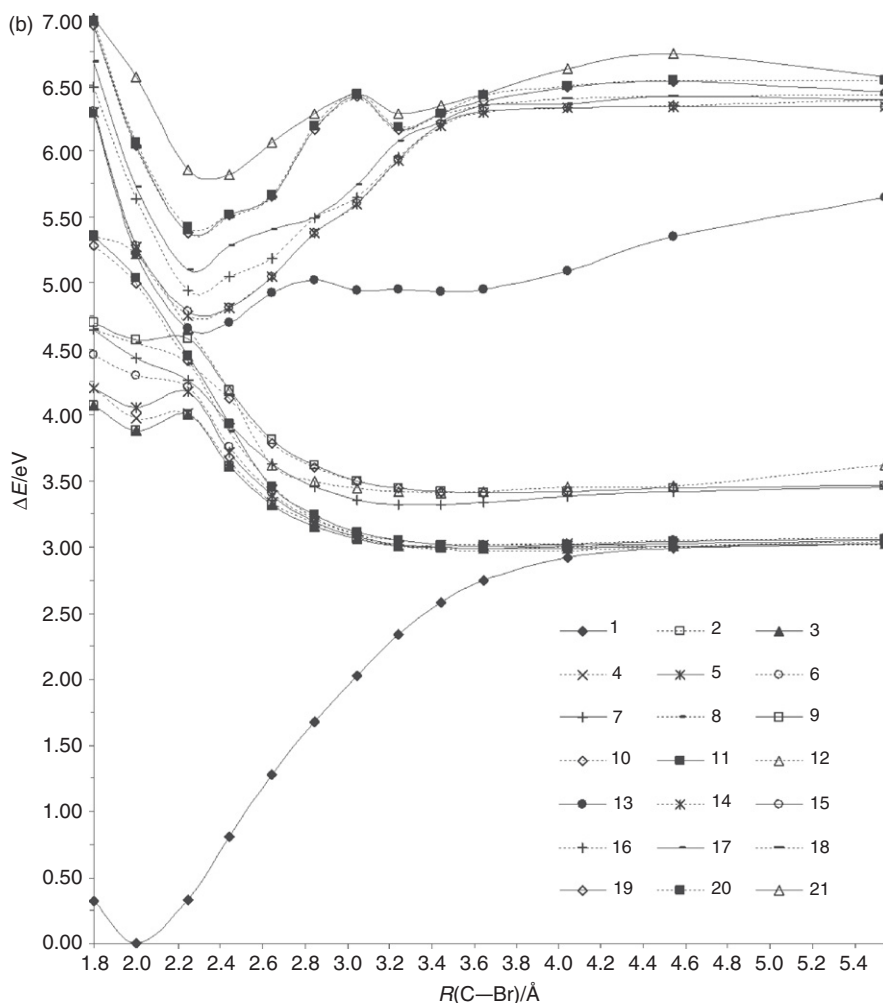


Figure 1.5 (Continued)

states 16 and 17 agree with the observed B band at 211 nm (5.88 eV). The PECs in Figure 1.5a and b indicate that these states are bound along the C—I and C—Br bond coordinates. However, by relaxation to nearby lower repulsive states through IC or ISC, a dissociation could be possible. In Figure 1.5a, it is found that populations in states 16 and 17 could be transferred to the repulsive states 9, 10, or 11 by crossing with the bound states 13 or 14. Then the repulsive states would dissociate to $\text{CH}_2\text{Br} + \text{I}(^2\text{P}_{1/2})$. In Figure 1.5b, it is

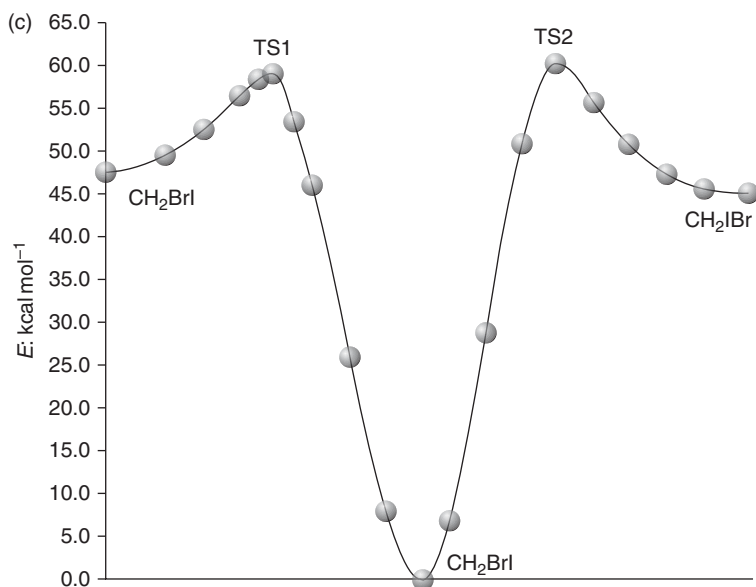


Figure 1.5 (Continued)

observed that populations in states 16 and 17 could relax to the repulsive states 12, 11, or 10 through crossing with states 15 or 14. These repulsive states dissociate to the ground $\text{CH}_2\text{I} + \text{Br}(^2\text{P}_{3/2})$ or $\text{CH}_2 + \text{Br}(^2\text{P}_{1/2})$. On comparing Figure 1.5a and b, it is noted that the PECs of states 16 and 17 with respect to the C—Br bond coordinate are easier to relax to the lower repulsive states as compared to the PECs along the C—I bond coordinate. Hence, the excitations in the B band will mainly break the C—Br bond.

The reaction between the two isomers was studied by the CASPT2 calculations. Figure 1.5c shows the PECs between the parent molecule and the two isomers. The frequencies of the two transition states, denoted as TS1 and TS2, compiled to $i266$ and $i248\text{ cm}^{-1}$, respectively. The spin-free CASPT2 relative energies are 59.2 and $60.0\text{ kcal mol}^{-1}$, respectively. Hence, in the gas phase, this energy profile would marginally favor iso- $\text{CH}_2\text{I}-\text{Br}$ in the isomerization process. However, in a solvent or a matrix, the process would be totally quenched by the loss of kinetic energy and yield only the parent species. The A- and B-band absorptions produce the two isomers in various ratios although one or the other of the isomers is strongly favored. However, the faster decay of iso- $\text{CH}_2\text{Br}-\text{I}$ as compared to iso- $\text{CH}_2\text{I}-\text{Br}$ would, on longer timescales, lead to only the latter species being observed.

To conclude, the spin-coupled states 8 and 9 are assigned to the observations in the A band, with the main photodissociation products identified as

$\text{CH}_2\text{Br} + \text{I}(^2\text{P}_{3/2})$ and the recombination product as iso- CH_2BrI . The spin–orbit-coupled states 16 and 17 are assigned to the observations in the B band. These states are, however, not repulsive but bound states along the coordinates of the C–I and C–Br bonds. Dissociation products $\text{CH}_2\text{I} + \text{Br}(^2\text{P}_{3/2})$ and $\text{CH}_2\text{I} + \text{Br}(^2\text{P}_{1/2})$ are predicted to dominate along with the recombination product of iso- CH_2IBr .

4.2. Dichloromethane (CH_2Cl_2)

Bar and coworkers [112,113] studied the photodissociation dynamics of pre-excited CH_2Cl_2 . The parent species were initially excited to the second, third, and fourth C–H stretch overtone regions and subsequently photodissociated by approximately 235 nm photons. The determined Cl^*/Cl branching ratios initiated from different overtone regions were found to be almost identical (about 0.5) in the products, which are higher than those obtained previously in 193 nm photodissociation of the vibrationless ground state [112,113]. Herein, we attempt to clearly interpret the experimentally observed photodissociation channels and discuss the reason that the vibrationally mediated photodissociation increases the branching ratio into Cl^* .

The PECs of the 12 spin-coupled states along C–Cl bond (which are composed of the first three singlet and first triplet spin-free states) were calculated by MS-CASPT2/CASSI-SO. As clearly shown in Figure 1.6, there are two groups of dissociation products as the C–Cl bond stretches to the dissociation limit. The energy difference between the two group products is 0.10 eV at $R(\text{C–Cl}) = 4.6 \text{ \AA}$. This value agrees with the present MS-CASPT2/CASSI-SO computed 0.13 eV energy difference between $\text{Cl}(^2\text{P}_{3/2})$ and $\text{Cl}^*(^2\text{P}_{1/2})$ and the experimental value 882 cm^{-1} (0.11 eV) [114]. So, we assigned the ground group products to $\text{CH}_2\text{Cl} + \text{Cl}(^2\text{P}_{3/2})$ and the upper group to $\text{CH}_2\text{Cl} + \text{Cl}^*(^2\text{P}_{1/2})$. The T_v values and characteristics of the 12 low-lying spin–orbital states of CH_2Cl_2 at the ground state minimum (where $R(\text{C–Cl}) = 1.794 \text{ \AA}$) and the point where $R(\text{C–Cl}) = 4.6 \text{ \AA}$ were compared. All states do not have strong spin–orbit coupling at the equilibrium structure. The spin-coupled state 11 is mainly composed of the first excited state 2^1A (92.9%), and the spin-coupled state 12 is mainly composed of the second excited state 3^1A (98.6%). However, along with the C–Cl bond stretching, the 2^1A and 3^1A states no longer only distribute in states 11 and 12, respectively. At the point where $R(\text{C–Cl}) = 4.6 \text{ \AA}$, the 2^1A state dispersed into spin-coupled state 12 with 35.3%, state 7 with 30.4%, state 8 with 25.3%, and state 11 with 6.8%. The 3^1A state dispersed into spin-coupled state 11 with 37.7%, state 8 with 30.0%, state 7 with 24.4%, and state 12 with 6.8%.

At the point where $R(\text{C–Cl}) = 4.6 \text{ \AA}$, states 7 and 8 are of the same T_v values of 3.33 eV, and states 11 and 12 are of the same T_v values of 3.23 eV. Based on the above analysis, the former two states will be responsible for the

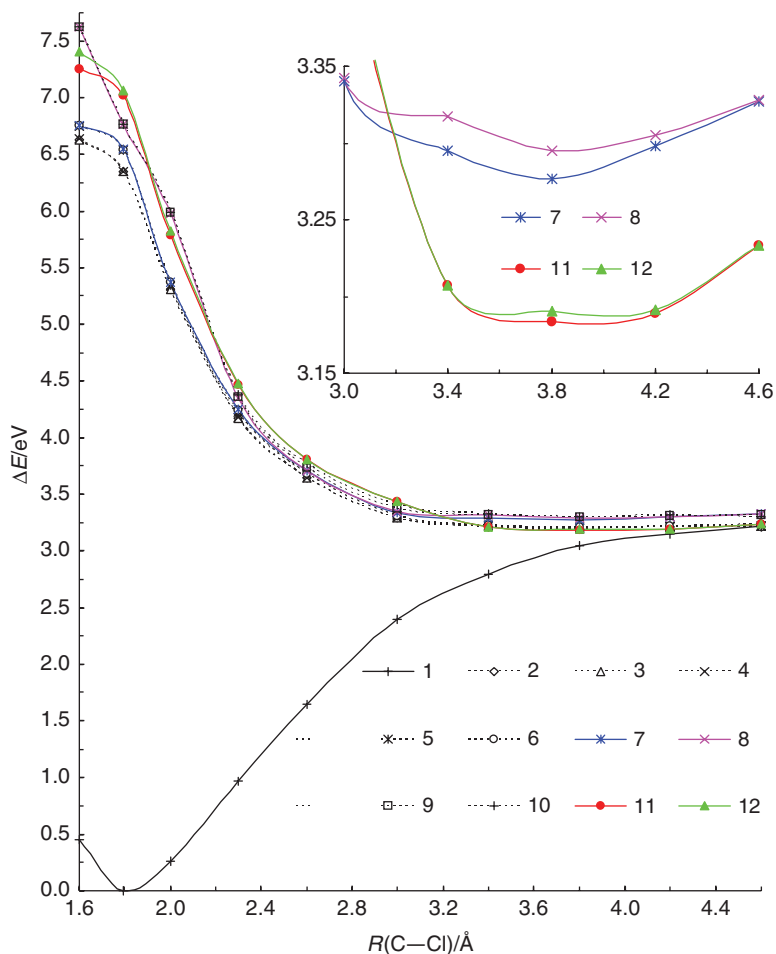


Figure 1.6 The spin-orbit-coupled MS-CASPT2(/CASSI-SO)//CASSCF PECs with respect to the C—Cl bond coordinate of CH_2Cl_2 .

products $\text{CH}_2\text{Cl} + \text{Cl}^*(^2\text{P}_{1/2})$ and the latter two states will be responsible for the products $\text{CH}_2\text{Cl} + \text{Cl}(^2\text{P}_{3/2})$. But which channel is more important? In other words, how to explain the Cl^*/Cl ratio difference of the vibrationless photodissociation and the vibrationally mediated ones? For the vibrationless photodissociation at 193 nm, Tiemann et al. [112] and Matsumi et al. [113,115] detected very similar Cl^*/Cl ratio as 0.33 ± 0.03 and 0.34 ± 0.07 , respectively. For the approximately 235-nm photodissociation on the initially prepared vibrationally excited states of the second, third, and fourth C—H overtone regions, the experiments [116] employed the combined energies are different as approximately 6.35, 6.68, and 6.99 eV, respectively.

Whereas, the corresponding Cl^*/Cl ratios are almost identical (0.55 ± 0.12 , 0.52 ± 0.11 , and 0.53 ± 0.12 , respectively) [116]. As presented in the inset of Figure 1.6, states 7 and 8 cross with states 11 and 12 around the point where $R(\text{C}–\text{Cl}) = 3.2 \text{ \AA}$. The channels leading to products $\text{CH}_2\text{Cl} + \text{Cl}(^2\text{P}_{3/2})$ via states 11 and 12 are more favorable since their PECs are steeper along the $\text{C}–\text{Cl}$ stretch than those of states 7 and 8. So, for vibrationless photodissociation, the product with Cl is dominant, whereas the product with Cl^* is minor, as the experiments [112,113] detected Cl^*/Cl ratio to be approximately 0.33. The vibrational excitation significantly enlarged the product Cl^*/Cl branching ratio to approximately 0.53. Firstly, we must rule out that the energy difference caused the Cl^*/Cl branching ratio alternation, since the combined energies (~ 6.35 , 6.68 and 6.99 eV , respectively) of the three vibrationally mediated photodissociation are above and below 193 nm (6.42 eV). The reasonable explanation is that the initial $\text{C}–\text{H}$ stretches reduce the symmetry of CH_2Cl_2 in Frank-Condon region, thus facilitating the transitions from S_1 to S_2 . Along with $\text{C}–\text{Cl}$ bond extending during the dissociation of CH_2Cl_2 , the spin-coupling effect of the first two singlet excited states and related triplet states is becoming stronger. According to above discussion, at the point where $R(\text{C}–\text{Cl}) = 4.6 \text{ \AA}$, the S_1 and S_2 states dispersed in four spin-coupled states 7, 8, 11, and 12. Around the region where $R(\text{C}–\text{Cl}) = 3.2 \text{ \AA}$, the Cl^* channels via states 7 and 8 cross the Cl channels via states 11 and 12. The strong spin-coupling effect could flip part of states 11 and 12 to states 7 and 8, subsequently increasing the Cl^*/Cl ratio.

4.3. Diiodomethane (CH_2I_2)

In gas phase, the first literature reference on the photodissociation of CH_2I_2 dates back to the molecular beam experiment at 300 nm by Kawasaki et al. in 1975 [117]. Following this article, photodissociation dynamics of CH_2I_2 excited at $365.5\text{--}247.5 \text{ nm}$ ultraviolet (UV) light have been investigated [118–122]. These studies came to the following conclusion: the dissociation takes place on a time scale shorter than the molecular rotation period [123], producing $\text{CH}_2\text{I} + \text{I}(^2\text{P}_{3/2})$ and $\text{CH}_2\text{I} + \text{I}^*(^2\text{P}_{1/2})$. The ratio of these products depends on the photolysis wavelength.

Compared with the experiments in the gas phase, the situation in condensed phase [124–139] is more complex and has controversial conclusions on the details of CH_2I_2 photodissociation dynamics [132,140]. Four possible photodissociation channels were proposed as shown in Figure 1.7a. Tarnovsky et al. [126–128] argued for the existence of a $\text{CH}_2\text{I}–\text{I}$ isomer formed by geminate recombination following dissociation of the initially excited CH_2I_2 (path D of Figure 1.7a). Transient resonance Raman spectroscopy [129–131], especially the very new experiment of time-resolved X-ray and electron diffraction [132], supported this interpretation. As Ref. [132] summarized, 38% of the photodissociated CH_2I_2 recombined to form

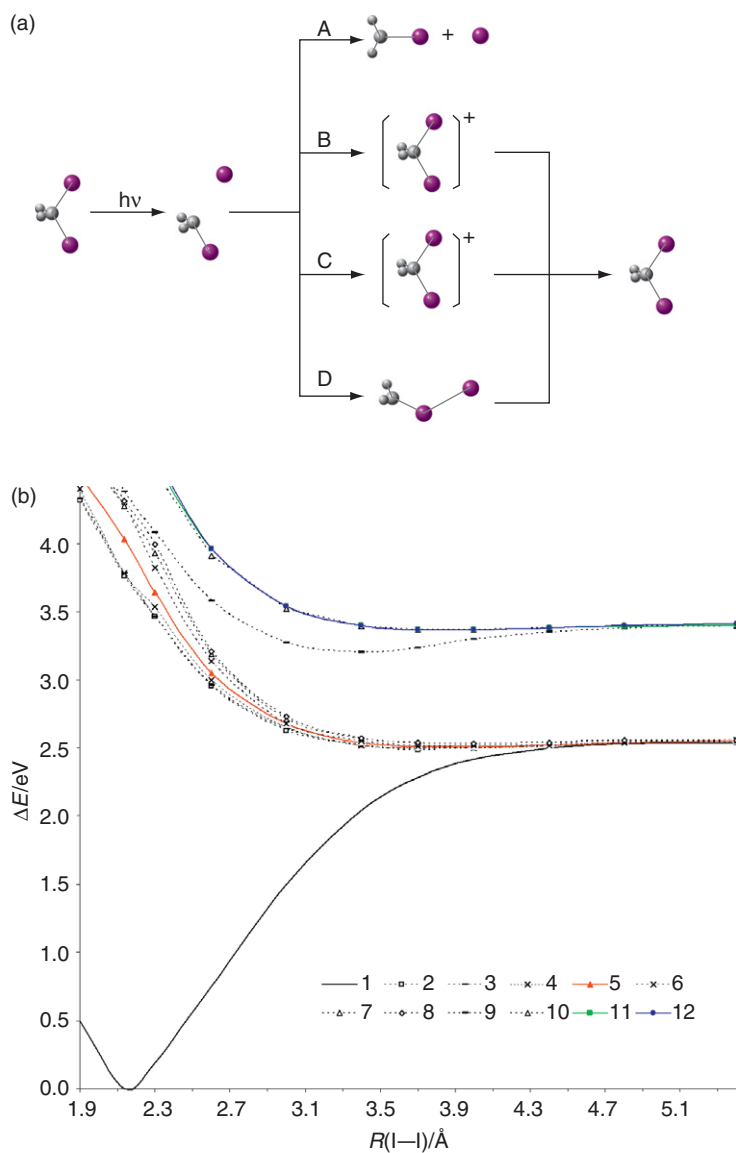


Figure 1.7 (a) The possible reaction pathways following the photodissociation of CH_2I_2 . (b) The spin-orbit-coupled MS-CASPT2(/CASSI-SO)//CASPT2 PECs with respect to the C—I bond coordinate of CH_2I_2 . (c) The spin-orbit-coupled MS-CASPT2(/CASSI-SO)//CASPT2 PECs with respect to the I—I bond coordinate of $\text{CH}_2\text{I—I}$.

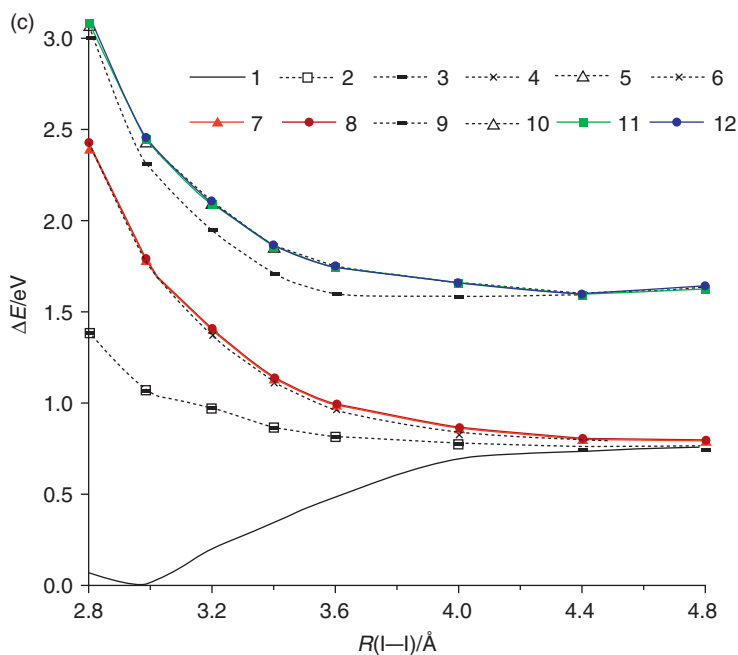


Figure 1.7 (Continued)

$\text{CH}_2\text{I–I}$ with a 4.2 ns half-life and a $3.02 \pm 0.02 \text{ \AA}$ I–I bond distance (path D), whereas the remaining 62% of photodissociated iodine radicals escaped the solvent cage (path A). Accordingly, the paths for the dissociated iodine radical rebounding back to CH_2I_2 via intermediates of a hot parent molecule CH_2I_2^* (path B) or CH_2I_2^+ (path C) are not favorable.

Despite the rich set of theoretical investigation [131,140–149], a clear reliable description of the photodissociation channels and conversion between CH_2I_2 and $\text{CH}_2\text{I–I}$ is missing. This can possibly be attributed to the fact that despite iodine being a heavy atom, all earlier computational studies excluded relativistic effects. The scalar relativistic terms calculated by Lazarou et al. [150] reached 6 kJ/mol/halogen atom. The energy difference between $\text{I}({}^2\text{P}_{3/2})$ and $\text{I}^*({}^2\text{P}_{1/2})$ due to spin–orbit interaction is about 1 eV, as discussed later. Such strong spin–orbit coupling effect is destined to affect the distribution of the photodissociation product fragments, since the obvious different translation energy of $\text{I}({}^2\text{P}_{3/2})$ and $\text{I}^*({}^2\text{P}_{1/2})$. This will subsequently affect the reaction of $\text{I}({}^2\text{P}_{3/2})$ and $\text{I}^*({}^2\text{P}_{1/2})$ with the solution. Without considering relativistic effect, one may ask whether the theoretical calculations on the reaction of I with the solution reflect the reality. In

addition, the PECs of spin–orbital coupling states leading to the products $I(^2P_{3/2})$ and $I^*(^2P_{1/2})$ are necessary to clearly describe the photodissociation channels. The current calculations on the photochemistry of CH_2I_2 included static and dynamic electron correlation, scalar relativistic effects, and spin–orbit interaction in conjunction with large all-electron relativistic basis sets.

We calculated the PECs of 12 spin-coupled states that are composed of the first three singlet states and first three triplet states at MS-CASPT2/CASSI-SO//CASPT2 calculation level. As presented in Figure 1.7b, there are two groups of dissociation products as the C–I bond is stretched. The ground group of the photodissociation is identified as $CH_2I + I(^2P_{3/2})$. The second group is identified as $CH_2I + I^*(^2P_{1/2})$. The computed energy difference between the two group products is 0.90 eV at $R_{C-I} = 5.4$ Å. This value agrees with the MS-CASPT2/CASSI-SO computed 0.87 eV energy difference between $I(^2P_{3/2})$ and $I^*(^2P_{1/2})$ [38]. The characteristics of the 12 low-lying spin–orbital states of CH_2I_2 show that most states have strong spin–orbit coupling. Similarly, the PECs of the corresponding 12 spin-coupled states of CH_2I-I are presented in Figure 1.7c. Here there are two groups of dissociation products as the C–I bond is stretched. The ground group of the photodissociation is identified as $CH_2I + I(^2P_{3/2})$, and the second group is identified as $CH_2I + I^*(^2P_{1/2})$, according to their energy difference (0.86 eV) at $R_{I-I} = 4.8$ Å and energy difference (0.87 eV) between $I^*(^2P_{1/2})$ and $I(^2P_{3/2})$ by the MS-CASPT2/L3/CASSI-SO calculations [38].

The UV photodissociation experiments [117–122] in gas phase drew unanimous conclusion: one C–I bond rupture to form $CH_2I + I(^2P_{3/2})$ or $CH_2I + I^*(^2P_{1/2})$. According to the characteristic of the spin-coupled states, the first spin-free excited state 2^1A (i.e., 1^1B_2) mainly disperses in the spin-coupled state 5 and the spin-coupled state 11. State 5 dissociates to the products $CH_2I + I(^2P_{3/2})$ and state 11 dissociates to $CH_2I + I^*(^2P_{1/2})$, as depicted in Figure 1.7b. State 12 is mainly composed by the 3^1A state (83.9%) and dissociates to $CH_2I + I^*(^2P_{1/2})$, as described in Figure 1.6b. That is to say, most of the second excited state 3^1A (i.e., 1^1B_1) dissociates to the products $CH_2I + I^*(^2P_{1/2})$. Figure 1.7b clearly assigns the fast dissociation channels observed by the experiments in gas phase [117–122]. The experiments also observed that the different ratio of $I^*(^2P_{1/2})$ and $I(^2P_{3/2})$ as dissociation channels depends on photolysis wavelength. The reason for this behavior can be given by the present calculation results. If the experimentally employed laser can reach both the 1^1B_2 and the 1^1B_1 states, three channels will open. State 5 dissociates to produce $I(^2P_{3/2})$ and states 11 and 12 dissociate to produce $I^*(^2P_{1/2})$. If the experimentally employed, laser can only reach 1^1B_2 , the third photodissociation channel from 3^1A leading to $I^*(^2P_{1/2})$ cannot occur. Hence, the ratio of I^*/I will be lower. For instance, the quantum yield for $I^*(^2P_{1/2})$ is 0.46 ± 0.04 at 248 nm, but 0.25 ± 0.02 at 308 nm [118]. The 248 nm (5.0 eV) wavelength photon can reach both the 1^1B_2 and the 1^1B_1 states, while at 308 nm (4.03 eV) only the

1^1B_2 state can be reached. The MS-CASPT2 (MS-CASPT2/CASSI-SO) excitation energies of the two states of interest were computed as 4.04 (4.03) and 4.37 (4.27) eV, respectively and experimentally observed values are 3.98 and 4.34 eV [117].

Davidsson et al. [132] summarized the photodissociation of CH_2I_2 in solution as paths A and D (see Figure 1.7a). With respect to the isomerization reaction, it is evident that the isomer CH_2I-I is responsible for the 570 nm (2.2 eV) transient absorption band observed after UV photolysis of CH_2I_2 [129], by the X-ray diffraction experiment [132] as clearly suggested by the MS-CASPT2 (MS-CASPT2/CASSI-SO) T_v value of 2.17 (2.36) eV of the $2^1A'$ state of CH_2I-I . The experiments [132,136,137] also observed that the further UV or visible excitation of the transient absorption bands leads to almost quantitative reformation of the parent CH_2I_2 molecule. There could be two pathways for CH_2I-I reforming to CH_2I_2 . The first pathway is via the isomerization. The isomerization reaction path from CH_2I-I to CH_2I_2 along the $I-I-C$ bond angle was calculated by the CASPT2 method. The calculated activation energy from CH_2I-I to CH_2I_2 is 14.9 kcal mol⁻¹ and 52.4 kcal mol⁻¹ for the inverse reaction. When the $C-I$ bond of CH_2I_2 stretched to $CH_2I + I$, the solvent induced the recombination of the $CH_2I\cdot$ and I fragments to CH_2I-I and CH_2I_2 . Considering that the dissociated fragments are vibrationally hot and that the energy barrier for the isomerization is small (14.9 kcal mol⁻¹), the recombination process will mostly produce CH_2I_2 , directly or via the isomerization. The second pathway is due to a secondary photodissociation of CH_2I-I to form $CH_2I + I$ and a subsequent recombination to CH_2I_2 . The $I-I$ bond of CH_2I-I is very weak: 2.985 Å bond distance as computed by the CASPT2 method, in agreement with an experimental value of 3.02 ± 0.02 Å [132]. Furthermore, the T_v values of CH_2I-I are much lower than the corresponding states of CH_2I_2 . The $I-I$ bond stretching of CH_2I-I leads to the direct photodissociation channels of the first and second singlet excited states, as presented in Figure 1.7c. According to the characteristic of the 12 spin-coupled states, the first spin-free excited state 2^1A ($1^1A''$) mainly disperses in the spin-coupled state 8 and spin-coupled state 11. The second spin-free excited state 3^1A ($2^1A'$) mainly disperses in the spin-coupled states 7 and 12. States 7 and 8 dissociate to the products $CH_2I + I(^2P_{3/2})$, and states 11 and 12 dissociates to $CH_2I + I^*(^2P_{1/2})$, as depicted in Figure 1.7c.

5. CONCLUSIONS

This chapter reviewed the mechanistic photodissociations of aryl halides (FBz, ClBz, BrBz, IBz, *o*-, *m*-, and *p*-diBrBz, 1,3,5-triBrBz, and *o*-, *m*-, and *p*-ClIT) by advanced ab initio calculations. The wavelength-dependent and geometrically memorized mechanisms for the photo-induced dissociations were elucidated through the computed PECs and the PESs crossing points. The heavy atomic

effect, substituent effect, employed photon energy effect, methyl rotation effect on the photodissociation channels and mechanisms were discussed. The photodissociation of CH_2BrI , CH_2Cl_2 , and CH_2I_2 have been investigated by spin-orbit *ab initio* calculations. The MS-CASPT2//CASSI-SO calculated PECs of the spin-coupled states clearly assigned the experimentally observed photodissociation channels and quantitatively described the photochemical and photophysical processes. The calculations indicated the importance of the relativistic effect on the photodissociations of heavy atomic molecules.

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CHAPTER 2

Quantum Linear Superposition Theory for Chemical Processes: A Generalized Electronic Diabatic Approach

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1. INTRODUCTION

Ever since the 1929 seminal paper by Dirac [1], the general quantum theory content has notoriously evolved in part due to developments in quantum field theory. The progress in technology allows for measurements of single system unheard to the pioneers jeopardizing aspects of the standard interpretation of QM itself. Reconciling principles of special relativity with QM has certainly produced a quantum field theory the way described by Weinberg by 1995 [2]. It has also made an impact on the way one can see QM itself in its nonrelativistic limit that is used to study chemical processes in a time-dependent regime. Here the focus is on basis states (BSs) search to describe quantum states of material systems and quantum states of particle systems, not the particles themselves.

Section 2 contains a description of chemical change in the framework of the linear superposition principle of abstract quantum physics where the axiom of wave function collapses and probability interpretation is replaced. Basic principles of QM are overviewed insofar as descriptions of chemical reactions are concerned.

In the nonrelativistic limit, the abstract formalism is summarized. Space–time projection in configuration space sharing origin with an inertial frame (I-frame) leads to wave functions over an abstract mathematical space, the dimension of which is determined by the number of degrees of freedom associated with the material system sustaining the quantum behavior. The coordinate set *does not* stand for position coordinates of electrons and nuclei; it points to an abstract (mathematical) fixed space. The Hilbert space associated with the system quantum states is constructed on special label wave functions; the elements of this set (eigenfunctions) have distinct symmetry properties. A quantum state being a linear superposition over a complete set of energy eigenfunctions does not necessarily have itself a symmetry label; thus time evolution of quantum states permits apparent changes of the amplitudes in the linear combination symmetry indexes if

appropriate interactions are allowed for. They open or close the material system's responses after external probes are directed to activate spectra rooted at a given BS; such interactions necessarily occur in laboratory (real) space demanding energy and momentum conservation laws. The square modulus directly yields a relative intensity to the response revealed by the measured spectrum. The probability interpretation while adequate for few specific situations cedes the place to the relative intensity response picture (cf. Appendix). These aspects are examined in Section 3 together with a first analysis of electronuclear wave functions; many states' reactivity models are examined in this general framework.

Computational quantum chemistry is deeply rooted in semiclassical models to QM based on the separation of electronic from nuclear degrees of freedom. In the Coulomb Hamiltonian, nuclei represented by discrete positive charge background (PCB) in real space are sources of potential for the electronic charges [3]. Classical and/or quantum mechanical aspects are associated with nuclear dynamics via an effective potential set up by the electronic quantum states; nuclear masses appear to fluctuate (vibrate) around equilibrium PCB configuration. The introduction of a second layer of classical representation is conveyed by the use of atomic basis sets located on top of PCB point sources in real space. Thus, while algorithms so derived have lost a clear connection to electronic Hilbert space characteristic of QM, they convey a definite chemical flavor originated in structural chemistry paradigms. Between these limit situations, a search for a quantum theory of chemical reactions is made by examining theory starting from abstract Hilbert space in terms of the linear superposition principle, then moving to projected formalism until getting at representations to semiclassical schemes that are able to maintain a version of the linear superposition principle while retaining aspects that are compatible to chemical paradigm.

2. BASIC QUANTUM MECHANICS AND CHEMICAL PROCESSES

In quantum mechanics (QM) [4], chemical processes can be expressed as change of quantum states sustained by given material systems, each one of them being defined by a fixed number of electrons and nuclei and referred to as a *1-system*. In terms of the linear superposition principle, an arbitrary quantum state $|\Psi\rangle$ is written with the help of (fixed) basis sets, $\{|n,n(m)\rangle\}$, where the quantum number n label the electronic spectrum and $n(m)$ a nuclear quantum number subsidiary to n to get

$$|\Psi, t\rangle = \sum_{n,n(m)} |n,n(m)\rangle \langle n,n(m)|\Psi, t\rangle = \sum_{n,n(m)} |n,n(m)\rangle C_{n,n(m)}(\Psi, t). \quad (1)$$

Time dependence enters in the set of amplitudes (complex numbers) $\{C_{n,n(m)}(\Psi,t)\}$ identifying the quantum state as a whole; moreover, the quantum state is normalized at all times: $\langle\Psi,t|\Psi,t\rangle = 1$. In this context, basis sets are fully independent from quantum states and time. The mapping relating Hilbert space to the set of complex numbers (amplitudes) requires the introduction of the dual conjugate space where the basis set are the bras $\{\langle n,n(m)|\}$ [4].

A generator of time displacement helps calculating amplitudes; this is the 1-system Hamiltonian operator, $\hat{H}$. It is self-adjoint with a complete set of energy eigenvalues, $\{E_{n,n(m)}\}$, and eigenvectors, $\{|n,n(m)\rangle\}$, related to the spectrum of the 1-system. The introduction of time, and later on a configuration space, requires an inertial frame (I-frame), the origin of which is located in laboratory space.

The spectrum provides a way to determine possible energy exchange mechanisms via the set of energy differences relating two base (eigen) states. Thus, even if the energy origin of the spectrum is arbitrary, measurable response quantities are not. Any energy level provides a root (state) wherefrom associated spectrum can be calculated and compared to experimental responses. Electromagnetic (EM) fields are implicitly taken to be sources/sinks of energy to fulfill energy conservation in the first place. The spectral response in intensity regime of a root state depends upon the square modulus of the amplitude, for example, $|C_{n,n(m)}(\Psi,t)|^2$, affecting it in a given quantum state or at a given time of its evolution; if the amplitude is zero, no physical response would be detected and if different from zero at a given time, the square modulus yields the relative intensity for the spectral response rooted there. Chemical spectroscopy is directly related to the elements defining the quantum state in the energy representation. This view of QM is taken from work published by Fiddler and the author [5].

For 1-systems, the standard probabilistic interpretation of QM is replaced by one based on linear response framework. Either a base state will serve as a root for a spectral family or not. In the former case, the amplitude must be different from zero, while in the latter the amplitude is zero. Because the quantum state is normalized, only relative intensities are sensed if a measurement in intensity is proposed [5].

For zero amplitude states (ZAS), the eigenstate offers “draining” amplitude possibilities for an energy probe (e.g., photon) that match the gap between the root (nonzero amplitude by definition) and the ZAS. These are real processes. A simple two-state time-dependent model illustrates amplitude evolution. If two energy levels showing the energy gap equal to a given photon frequency are both ZAS, no response could be detected, and no energy exchange between photon field and the 1-system would take place.

Sensing a chemical process would correspond to the emergence of amplitudes at those base states related to products that chemists might have prepared with zero value at the initial state, for example,

$$C(t_0) = [C_{0,0(0)}(t_0), C_{0,0(1)}(t_0), \dots, 0_{n,n(0)}(t_0), 0_{n,n(1)}(t_0), \dots, \\ 0_{k,k(0)}(t_0), 0_{k,k(1)}(t_0), \dots]. \quad (2)$$

A symbol such as $0_{k,k(1)}$ indicates zero amplitude at base state $|k,k(1)\rangle$, and of course, it would not explicitly appear in the linear superposition; the base state does not disappear however, so that to keep the ordering of energy labeling the column vector must explicitly have zero amplitudes when it cannot put up a response to external probes. The set $C_{0,0(0)}(t_0), C_{0,0(1)}(t_0)$ stands for reactant amplitudes with one vibration state that can set up a response to external probes. Excited states from the reactant system are compiled in set $0_{n,n(0)}(t_0), 0_{n,n(1)}(t_0), \dots$; the set $0_{k,k(0)}(t_0), 0_{k,k(1)}(t_0)$ stands for amplitudes at the k th electronic state of the 1-system that characterizes products, namely, they would have spectral response corresponding in a chemical sense to a new chemical species if they were different from zero.

Note that the series $E_{0,0(0)}, E_{0,1(0)}, \dots, E_{n,0(n)}, \dots$ if ordered with respect to the electronic quantum number and ground nuclear states would look like

$$E_{0,0(0)} < E_{k,k(0)} < E_{1,1(0)} < \dots < E_{n,n(0)} \dots \quad (3)$$

The particular case chosen here, the product $E_{k,k(0)}$, has ground state energy below the reactants' first excited state $E_{1,1(0)}$ as it might be detected in a laboratory bench. Thus, there might exist nuclear quantum numbers related to $E_{0,0(0)}$ that are in almost resonance to products states, namely, $\{E_{0,0(j)}\} \sim E_{k,k(0)}$. Before examining cases where amplitudes at product state may become different from zero, let us define some other supplementary aspects.

After time evolution, we take as example a system that can show spectral response at the family of k -states (products) as well as the reactant, for example,

$$C(t) = [C_{0,0(0)}(t), C_{0,0(1)}(t), \dots, 0_{n,n(0)}(t), 0_{n,n(1)}(t), \dots, C_{k,k(0)}(t), C_{k,k(1)}(t), \dots]. \quad (4)$$

Amplitudes, as time goes on, would eventually change to showing nonzero values at the quantum base states recognized as products. How do we know something has changed? The knowledge we talk about is obtainable from experiment. This would imply that time evolution one theoretically follows in Hilbert space is to be perturbed by an experiment designed to probe a product response (k -states in this case). Whether the decision is taken by a (automated) device external to the evolving quantum system or an experimentalist, you cannot expect that QM would be able to tell you something about such an event. Events are characteristics of real space processes. But once the event takes place, the measurement probes the quantum state Eq. (4) as is at that moment. There will be nonzero responses for those base states having nonzero amplitudes. If an experimental set up able to

detect coherent superpositions is at hand, the response will be expressed by the set of amplitudes (complex spectra). For experiments able to detect relative intensities, there will be a superposition of spectral response that can be filtered out. In all circumstances, only nonzero amplitudes open the material system to spectral responses.

Pump-probe experiments show this type of structure [6]. Any chemical process followed with spectroscopic techniques can be described in this framework.

Chemistry is characterized by the varied energy orderings that cannot be simply predicted. In the example shown here, $E_{0,0(0)}, E_{0,0(1)}, \dots, E_{0,0(n)}, \dots$ stands for spectral elements of the keto-form, while $E_{k,k(0)}, E_{k,k(1)}, \dots, E_{k,k(m)}, \dots$ stands for the spectra of the enol-form. One has to disentangle the spectrum of the 1-system following a chemical labeling.

But remember, Hilbert space does not include object description, only quantum states. Any “population” view is not granted here, and because it is a 1-system there is no place for probabilistic views. Yet, spectral responses used as identifiers lead to base states labeled, for instance, with chemical graphs: $|H_2CO\rangle$, $|H_2\rangle|CO\rangle$, $|H_2CO, n\pi^*, S=1\rangle$, $|H_2CO, n\pi^*, S=0\rangle$, $|HCO\rangle|H\rangle$, $|HCO:H, S=0\rangle$, $|HCO:H, S=1\rangle$, $|H_2O\rangle|C\rangle$, and so on. This would mean the spectra associated with these names can be used as *labels* to BSs. Observe that the composition of the 1-system is invariant; the symbol “:” is used to indicate repulsive interaction for the one I-frame state either with spin singlet ($S=0$) or triplet ($S=1$) (cf. Sections 6.1.3 and 6.3.1). Thus, starting from the 1-system related to this symbol, a partitioning procedure could be implemented to make descriptions to share a chemical flavor via the spectral response. Yet, no object hood would be implied; the chemical substances belong to real space laboratory shelf and, while a seasoned chemist may produce systems related to a quantum state such as Eq. (5), spontaneous time evolution from Eq. (2) would not lead to Eq. (5):

$$[0_{0,0(0)}(t), 0_{0,1(0)}(t), \dots, 0_{n,0(n)}(t), 0_{n,1(n)}(t), \dots, C_{k,0(k)}(t), C_{k,1(k)}(t), \dots]. \quad (5)$$

Reasons for this statement will be discussed later on because the external energy sources/sinks have not yet entered the discussion. Pure QM examine all possibilities a system may display only. However, at the laboratory place such state can be prepared as initial state.

Chemical species can be (and are) identified with probing of specific subsets of electronic quantum numbers. Detection of a quantum state $|\Psi\rangle$ would require probing with a frequency palette – frequency range – covering all root base states deemed relevant.

Because the number of elementary components is fixed, whatever change induced and sensed, for instance as a chemical or biochemical process, must be represented as a change of quantum state, namely, that which is expressed in the amplitudes of the linear superposition [e.g., Eq. (1)].

Ordering the ground states so that different chemical labels are located along a “reaction coordinate” (RC), one can discuss a great deal of mechanisms that might be associated with actual time evolution. What does it take in this picture to prompt for appearance of nonzero amplitudes at the channel standing for products?

Assume there is a controlled external source of energy. A first requisite is to get at (almost) resonance between the spectrum of reactant and product. Because the off-diagonal elements $\langle 0, j(0) | \hat{H} | k, k(m) \rangle$ are always zero, the initial amplitudes would stay put, only time-dependent phases change: *No chemistry with isolated material Hamiltonians* and physics for that matter. This result is important because in molecular quantum chemistry such types of Hamiltonians are central to the study of chemical reaction rates.

Therefore, to promote time evolution, there is need for a nondiagonal operator coupling eigenstates via external fields. Let $\hat{V}(\mathbf{A})$ be such an operator coupling the material system states to the EM vector potential $\mathbf{A}$ [7]. Assume there is energy available to change the state of our system. Take a set of almost degenerate levels: $\{E_{0,0(j)}, E_{0,0(j+1)}, \dots, E_{0,0(j')}\}$ and $\{E_{k,k(m)}, E_{k,k(m+1)}, \dots, E_{k,k(m+m')}\}$. The nearest excited state is taken to be $E_{1,1(0)}$ with energy above $E_{0,0(j')}$ and $E_{k,k(m+m')}$.

Thus, if we put energy in the reactant manifold, that is, put amplitudes different from zero, a successful time evolution, and with this we mean that amplitudes at the product manifold become different from zero, the region where manifolds between reactant and product overlap can provide possible energy funnels. How to detect it? Well, start probing spectral response from those levels that make part of the funnel; this situation would resemble a pump-probe femtosecond experiment. Thus, detection of nonzero amplitudes at the product states is the necessary condition to prompt for energy transfer. However, it is not sufficient as discussed later on.

As it is well known, such a time evolution is possible if the matrix element $\langle 0,0(j) | \hat{V}(\mathbf{A}) | k,k(i) \rangle$ is different from zero. The linear superposition would cover excited states over the product BSs. The possibility exists that by spontaneous emission from the product manifold, the system would relax by emitting vibration quanta down to the ground state $|k,k(0)\rangle$, namely, a nonzero amplitude $C_{k,k(0)}$ may appear. Thus, energy is sent out to the EM field and another part is stored at the product ground state. Thus, a trace of chemical process is just there. As described, such a process would be irreversible due to the high degeneracy of the EM field.

There are a number of the so-called closed shell systems for which the standard coupling operator between EM field and electric dipole operator from the 1-system always has $\langle 0,0(j) | \hat{V} | k,k(i) \rangle$ equal to zero. This would be the case for chemical reactions where reactants and products are closed shell. A third electronic state is required to produce a coupling. A three-state where an excited state manifold $\{E_{1,1(0)}, E_{1,1(1)}, \dots\}$ have the right electronic parity. The development of amplitudes at the product in the quantum

state is mediated by an excited state having $\langle 0,0(j)|\hat{V}|1,1(i)\rangle$ and $\langle 1,1(i)|\hat{V}|k,k(m)\rangle$ different from zero. We call this excited state by the name of transition state; as a matter of fact, it is a manifold of vibration state. Note that energy is not funneled by actually exciting the system.

A simple three-state model would help discussing some issues. Take the sequence $|0,0(j)\rangle \rightarrow \psi_1, |k,k(i)\rangle \rightarrow \psi_2$, and $|1,1(0)\rangle \rightarrow \psi_3$ and EM vector field $\mathbf{A}$ [8]:

$$\Phi(\mathbf{A}) = c_1(\mathbf{A}) \psi_1 + c_2(\mathbf{A}) \psi_2 + c_3(\mathbf{A}) \psi_3. \quad (6)$$

Parity considerations ensure that $V_{12} = \langle \psi_1 | \hat{V} | \psi_2 \rangle = 0$ for any couple of vibration numbers, which means that there is no direct amplitude evolution from one set of states toward the other. Moreover, $V_{13} = \langle \psi_1 | \hat{V} | \psi_3 \rangle$ and $V_{23} = \langle \psi_2 | \hat{V} | \psi_3 \rangle$ are different from zero and depend upon the external transverse potential $\mathbf{A}$. The Hamiltonian matrix includes coupling terms, and the secular determinant required to obtain amplitudes is

$$\left| \left[\hat{H} + \hat{V} \right]_{ij} - E \delta_{ij} \right| = \begin{vmatrix} U_1 - E & 0 & V_{13} \\ 0 & U_2 - E & V_{23} \\ V_{13} & V_{23} & U_3 - E \end{vmatrix} = 0. \quad (7)$$

Diagonal elements $U_j = [\hat{H}]_{jj} = \langle \psi_j | \hat{H} | \psi_j \rangle$. Finally, the changes in amplitudes for the lowest root leading to the general ground quantum state are given by Arteca and coworkers [8–14]:

$$\begin{aligned} |c_1| &= \frac{|V_{13}c_3|}{|E_{\text{fml}} - U_1|}, \quad |c_2| = \frac{|V_{23}c_3|}{|E_{\text{fml}} - U_2|}, \\ |c_3| &= \left\{ \left(\frac{V_{13}}{|E_{\text{fml}} - U_1|} \right)^2 + \left(\frac{V_{23}}{|E_{\text{fml}} - U_2|} \right)^2 + 1 \right\}^{-\frac{1}{2}}. \end{aligned} \quad (8)$$

Let us now extract some information relevant to a description of chemical processes. As the equations above are generic and will be used to distill some time-dependent clues that belong to time evolution formalism, no exact solutions are required for this endeavor. Using our nomenclature $c_1 \rightarrow c_{00(m)}$, the amplitude $c_2 \rightarrow c_{kk(j)}$ and $c_3 \rightarrow c_{11(i)}$, and we use three fixed states for discussing situations that might be happening as energy is transferred from the EM to the reacting model.

Preparing the system with $c_2(t_o) = c_{kk(j)} = 0$ for all j 's and $c_3(t_o) = c_{11(i)} = 0$ for all i 's, the amplitude would be one at the ground state of reactants: $c_1(t_o) = c_{00(0)} = 1$.

Energy is required to activate the system. Because all amplitudes but one are zero once we switch on the EM field, the only open channel to funnel energy is the ground state $|\psi_1\rangle \rightarrow |00(0)\rangle$. Of course, potentially, all base state could provide a channel but they have to have a nonzero amplitude.

Now, assume there is a frequency such that the state $|00(1)\rangle$ becomes entangled with the ground state thereby showing (time dependent) amplitude at the first harmonic. Thus, having a $c_{00(1)} \neq 0$, a possibility exists to get at a $c_{00(2)} \neq 0$ and so on until getting energy levels in the reactant spectra, say $c_{00(n)} \neq 0$, that (almost) matches energy levels of product spectra.

At domain where energy levels from reactant and product spectra overlap will be referred to as a funnel domain. Because $\langle \psi_1 | \hat{V} | \psi_2 \rangle = 0$ for all vibration levels, there is no mechanism to directly produce amplitude at the product channel starting from one of the energy levels in the reactant funnel.

When and how c_3 amplitudes start to grow up? In our model [8–12], this would begin to happen when the energy gap $|E_{\text{fml}} - U_1|$ decreases and such decrement occurs as the amplitudes of the excited vibration states reach energy levels nearer those in the funnel. Observe that because at the product channel amplitudes are zero, no change in the gaps can be produced. We define the lower energy of the reactant funnel as the one where the amplitude c_3 begins to increase. To have a nonzero amplitude at the excited state does not mean that there is a “population” of such state. It means only that coherent quantum states may have amplitudes at base states even if there is not enough energy to actually make possible a unit amplitude there. What we have obtained so far is a standard quantum mechanical evolution description with the help of the model equations above.

As soon as amplitude c_3 becomes sizable, an energy funnel would open if there is an appropriate energy level at the product channel; in other words, such levels define the funnel support from the product side. The connection between both funnels is hence achieved by the coupling to transition state but at energies below the chosen electronic excited state $E_{11(0)}$. Resonance at the joint funnel domain would make amplitude c_2 to change in time. Under particular conditions, c_2 may go through unit value. Translating this situation to real life, a possibility opens for the material system to emit a photon and get trapped in the product manifold if the photon field loses coherence. In this case, a chemical event would have taken place. If no event is detected (seen as it were), the system would evolve coherently at the joint funnel domain.

We may conclude that the formalism permits understanding chemical processes as time evolution of the quantum state sustained by the material system when EM fields are coupled to the system. At a laboratory level, the same material system sustains varied chemical species and metastable states. Thus, the physical chemical process finds a natural space to be theoretically studied in the corresponding Hilbert space implemented at a boundary between Hilbert and real spaces; we call it a Fence.

Relating the abstract formalism to one more akin to laboratory world is the targeted issue. For this, the space–time projection leads to equations where at least some elements of the formalism show a relationship to real space characteristics.

3. BASIC SPACE–TIME-PROJECTED QUANTUM FORMALISM

The introduction of inertial frames characteristic of special relativity is a key step to get meaningful projected formalisms. The frame's origin is located in laboratory space (or any space defined by specific mass distributions), and transformations relating families of such frames form the Lorentz group. There are then communication protocols between two I-frames in relative velocity $\mathbf{v}$ leading to specific coordinate transformations. The classical concept of relative velocity applies to frames. These frames are used to define configuration spaces appearing in projecting abstract quantum states. Configuration spaces are mathematical constructs that lend the origin to an inertial frame. Abstract quantum states are henceforward projected on such spaces.

3.1. Time-projected formalism

At this level, time and space are separately treated, this is a special inertial frame where space rotations and space and time translations are studied, the aim is the construction of basis sets; boosts are left outside for the time being. This is a nonrelativistic limit for situations where $|\mathbf{v}| \ll c$, the speed of light in vacuum. Thus, the full 3-space is labeled by one time.

Formally, time evolution is relative to a quantum state prepared at a given time t_o , namely, $|\Psi, t_o\rangle$, that is time-transported by the unitary time evolution operator $\hat{U}(t, t_o)$: $|\Psi, t\rangle = \hat{U}(t, t_o)|\Psi, t_o\rangle$.

This operator fulfills the differential equation $i\hbar \partial \hat{U}(t, t_o)/\partial t = \hat{H} \hat{U}(t, t_o)$. Thus, multiplying from the right with $|\Psi, t_o\rangle$, one gets the form of standard Schrödinger time-dependent equation:

$$\left(i\hbar \frac{\partial}{\partial t} - \hat{H} \right) |\Psi, t\rangle. \quad (9)$$

The operator $\hat{H}$ is the generator of time displacement. This operator defined for a 1-system is the Hamiltonian having the dimension of energy. The material characteristics of the 1-system would enter as parameters of the Hamiltonian operator.

For a conservative, isolated 1-system, the Hamiltonian is time independent; the mapping $|\Psi, t\rangle \leftrightarrow |\Psi\rangle|t\rangle$ holds thereby leading to the eigenvalue equation where the separation constant E (dimension of energy) is taken as a parameter:

$$\hat{H}|\Phi\rangle = E|\Phi\rangle \quad \text{and} \quad i\hbar \partial|t\rangle = E|t\rangle. \quad (10)$$

With $\hat{H}$ being self-adjoint, in principle, the eigen value in Eq. (11) holds:

$$\hat{H}|n, n(m)\rangle = E_{n, n(m)}|n, n(m)\rangle. \quad (11)$$

The eigenvectors are orthonormal for the scalar product fulfills the special form: $\langle n, n(m) | \mathbf{n}', \mathbf{n}'(m') \rangle = \delta_{nn'} \delta_{n'(m)n'(m')}$. Nuclear degrees of freedom for the same electronic state (quantum number) have orthogonal nuclear BSs. For different electronic states, the matrix elements $\langle n(m) | \hat{V} | \mathbf{n}'(m') \rangle \rightarrow \hat{V}_{nm'} S_{mm'}$ relate to well-known Franck–Condon factors ($S_{mm'}$).

The energy scale can be changed at will. In practice, *energy differences* are the magnitudes that can be related to physical processes at a Fence. The time-dependent amplitudes look like $C_{nm(m)}(\Psi, t) = C_{nm(m)}(\Psi) \exp(iE_{nm(m)}t/\hbar)$. Changing the origin of the energy axis by Δ , all phases are equally affected. The time-dependent quantum state for the isolated 1-system can be written to within the phase factor as $|\Psi, t\rangle = \exp(i t\Delta/\hbar) \sum_{nm(m)} |n, n(m)\rangle C_{nm(m)}(\Psi) \exp(i(E_{nm(m)} - \Delta)t/\hbar)$. The global phase factor indicates the chosen energy gauge. The separation *parameter* E as being conjugate to time may vary from $-\infty$ to $+\infty$ *to the extent it is a label* that can be used to identify a basis vector $|E\rangle$; endowing this quantity with a dynamical meaning concerning real physical systems requires further developments.

The exact Hamiltonian $\hat{H}$ as defined cannot drive a productive time evolution [15]. Of course, the situation does not change once the formalism is projected in configuration space. The projection procedure shown below would serve to define the language to be used later on.

3.2. Configuration space basis

Above, abstract quantum states $|\Psi\rangle$ were projected in (mathematical) time space: the mapping $\langle t | \Psi \rangle$ corresponds to a complex function $\Psi(t)$ with argument on a real-time axis. In Hilbert space, the time variable is just a mathematical construct until the concepts of process is used to introduce physical (measurable) time; this requires introduction of a different space, a Fence space.

The I-frame locates the origin of an abstract configuration space with elements $\mathbf{q} = (q_1, q_2, q_3, \dots, q_{1k}, q_{2k}, q_{3k}) = (\mathbf{q}_1, \dots, \mathbf{q}_k)$, where k corresponds to the material system elements, $k = 3n + 3m$, the mathematical configuration space is a real space R^{3k} . In the special I-frame chosen, a time variable labels the whole configuration space at once.

Given a configuration space, the symbol $\mathbf{q}$ is used as a label to identify a quantum base state $|\mathbf{q}\rangle = |q_1, q_2, q_3\rangle = |q_1\rangle |q_2\rangle |q_3\rangle$. A configuration operator $\hat{q}$ is defined in such a way that [16–18]

$$\hat{q}|\mathbf{q}\rangle = \mathbf{q}|\mathbf{q}\rangle. \quad (12)$$

The configuration operator $\hat{q}$ is Hermitian; coordinates are real numbers.

Consider a commutative space, meaning by this sentence that the operators products $\hat{q}_i \hat{q}_j$ commute for all pairs i, j , that is, $[\hat{q}_i, \hat{q}_j] = \hat{q}_i \hat{q}_j - \hat{q}_j \hat{q}_i$ is equal to the zero operator, $\hat{0}$. Thus, $\mathbf{q}$ can represent a vector with well-defined coordinate labels.

The set of configuration base states $\{|q\rangle\}$ is orthonormal in a generalized function sense, namely, $\langle q'|q\rangle = \delta(q - q')$. Symbol $\delta(q - q')$ stands for a measure, or Dirac's function. It is not difficult to check that a unit operator can be defined as

$$\hat{1} = \int dq' |q'\rangle \langle q'|. \quad (13)$$

An abstract quantum state $|\Psi\rangle$ of a 1-system in configuration space is given as a linear superposition:

$$|\Psi\rangle = \hat{1}|\Psi\rangle \rightarrow \int dq' |q'\rangle \langle q'|\Psi\rangle = \int dq' |q'\rangle \Psi(q'). \quad (14)$$

Note two things: (i) the symbol Ψ is used for two different situations: (a) as a label (name) and (b) as a mathematical function (mapping). Therefore, even if one gets mathematical solutions to differential equations, they would not necessarily map out abstract quantum states. From this equation, it is clear that we have to have the wave function defined in a neighborhood dq' of the point q' . Exact reconstruction of the quantum state implies knowledge of the wave function at all points in configuration space. There can be partial reconstructions starting from knowledge limited to finite domains. (ii) An arbitrary mathematical function $F(q')$ does not necessarily represent a projection of a quantum state into configuration space.

Hilbert space states do not depend upon configuration coordinates. This is apparent from the amplitudes $C_i(\Psi)$. The question now is to study the behavior of space eigenkets ($|q'\rangle$) toward an origin translation of the I-frame. While the quantum state is frame independent, the projections given by $\langle q'|\Psi\rangle$ may show specific properties under origin translation. We now study some issues.

3.2.1. Infinitesimal translations

Let $\hat{T}(dq')$ be the operator accomplishing an infinitesimal translation: $\hat{T}(dq')|q'\rangle = |q' + dq'\rangle$. This operation amounts shifting the I-frame's origin by dq' thereby implying presence of at least two I-frames. What effect would produce the translation operator of the quantum state represented in Eq. (14)? Use the neighborhood of $|q'\rangle \langle q'|\Psi\rangle$:

$$\hat{T}(dq')|q'\rangle \langle q'|\Psi\rangle = |q' + dq'\rangle \Psi(q') = |q'\rangle \Psi(q' - dq'). \quad (15)$$

The last equality follows from a change of dummy labels (variables) that would appear when integration as in Eq. (14) is performed.

Thus, a displacement in a given direction of a configuration ket label corresponds to a translation of the wave function argument in the opposite direction. The change in the ket label amounts to an origin shift in laboratory space.

With the help of a generator of translation operator $\hat{k}$ showing dimension as inverse of length one gets in a standard fashion,

$$\hat{T}(\mathbf{d}\mathbf{q}) = \hat{1} - i \hat{k} \cdot \mathbf{d}\mathbf{q}. \quad (16)$$

The reciprocal space $\mathbf{k}$ enters into the handling of translation operators. This is just dimensional analysis, the translation operator is dimensionless, so must be for the product $\hat{k} \cdot \mathbf{d}\mathbf{q}$.

The vector operator $\hat{k}$ must hence be Hermitian in order to be norm conserving, with inverse of length as the appropriate dimension: $\hat{k}$ is the *generator* of displacement in configuration space. The direct and inverse spaces share the origin we have located with an external I-frame.

3.2.2. Reciprocal space

Eigenvectors for the wave operator $\hat{k}$ are labeled as $|k_1, k_2, k_3\rangle$ in the understanding that operator components commute among themselves. Thus,

$$\hat{k}|\mathbf{k}\rangle = \mathbf{k}|\mathbf{k}\rangle. \quad (17)$$

The eigenvalues of $\hat{k}$ are real numbers as they should. In $\mathbf{k}$ -space, the scalar product is a generalized function (distribution) that only makes sense inside an integral:

$$\langle \mathbf{k} | \mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}'). \quad (18)$$

With these properties, it is easy to show a resolution of the identity in $\mathbf{k}$ -space:

$$\hat{1} = \int \mathbf{d}\mathbf{k}' |\mathbf{k}'\rangle \langle \mathbf{k}'|. \quad (19)$$

An arbitrary quantum state $|\Psi\rangle$ can be expanded in $\mathbf{k}$ -space:

$$|\Psi\rangle = \hat{1}|\Psi\rangle = \int \mathbf{d}\mathbf{k}' |\mathbf{k}'\rangle \langle \mathbf{k}' | \Psi \rangle. \quad (20)$$

$\langle \mathbf{k}' | \Psi \rangle$ is the wave function standing for the quantum state $|\Psi\rangle$ in reciprocal space, $\Psi(\mathbf{k}')$.

Multiplying Eq. (20) from the left with the bra $\langle \mathbf{q}' |$, one gets

$$\langle \mathbf{q}' | \Psi \rangle = \int \mathbf{d}\mathbf{k}' \langle \mathbf{q}' | \mathbf{k}' \rangle \langle \mathbf{k}' | \Psi \rangle. \quad (21)$$

This equality leads to the definition of the transformation function: $\langle \mathbf{q}' | \mathbf{k}' \rangle$. Now, using Eq. (20) and multiplying by the bra $\langle \mathbf{k}' |$, one gets

$$\langle \mathbf{k}' | \Psi \rangle = \Psi(\mathbf{k}') = \int \mathbf{d}\mathbf{q}' \langle \mathbf{k}' | \mathbf{q}' \rangle \langle \mathbf{q}' | \Psi \rangle = \int \mathbf{d}\mathbf{q}' \langle \mathbf{k}' | \mathbf{q}' \rangle \Psi(\mathbf{q}'). \quad (22)$$

Note that the symbol Ψ is used in both cases because it is the same abstract quantum state projected in two different basis sets. This is not to convey that the functions have the same form. The set $\{\langle \mathbf{q}' | \mathbf{k}' \rangle\}$ is basis function in Eq. (21) and the set $\{\langle \mathbf{k}' | \mathbf{q}' \rangle\}$ is basis function in Eq. (22).

Projection of $\hat{k}$ -operator in variables belonging to the configuration space reads as

$$\hat{k} = -i \left(\frac{\partial}{\partial \mathbf{q}'} \right). \quad (23)$$

The matrix elements of this operator are as follows.

$$\langle \mathbf{q}' | \hat{k} | \mathbf{q}'' \rangle = -i \left(\frac{\partial}{\partial \mathbf{q}'} \right) \delta(\mathbf{q}' - \mathbf{q}''). \quad (24)$$

Moreover,

$$\begin{aligned} \langle \mathbf{q}' | \hat{k} | \Psi \rangle &= \int d\mathbf{q}'' \langle \mathbf{q}' | \hat{k} | \mathbf{q}'' \rangle \Psi(\mathbf{q}'') = \int d\mathbf{q}'' -i \left(\frac{\partial}{\partial \mathbf{q}'} \right) \delta(\mathbf{q}' - \mathbf{q}'') \Psi(\mathbf{q}'') \\ &= -i \left(\frac{\partial \Psi(\mathbf{q}')}{\partial \mathbf{q}'} \right) = -i \left(\frac{\partial}{\partial \mathbf{q}'} \right) \langle \mathbf{q}' | \Psi \rangle. \end{aligned} \quad (25)$$

The transformation function connecting representations $\mathbf{q}$ to $\mathbf{k}$ is obtained when $|\Psi\rangle \rightarrow |\mathbf{k}'\rangle$ in Eq. (25). Bearing in mind that $\hat{k}|\mathbf{k}'\rangle = \mathbf{k}'|\mathbf{k}'\rangle$

$$\mathbf{k}' \langle \mathbf{q}' | \mathbf{k}' \rangle = -i \left(\frac{\partial \langle \mathbf{q}' | \mathbf{k}' \rangle}{\partial \mathbf{q}'} \right). \quad (26)$$

The solution to this differential equation is the transformation function

$$\langle \mathbf{q}' | \mathbf{k}' \rangle = A \exp(i\mathbf{k}' \cdot \mathbf{q}'), \quad (27)$$

where $A = 1/\sqrt{2\pi}$. Thus, the projected base function of a reciprocal space eigenvector is a plane wave. Furthermore, $\langle \mathbf{k}' | \mathbf{q}' \rangle = (1/\sqrt{2\pi}) \exp(-i\mathbf{k}' \cdot \mathbf{q}')$ so that the wave function in $\mathbf{q}$ -space is related to its wave function in $\mathbf{k}$ -space via the Fourier transform:

$$\Psi(\mathbf{q}') = \left(\frac{1}{\sqrt{2\pi}} \right) \int d\mathbf{k}' \exp(i\mathbf{k}' \cdot \mathbf{q}') \Phi_{\Psi}(\mathbf{k}') \quad (28)$$

$$\Phi_{\Psi}(\mathbf{k}') = \left(\frac{1}{\sqrt{2\pi}} \right) \int d\mathbf{q}' \exp(-i\mathbf{k}' \cdot \mathbf{q}') \Psi(\mathbf{q}'). \quad (29)$$

The set of plane waves form a complete set of eigenfunctions. Either $\Phi_{\Psi}(\mathbf{k}')$ is given or its Fourier transform can be calculated or vice versa. At variance with standard textbooks, here we use the same symbol Ψ as subindex to

emphasize that it is the same abstract quantum state that is projected on either space. The analytical forms differ.

3.2.3. Rotational invariance: angular momentum

Abstract quantum states projected in a 4D special relativity frame are invariant to rotations in 3-space and origin translations. The generator of 3-rotations form a vector $\hat{J} = (\hat{J}_1 \hat{J}_2 \hat{J}_3)$, while rotations involving the time axis are noted by the vector $\hat{K} = (\hat{K}_1 \hat{K}_2 \hat{K}_3)$, which are known as boost 3-vector. Angular momentum is conserved while the boost is not. The eigenvalues of $\hat{J}$ are hence used to label BSs.

Once the commutation relations are known, the eigenvalue equations and eigenvalues can be worked out. This is a lengthy task that would take us far away from our more modest objectives. There is, however, an excellent article in this series from Wormer and Paldus [19] where angular momentum diagrams are masterly presented, see also [4,20].

All kinematical elements are in place to examine a space–time-projected Schrödinger scheme, schematically presented below.

We now come to an important point. The configuration space vectors actually are labels to basis vectors. This applies to the reciprocal space vectors: they are labels to those basis vectors. Even if it is a common procedure to change dimension of the reciprocal space operator and labels into momentum dimension by using Planck constant, unless an explicit dynamical theory is defined, for vectors $|\mathbf{p}\rangle$, the symbol inside the ket is just a label. If we stick to this rule, one cannot compare the absolute value $|\mathbf{p}|$ with the relativistic momentum of a particle of mass M , namely, the product: M times c . The latter is a typical magnitude at the real space (laboratory) level. The formalism examined so far belongs to a rigged Hilbert space [18]. They are not yet commensurable.

By shifting the theory to quantum states sustained by a material system, the search for basis sets becomes independent from actual situations in which the material system may be found. To use the angular momentum, basis set does not imply a rotational symmetry of the actual material systems. Linear combinations over these basis sets do not have full symmetry. Chemists know about hybrid orbitals, particular linear combinations that have symmetries far from spherical. The point made all along this chapter consists in a clear distinction between basis sets and quantum states.

4. ABSTRACT QUANTUM FORMALISM

In the abstract formalism, the configuration space is a pure, multidimensional Euclidean space of appropriate dimension. No reference is made to a particle model. This latter is akin to semiclassical views some of which are examined in Section 5.

4.1. Schrödinger equation in configuration space

The general structure of QM does not require a particle or a wave model, not even at a Fence. This results in an abstract modern quantum theory separating “kinematic” from “dynamic” aspects as long as no specific calculation is in demand. Projecting the abstract framework in configuration space, that is a pure mathematic space, the time-dependent Schrödinger Eq. (32), namely, $(i\hbar) \partial|\Psi,t\rangle/\partial t = \hat{H}|\Psi,t\rangle$, becomes with the help of unit projector operator $\hat{1}$ a linear superposition:

$$\int d\mathbf{q}'|\mathbf{q}'\rangle \left\{ (i\hbar) \frac{\partial\langle\mathbf{q}'|\Psi,t\rangle}{\partial t} - \int d\mathbf{q}''\langle\mathbf{q}'|\hat{H}|\mathbf{q}''\rangle\langle\mathbf{q}''|\Psi,t\rangle \right\} = 0. \quad (30a)$$

Another aspect of the importance of the superposition principle approach is apparent in this equation. At any neighborhood of a point in configuration space, the term in curly brackets must be zero thereby leading to an equation that is formally equivalent to Eq. (9) valid everywhere in configuration space.

To construct an equation showing the same form introduce a diagonal model ansatz: $\langle\mathbf{q}'|\hat{H}|\mathbf{q}''\rangle = \delta(\mathbf{q}' - \mathbf{q}'')\langle\mathbf{q}'|\hat{H}|\mathbf{q}'\rangle$. Put this equation into (30a); after performing the integration over measure $d\mathbf{q}''$ the result is

$$\left\{ (i\hbar) \frac{\partial\langle\mathbf{q}'|\Psi,t\rangle}{\partial t} - \langle\mathbf{q}'|\hat{H}|\mathbf{q}'\rangle\langle\mathbf{q}'|\Psi,t\rangle \right\} = 0. \quad (30b)$$

Performing integration similar to Eq. (30a), for the linear superposition to hold it is necessary and sufficient that for any neighborhood of a configuration point $\mathbf{q}'$ and the entire integration domain (configuration space), the term in curly brackets be equal to zero. One gets the same form for Schrödinger equation projected in configuration space this time. To close this analysis, one makes the assignment:

$$\langle\mathbf{q}|\hat{H}|\mathbf{q}\rangle\langle\mathbf{q}|\Psi,t\rangle \rightarrow \hat{H}(\hat{q})\langle\mathbf{q}|\Psi,t\rangle. \quad (31)$$

This rearrangement, once introduced in Eq. (30b), leads to the time-dependent equation having the form of Schrödinger's used in his seminal paper [21]. The term appearing in the curly bracket must then be equal to zero in order to fulfill the new Eq. (32):

$$\left\{ i\hbar \frac{\partial}{\partial t} - \hat{H}(\hat{q}) \right\} \Psi(\mathbf{q},t) = 0. \quad (32)$$

The introduction of $\hat{H}(\hat{q})$ is not a logical step. It is a hypothesis that permits giving to Schrödinger equation, in configuration space, the same form as in abstract space. We assume that the mapping $\hat{H} \rightarrow \hat{H}(\hat{q})$ holds true.

Abstract Eqs (9–11) have correlates in configuration space-projected Schrödinger equation. There are families of functions independent of the

time parameter that must fulfill the equation: $\hat{H}(\hat{q}) \Psi(\mathbf{q}) = E\Psi(\mathbf{q})$. This eigenvalue equation defines a complete set of denumerable functions when the operator is self-adjoint. The equation defines eigenfunctions and energy eigenvalues sustained by a material system with Hamiltonian $\hat{H}(\hat{q})$. With the spectra, families of spectral response (based on energy differences) can be constructed and compared to experiment at a Fence.

Thus, $\hat{H}(\hat{q})\Psi(\mathbf{q}) = E\Psi(\mathbf{q})$ opens the possibility to calculate the spectrum associated with $\hat{H}(\hat{q})$, but it falls short to provide the ultimate oracle of chemical knowledge. Spectra and basis functions are the primary constituents of a Hilbert space representation of arbitrary quantum states via a principle of linear superposition. This time we have the basic elements projected with the help of inertial frames, and consequently, the localization of such frames in laboratory space puts the framework back into real world.

Abstract QM deals with quantum states sustained by the given material systems. It does not deal with the material constituents as objects. This point is important to get a more clear understanding of the theory.

4.2. Electronuclear configuration space

The material systems of interest are made of nuclei and electrons, the atomic number assigning chemical identity. To follow as near as possible, quantum chemical practices, the configuration space of electrons, and nuclei degrees of freedom are labeled as $(\mathbf{x}, \mathbf{X})$. The base vectors $|\mathbf{x}, \mathbf{X}\rangle$, the $3n - D$ vector $\mathbf{x}$, and $3m - D$ vector $\mathbf{X}$ are configuration spaces where electronic and nuclear states are projected. The convention does not alter the abstract nature of configuration space. It is the dimension that is dictated by the system's degrees of freedom. The origin of the I-frame is defined with respect to another I-frame; both are located in laboratory space.

Full configuration space points show the same time label. The whole I-frame can eventually move with velocity $\mathbf{v}$ with respect to another I-frame that you might deem relevant when a specific problem is under scrutiny. Lorentz group of transformations applies to the I-frames.

An electronuclear basis wave function $\Phi_{n,n(m)}(\mathbf{x}, \mathbf{X}) = \langle \mathbf{x}, \mathbf{X} | n, n(m) \rangle$ is then a projection of the abstract base state. From now on, we use a Φ -label for basis functions. Each basis function shows a characteristic nodal pattern (NP). For the electronic system, the node pattern is independent from the point in nuclear configuration space. This property is crucial to understand differences between semiclassical models used in the literature. The mapping (function) $\Phi_{n,n(m)}$ is fixed for given quantum numbers. $\Phi_{n,n(m)}(\mathbf{x}, \mathbf{X})$ is a complex valued mathematical function calculated at the point $(\mathbf{x}, \mathbf{X})$. The measure $d^{3n}\mathbf{x} d^{3m}\mathbf{X}$ (volume element) is associated with the system having n -electrons and m -nuclei of a given kind. The integral $\int \Phi_{\mathbf{n}', \mathbf{n}'(m')}(\mathbf{x}, \mathbf{X}) \Phi_{n,n(m)}(\mathbf{x}, \mathbf{X}) d^{3n}\mathbf{x} d^{3m}\mathbf{X}$ gives the same information as the abstract quantum BS: $\langle n, n(m) | \mathbf{n}', \mathbf{n}'(m') \rangle = \delta_{\mathbf{n}\mathbf{n}'} \delta_{\mathbf{n}'(m)\mathbf{n}'(m')}$.

Thus, the complete set $\{\Phi_{n,n(m)}(\mathbf{x},\mathbf{X})\}$ where the variables are the quantum numbers constitutes a basis set to represent arbitrary quantum states within the principle of linear superposition: $\Psi(\mathbf{x},\mathbf{X},t) = \sum_{n,m} \Phi_{n,n(m)}(\mathbf{x},\mathbf{X}) C_{nm(m)}(\Psi,t)$. Knowledge about the quantum state resides in the set of amplitudes that differ from zero. Amplitudes relate at a Fence the response of a quantum system to external probes.

The time dependence of amplitudes in the interaction representation is then

$$C_{k,k(j)}(\Psi_I,t) = \sum_{n,n(m)} C_{n,n(m)}(t_0) \int \int \Phi_{k,k(j)}^*(\mathbf{x}',\mathbf{X}') \times \exp\left(\frac{i\hat{V}_I(\mathbf{x}',\mathbf{X}')t}{\hbar}\right) \Phi_{n,n(m)}(\mathbf{x}',\mathbf{X}') d^{3n}\mathbf{x}' d^{3m}\mathbf{X}'. \quad (33)$$

Only basis functions for which the initial quantum state has nonzero amplitudes will contribute to create amplitudes that might have been zero when the system was prepared. The necessary and sufficient condition to detect a response is that the transition amplitude $\int \int \Phi_{k,k(j)}(\mathbf{x}',\mathbf{X}') \exp(i\hat{V}_I(\mathbf{x}',\mathbf{X}')t/\hbar) \Phi_{n,n(m)}(\mathbf{x}',\mathbf{X}') d^{3n}\mathbf{x}' d^{3m}\mathbf{X}'$ be nonzero for the label $k,k(j)$; we are interested to sense its response with some probe external to the 1-system.

If the quantum state is normalized to 1 at all times, then $|C_{k,k(j)}(\Psi,t)|^2$ would represent the relative response intensity if you decide probing the spectra rooted at $\Phi_{k,k(j)}$. If the spectral response can be probed on copies all prepared in the same manner with time-delayed techniques to obtain a mapping of $|C_{k,k(j)}(\Psi,t)|^2$ as a function of time that is detectable at the laboratory, then this corresponds to intensity regime measurement.

Measurements in amplitude permit detecting aspects of these coherent states [5]. Here, actual measuring devices are not made explicit; only the wave function assumed to represent a quantum state is determined explicitly.

A final and key point on basis functions concerns the quantum numbers and the domain where the mathematical function is defined: $\Phi_{n,n(m)}(\mathbf{x},\mathbf{X})$. The *quantum numbers are independent from the configuration space location*.

The following stage requires the construction of appropriate model differential equations. For this purpose, we briefly examine the construction of model Hamiltonian operators; it is perhaps relevant to note a basic point, namely, solutions to differential equations are mathematical constructs on their own, so that results must be checked against experiments.

4.3. Hamiltonians

Special relativity opens a royal path to construct model Hamiltonians. One reason, simple to apprehend, lies in the fact that the norm of a 4-vector

remains invariant to Lorentz transformations. For two I-frames in relative motion (velocity $\mathbf{v}$), equations we know that its form from a moving frame can be transformed back to the one serving the purpose of a fixed frame. The equations are said to be covariant. In this manner, the velocity factor would enter the theoretical description, and the study is carried out in a “fixed” framework. Moreover, the dynamics of general relativity concerns 3D things. The mathematical object that changes is not the 4D distances within space–time, but distances within 3D spaces nested in space–time [22]. Thus, the projection procedures at a given time used so far are sufficiently general. The *form* of Eqs. (9) and (31) holds in relativistic and nonrelativistic limits.

So far, the wave function has been taken as a projection of a quantum state in a generic basis set. The search for a basis set is hence of primary importance. The operator $\hat{H}(\hat{q})$ is transformed into partial differential operators, and consequently, the calculation of basis sets is shifted toward analytical solutions of model systems or to numerical solutions of the equations using complete sets of special mathematical functions. Many computer algorithms derive from such representations. In principle, the abstract formalism is realized via partial differential equations, and the experimental data about the spectra and the responses toward external probes must be checked for each particular case.

4.3.1. Single-particle model Hamiltonians

For charged systems, relativistic invariant Hamiltonians, such as the Klein–Gordon and Dirac forms (see Ref. [2] Chapter 1), have a supplementary symmetry related to charge conjugation. The solutions of such equation permit treatment of basis sets for the conjugated positive and negative charge material species (e.g., positron and electron states). The label E used as separation constant can have positive or negative values, while the eigenstates energies are always positive. Dirac equation describes electronic base states with mathematical objects with four dimensions, 4-spinors. In the nonrelativistic limit, the equation reduces to Pauli equation expressed in 2-spinor forms characteristic of spin 1/2 base states defining fermion states. The scalar wave function multiplying the 2-spinor fulfills Schrödinger equation for the material system interacting with external EM fields. Pauli equation includes spin–orbit terms plus operators leading to spin coupling to external magnetic fields.

The Pauli Hamiltonian model for a material system with mass M , charge e in the EM field plus Coulomb field takes on the form

$$\left\{ i\hbar \frac{\partial}{\partial t} - \left(\frac{1}{2m} \right) \left[\sigma \left(\hat{p} - \left(\frac{e}{c} \right) \mathbf{A}(\hat{q}) \right) \right] \left[\sigma \left(\hat{p} - \left(\frac{e}{c} \right) \mathbf{A}(\hat{q}) \right) \right] - eV(\hat{q})\sigma_0 \right\} \Psi = 0. \quad (34)$$

Here, Ψ is a 2-spinor, $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ is a vector where $\sigma_{\mathbf{k}}$ ’s are Pauli spin 2×2 matrices, and $V(\hat{q})$ is a Coulomb potential operator (multiplied by a

2×2 unit matrix, σ_0). The momentum operator is given by $\hat{p} = i\hbar \hat{k}$, where $\hat{k}$ is the generator of displacement in configuration space appearing in Eq. (16). The total Hamiltonian including the transverse EM potential takes on the form

$$\hat{H}_T(\hat{q}, \mathbf{A}, \sigma) = \hat{H}(\hat{q}) + \hat{V}_1 + \hat{V}_2. \quad (35)$$

The interaction operators read as

$$\hat{V}_1 = - \left\{ \left(\frac{e}{mc} \right) (\hat{p} \cdot \mathbf{A}(\hat{q}) + \mathbf{A}(\hat{q}) \cdot \hat{p}) + \left(\frac{e\hbar}{2mc} \right) \sigma \cdot \nabla \wedge \mathbf{A}(\hat{q}) \right\} \quad (35a)$$

$$\hat{V}_2 = \left(\frac{e^2}{2mc^2} \right) \mathbf{A}(\hat{q}) \cdot \mathbf{A}(\hat{q}). \quad (35b)$$

The intended coupling operator $\hat{V}$ introduced in Section 2 can be taken now as $\hat{V}_1$, for instance.

Schrödinger operator coming from Eq. (32) takes on the form

$$\hat{H}(\hat{q}) = \left(\frac{1}{2m} \right) \hat{p}^2 + eV(\hat{q}). \quad (36)$$

The longitudinal Coulomb interaction is given by $eV(\hat{q})$.

The Schrödinger Hamiltonian operator $\hat{H}(\hat{q})$ commutes with the total spin operator $\hat{S}$: $\hat{S}\hat{H}(\hat{q}) - \hat{H}(\hat{q})\hat{S} = 0$. The spin quantum numbers (S, M_S) provide labels to the basis functions of a 1-system. For the sake of analysis, basis functions are taken as products of space and spin functions each with its own permutation symmetry. This procedure is preferable so far one is building up basis sets; processes description may require adjustments that are specific to cases under study.

4.3.2. Coulomb Hamiltonian

For a 1-system defined by n -electrons and m -nuclei of certain defined kinds, Eq. (36) can explicitly be written as

$$\hat{H}(\hat{q}) = \hat{H}_e(\hat{q}_e) + \hat{H}_N(\hat{q}_N) + V(\hat{q}_e, \hat{q}_N) \quad (37a)$$

$$\hat{H}_e(\hat{q}_e) \rightarrow \sum_i \left\{ \left(\frac{1}{2m} \right) \hat{p}_i^2 + \sum_{j \neq i} e_j V_i(\hat{q}_e) \right\} \quad (37b)$$

$$\hat{H}_N(\hat{q}_N) \rightarrow \sum_k \left\{ \left(\frac{1}{2M_k} \right) \hat{p}_{kN}^2 + \sum_{k' \neq k} Z_k e V_{k'}(\hat{q}_N) \right\}. \quad (37c)$$

Note that unless these operators act on a wave function or a basis function, the Cartesian form of the operators is not realized. Thus, $\hat{H}(\hat{q})\Phi_{n,n(0)}(\mathbf{x},\mathbf{X})$ transforms into $\hat{H}(\mathbf{x},\mathbf{X})\Phi_{n,n(0)}(\mathbf{x},\mathbf{X})$ and any mathematical operation on the coordinates must be carefully analyzed. One cannot substitute the I-frame without further ado as it is common practice in computational quantum chemistry.

The Hamiltonian $\hat{H}(\mathbf{x},\mathbf{X})$ assumes the presence of a configuration space and takes on the form

$$\begin{aligned} \hat{H}(\mathbf{x},\mathbf{X}) \rightarrow \sum_i \left\{ \left(\frac{-\hbar^2}{2m} \right) \nabla_i^2 + \sum_{j \neq i} \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_j|} \right. \\ \left. + \sum_k \left\{ \left(\frac{-\hbar^2}{2M_k} \right) \nabla_k^2 + \sum_{\mathbf{k}' \neq \mathbf{k}} Z_k Z_{\mathbf{k}'} \frac{e^2}{|\mathbf{X}_k - \mathbf{X}_{\mathbf{k}'}|} - \sum_i \sum_k Z_k \frac{e^2}{|\mathbf{x}_i - \mathbf{X}_k|} \right\} \right\}. \end{aligned} \quad (38)$$

The interaction with external EM field is obtained by adapting Eqs (35a) and (35b). This closes the construction of the Coulomb Hamiltonian for a 1-system.

The Coulomb terms in Eq. (38) depend upon distances calculated with points from the abstract configuration space. Therefore, Coulomb terms are invariant to I-frame rotations and origin translations. The kinetic energy operators are also invariant to I-frame rotations and origin displacements. These latter operators sense curvatures for the wave function. In spite of appearances, this is not yet a particle operator. To get such a model, one has to endow the configuration space with the particle model interpretation.

4.4. Abstract generalized electronic diabatic model

The abstract GED model retains the abstract nature of the whole configuration space. The space associated with the pure quantum mechanical degree of freedom must be incorporated now. Quantum numbers of neither spin- nor space-projected basis functions depend upon the domain where the function can be evaluated. This fact should be reminded.

The electronuclear basis function is denoted as $\Phi_{n,n(m)}(\mathbf{x},\mathbf{X};L,M_L;S,M_S;I,M_I)$ or in a more simple way: $\Phi_{n,n(m)}(\mathbf{x},\mathbf{X};^{2S+1}L_J;I,M_I)$. Nuclear spin label is indicated in a simple manner. Note that spin quantum numbers are put inside the function argument to alleviate nomenclature. The basis sets are constructed with Schrödinger's operators equivalent to Eq. (36).

The degrees of freedom of the configuration space, $\mathbf{q}_1, \dots, \mathbf{q}_n$, are now supplemented with a new spin space where the total spin operator is a sum of 1-spin operators: $\hat{S} = \sum_{j=1,n} \hat{S}_j$. The total spin fulfills the equations

$$\hat{S}^2 |S, M_S\rangle = S(S+1) |S, M_S\rangle \quad \text{and} \quad \hat{S}_3 |S, M_S\rangle = M_S |S, M_S\rangle. \quad (39)$$

The spin basis function $\Xi_n(S, M_S; 1, \dots, n)$ is constructed in such a way that the product with the configuration space part $\Phi_{n,n(m)}(\mathbf{x}, \mathbf{X})$ be antisymmetric under permutations of electronic labels. To this product, one has to include the nuclear spin $\Xi(I, M_I; 1, \dots, m)$. We assume that the direct product basis functions are taken to have the appropriate permutation symmetry. Note that the concept of spin orbital is avoided.

Projecting abstract quantum states has lead to the construction of partial differential equations for mathematical functions $\Psi(\mathbf{x}, \mathbf{X})$. Imposing appropriate boundary conditions, one may calculate basis functions $\Phi_{j,j(m)}(\mathbf{x}, \mathbf{X})$ that are solutions to the exact Coulomb Hamiltonian $\hat{H}(\mathbf{x}, \mathbf{X})$ from Eq. (38):

$$\hat{H}(\mathbf{x}, \mathbf{X})\Phi_{j,j(m)}(\mathbf{x}, \mathbf{X}) = E_{j,j(m)}\Phi_{j,j(m)}(\mathbf{x}, \mathbf{X}). \quad (40)$$

The connection between the abstract base ket $|j,j(m)\rangle$ and the mathematical basis function $\Phi_{j,j(m)}(\mathbf{x}, \mathbf{X})$ emphasizes the relevance of quantum numbers; the configuration space is an auxiliary support; the form is symbolized by $\Phi_{j,j(m)}$. The trouble is to actually compute solutions to this eigenvalue problem. There is need to somehow separate the electronic from the nuclear degrees of freedom.

We noted some time ago that a separation of electronic from nuclear degrees of freedom suggests itself via the eigenvalues. The aim is the construction of effective equations to calculate electronic basis functions with quantum numbers that are independent from the nuclear configuration space [14,15]. As focus is on quantum numbers, the construction addresses only the set of basis functions and not general quantum states that are linear superpositions where one sums over basis quantum numbers that serve as dummy indexes.

Note again that quantum numbers do not depend upon where in configuration space an evaluation of the basis function is realized. The approach used to get differential equations for the electronic part is based on a separation leading from $\Phi_{j,j(m)}(\mathbf{x}, \mathbf{X})$ to a diabatic ansatz, for example, $\Omega_j(\mathbf{x})\Gamma_{j(m)}(\mathbf{X})$. The energy eigenvalue $E_{j,j(m)}$ is written as a sum of two terms: $E_j + E_{j(m)}$. The word diabatic refers to this $\mathbf{X}$ -independence of the electronic basis functions, $\Omega_j(\mathbf{x})$. The word adiabatic concerns the total wave function and indicates that the structure of the linear superposition in terms of the location of energy expectation value does not change with changes applied to the $\mathbf{X}$ -space, for example, by selecting always the linear superposition yielding the lowest energy value for every $\mathbf{X}$ -point one gets an adiabatic energy profile.

The hypothesis implicit in the diabatic ansatz concerns the character of the electronic base state. The NP would impose an electron–nuclear attractor energy that is in absolute value the largest at a point around which one can get a lowest energy vibration state $\Gamma_{j(0)}(\mathbf{X})$ for a given diabatic electronic basis function. We designate such configuration point as $\mathbf{X}^{(j)}$. We call this

point an attractor and use it to define a new origin for an I-frame if necessary.

The average $\langle \Phi_{jj(0)}(\mathbf{x}, \mathbf{X}) | \{ \hat{H}_e(\hat{q}_e) + V(\hat{q}_e, \hat{q}_N) + V(\hat{q}_N, \hat{q}_N) \} | \Phi_{jj(0)}(\mathbf{x}, \mathbf{X}) \rangle_{\mathbf{X}}$ over nuclear configuration space when it is carried out over the diabatic model permits defining the energy functional:

$$U[\Omega_j; \mathbf{X}^{(j)}] = \langle \Omega_j(\mathbf{x}) | \{ \hat{H}_e(\hat{q}_e) + \langle V(\hat{q}_e, \hat{q}_N) \rangle_{j(0)} + \langle V(\hat{q}_N, \hat{q}_N) \rangle_{j(0)} \} | \Omega_j(\mathbf{x}) \rangle_{\mathbf{X}}. \quad (41)$$

Then, the configuration $\mathbf{X}^{(j)}$ which the nuclear system would fluctuate around is used to construct the model:

$$\langle V(\hat{q}_N, \hat{q}_N) \rangle_{j(0)} \rightarrow V_{NN}(\mathbf{X}^{(j)}) \quad \text{and} \quad \langle V(\hat{q}_e, \hat{q}_N) \rangle_{j(0)} \rightarrow V(\hat{q}_e, \mathbf{X}^{(j)}). \quad (42)$$

The nuclear part is being transformed into a *fixed source* of Coulomb potential; this one acts back over the electronic system, $V(\hat{q}_e, \mathbf{X}^{(j)})$.

The symmetry of the abstract nuclear configuration space is broken. Now, one can define a nuclear configuration space relative to the attractor $\mathbf{X}^{(j)}$, $\delta\mathbf{X} = \mathbf{X} - \mathbf{X}^{(j)}$, and make the hypothesis that the following substitution holds:

$$U[\Omega_j; \mathbf{X}^{(j)}] \rightarrow U[\Omega_j; \delta\mathbf{X}] = U[\Omega_j; \mathbf{X} - \mathbf{X}^{(j)}] \rightarrow U[\Omega_j; \mathbf{X}]. \quad (43)$$

This ansatz moves the formalism away from the exact solution in abstract configuration space with coordinates $(\mathbf{x}, \mathbf{X})$ into symmetry-broken patches around the attractors $\{\mathbf{X}^{(j)}\}$. This approach defines a general semiclassical procedure referred to as abstract generalized electronic diabatic (a-GED) scheme. The concept of abstract refers to the electronic configuration space only.

The last functional form in Eq. (43) can be used to calculate electronic diabatic basis function once the constraint below is fulfilled [3,8–15], namely

$$\frac{\partial U[\Omega_j; \mathbf{X}]}{\partial \mathbf{X} |_{\mathbf{X}=\mathbf{X}^{(k)}}} = 0. \quad (44)$$

The lowest energy eigenvalue is found from Eq. (45):

$$\left\{ \hat{H}_e(\hat{q}_e) + V(\hat{q}_e, \mathbf{X}^{(k)}) + V_{NN}(\mathbf{X}^{(k)}) \right\} \Omega_{\mathbf{k}'}(\mathbf{x}) = U_{\mathbf{k}'}[\Omega_k; \mathbf{X}^{(k)}] \Omega_{\mathbf{k}'}(\mathbf{x}). \quad (45)$$

The lowest energy value $U_k[\Omega_k; \mathbf{X}^{(k)}]$ is a true eigenvalue while remaining energy roots $U_{\mathbf{k}'}[\Omega_k; \mathbf{X}^{(k)}]$ can be related to eigenvalues of an electronic Hamiltonian at $\mathbf{X}^{(k')}$, that is $U_{\mathbf{k}'}[\Omega_{\mathbf{k}'}; \mathbf{X}^{(k')}]$. Here lies the seeds for the diabatic potential energy surfaces (D-PES) because from the inequality

$$U_{\mathbf{k}'}[\Omega_k; \mathbf{X}^{(k)}] > U_{\mathbf{k}'}[\Omega_{\mathbf{k}'}; \mathbf{X}^{(k')}] ,$$

one can bridge these points with the functional $U_{\mathbf{k}'}[\Omega_{\mathbf{k}'}; \mathbf{X}] \equiv U_{\mathbf{k}'}[\mathbf{X}]$, with obvious notation.

The solutions to the Eq. (45) once the optimization implied by Eq. (44) is carried out contains all eigenfunctions with an energy order determined by the attractor: one gets for the lowest eigenvalue obtained at $\mathbf{X}^{(k)}$.

Vibration levels can hence be obtained from

$$\left\{ \hat{K}_N + U_j[(\mathbf{X} - \mathbf{X}^{(j)})] \right\} |\Gamma_{j(k)}(\mathbf{X} - \mathbf{X}^{(j)})\rangle = E_{j(k)} |\Gamma_{j(k)}(\mathbf{X} - \mathbf{X}^{(j)})\rangle. \quad (46)$$

The nuclear configuration $\mathbf{X}^{(j)}$ introduces a structural element in the description of the electronuclear quantum states of the material 1-system. The model strongly reminds semiclassical approaches. Before dwelling into them, let us examine some general features from the preceding exact diabatic approach.

4.4.1. a-GED spectra

Consider the lowest electronic energy level. Assume that somehow the nuclear configuration point is known so that $U[\Omega_j; \mathbf{X}^{(0)}]$ is the lowest energy when $j=0$. As the electronic function is known, the generalized functional fulfills the inequality:

$$U[\Omega_{j=0}; \mathbf{X}] \geq U[\Omega_{j=0}; \mathbf{X}^{(0)}]. \quad (47)$$

The functional $U[\Omega_{j=0}; \mathbf{X}]$ is a *diabatic* potential energy hypersurface determined by the basis function $\Omega_{j=0}$.

The functional Eq. (43) for $U[\Omega_{j=0}; \mathbf{X}^{(0)}]$ defines a fixed Hamiltonian, bounded from below and self-adjoint, namely,

$$\hat{H}_e(\hat{q}_e) + V(\hat{q}_e, \mathbf{X}^{(0)}) + V_{NN}(\mathbf{X}^{(0)}) = \hat{H}(\hat{q}_e; \mathbf{X}^{(0)}). \quad (48)$$

One would then get a complete set of electronic diabatic functions $\{\Omega_k\}$ [15]. The number and quality of nodes characterize these functions. Thus, the diabatic function Ω_k obtained from its own functional form $U[\Omega_k; \mathbf{X}^{(k)}]$ in so far nodal properties are concerned is identical to the one found with $U[\Omega_k; \mathbf{X}^{(0)}]$. The energy of course is totally different:

$$U[\Omega_k; \mathbf{X}^{(0)}] > U[\Omega_k; \mathbf{X}^{(k)}]. \quad (49)$$

The invariance of the nodal characteristic of basis functions Ω_k with respect to the stationary point in nuclear configuration space is a fundamental property. Note that at another stationary nuclear geometry, $\hat{H}(\hat{q}_e; \mathbf{X}^{(k)})$ is bound from below and addresses the same number of electrons than $\hat{H}(\hat{q}_e; \mathbf{X}^{(0)})$, thus the set of eigenfunctions should include all symmetries but energy ordered differently due to different external potential.

4.4.2. a-GED: D-PES

The functional defining D-PES has the form $U[\Omega_k; \mathbf{X} - \mathbf{X}^{(k)}] \equiv U_k(\mathbf{X} - \mathbf{X}^{(k)})$; this notation is simplified as $U_k(\mathbf{X})$ if there is no risk of ambiguity. The

continuity of $U_k(\mathbf{X})$ means that if the limit $\mathbf{X} - \mathbf{X}^{(k)} \rightarrow \mathbf{0}$, then $U_k(\mathbf{X}) \rightarrow U_k(\mathbf{X}^{(k)})$ in such a way that $\partial U_k(\mathbf{X})/\partial \mathbf{X}$ tends to zero vector when $\mathbf{X} \rightarrow \mathbf{X}^{(k)}$.

The curvature of a D-PES for a basis function at the stationary configuration is positive by construction. The configuration $\mathbf{X}^{(k)}$ is an attractor in the sense that comes from an operator bounded from below so that in a neighborhood of this stationary point, the curvature must be positive. These assumptions configure the model.

In the present diabatic model, there are PESs that might have their minima at different fixed points in the nuclear configuration space. This means that many different D-PESs would cross at definite regions.

Crossings of D-PESs do not create difficulties because the diabatic basis are obtained as solutions from Hamiltonians families $\{\hat{H}(\hat{q}_e; \mathbf{X}^{(k)})\}$. Each one of these operators is well defined, in principle.

Take the case

$$U[\Omega_0; \mathbf{X}^{(0)}] < U[\Omega_k; \mathbf{X}^{(k)}] < U[\Omega_{k'}; \mathbf{X}^{(k')}] \quad (50)$$

Now, let us go back to our example in Section 2 and assign $\mathbf{k}' = 1$ to make the map more precise. Thus, $U[\Omega_{\mathbf{k}'=1}; \mathbf{X}^{(\mathbf{k}'=1)}]$ is a model for an excited electronic state and $U[\Omega_{k=3}; \mathbf{X}^{(k=3)}]$ is the chemical product for the eigenstate. The model quantum state reads

$$\Phi(\mathbf{x}; \mathbf{X}, \mathbf{A}) = c_0(\mathbf{A}; \mathbf{X})\Omega_0(\mathbf{x}) + c_2(\mathbf{A}; \mathbf{X})\Omega_2(\mathbf{x}) + c_3(\mathbf{A}; \mathbf{X})\Omega_3(\mathbf{x}). \quad (51)$$

It can be shown that there would be no chemical change, meaning that the amplitudes of the initial quantum state stay put, unless we switch on the operators coupling electronic states and fulfill energy–momentum conservation laws at the laboratory level.

The linear superposition shown in Eq. (51) is the nearest one can get to a full quantum mechanical approach. The quantum state coupled to an external field $\Phi(\mathbf{x}; \mathbf{X}, \mathbf{A})$ is hence separable in the abstract diabatic framework.

By considering the nuclear configuration to play an autonomous role, the classical concept of molecular structure glimpses via the set of $\mathbf{X}^{(k)}$ -coordinates. Yet, such coordinates are not real space coordinates; that is the very concept that might help bridging abstract to classical or semiclassical representations.

5. SEMICLASSICAL MODELS

Full quantum mechanical treatment for a 1-system model requires only one I-frame, the origin of which can be located in the laboratory space. This frame, by introducing appropriate configuration spaces, serves to *project* abstract quantum states.

Abstract quantum states are axiomatically introduced. This procedure leads to a well-defined mathematical representation of QM (cf. the overview presented in preceding sections).

In “real” life, the 1-system’s material elements can be arranged in different manners, call them fragments, so that the sum of their elementary components adds up to the 1-system of interest. Each fragment is endowed with an abstract system of quantum states that can be projected onto an inertial frame, I_k -frame. The set of I_k -frames located in the laboratory space are manipulated to device experiments. The Hamiltonian for the set of fragments corresponds to the sum of noninteracting I_k ’s Hamiltonians. For noninteracting fragments there is no problem. Each one can be identified by the response to EM fields. The interesting situation happens when such fragments are put in interaction. In chemistry such is the standard situation. For example, take H_2 “fragments,” make them interact with O_2 ones, and a possible result will be the emergence of a 1-system H_2O . This chemistry would require the passage from a two-I-frame system to a one-I-frame system. The problem is the passage from laboratory space to the space characteristic of semiclassical quantum mechanical schemes, that is, to make the set of I-frame subsystems commensurate to the global 1-system.

There are important classical physics aspects related to frames location and possibly orientation that ought to be conserved. The invariant element for these systems is the fermion nature of the electronic part. It is then the nuclear part that can contingently change with the isotope constitution as well as spin states, the nuclear charge is invariant: a PCB in real space. The model implies a separation between electronic from nuclear degrees of freedom. This is a step in the way to construct electronic basis functions.

For a 1-system, there is also the possibility to separate the nuclear from the electronic degrees of freedom by treating the massive nuclear system as charge located in real space. In this context, focus is on the semiclassical treatment of the 1-system where we distinguish two broad classes of diabatic semiclassical models: class I and class II. Finally, we distinguish class III systems associated with processes involving passage from many-to-one I-frames and vice versa.

Class I corresponds to the case where the abstract nuclear configuration space is mapped onto the space of nuclear positions with respect to the chosen I-frame. These new vectors belong to real space. We will refer to them as a PCB model. The electronic configuration space keeps its abstract form. It is a pure mathematical space. Here, we insist in handling quantum states instead of particles. The Schrödinger equation corresponds to electronic 1-system submitted to the effect of an external (Coulomb) potential.

Class II semiclassical approach, both electronic and nuclear configuration spaces, describes real particles with position vectors referred to the origin of an I-frame located in a laboratory setting. This approach is well adapted to introduce computer algorithms. It is extensively used in quantum chemistry.

Class III systems incorporate situations such as scattering, matter–EM interactions, dissociation/association reactions, Bose–Einstein condensation,

and ionization processes. Self-consistent reaction field theories for solvent effects, measurement devices, and much more belong to class III. The theoretical study belongs to the realm of semiclassical models to the extent one has to mix spaces with one to several I-frames.

5.1. Class I models: a-BO and GED schemes

BO scheme, as it is commonly used, actually belongs to class II and III models. We elaborate in this section a new blend called abstract Born–Oppenheimer framework (a-BO). Thus, we do not handle electrons as particles but quantum states sustained by the electronic part of the 1-system, the electron number is constant anyway. The space of nuclear degrees of freedom is defined with position vectors in real space, yet the I-frame remains the same. A conspicuous example is the calculation by Schrödinger of the nonrelativistic electronic spectra of the 1-system standing for the hydrogen atom at the birth of wave mechanics in 1926 [21]. Dirac’s calculation of hydrogen atom with his relativistic method in 1927 is another example.

5.1.1. Abstract BO scheme

The abstract diabatic model was discussed in Section 3.5 and now named as a-GED approach. Here we focus the BO scheme and make some comparisons to a-GED at the end of this section. The aim of such comparison being to show the close relationships and complementary nature that exists between a-BO and a-GED schemes.

The approach directs to the calculation of the quantum state in real nuclear configuration space ξ . In this context, consider the model electronic Hamiltonian

$$\hat{H}(\hat{q}_e, \xi) = \left\{ \hat{H}_e(\hat{q}_e) + V_{Ne}(\hat{q}_e, \xi) + V_{NN}(\xi) \right\}. \quad (52)$$

This operator corresponds to a replacement in Eq. (38) of the abstract nuclear configuration space $\mathbf{X}$ by ξ . The exact wave function for the 1-system, $\Psi(\mathbf{x}, \xi)$, is modeled within BO framework as the product: $\Psi(\mathbf{x}, \xi) \rightarrow \Psi(\mathbf{x}; \xi) \Gamma(\xi)$.

The a-BO energy functional $W^{a-BO}(\xi)$ reads as

$$W^{a-BO}(\xi) = \langle \Psi(\mathbf{x}; \xi) | \hat{H}(\hat{q}_e, \xi) | \Psi(\mathbf{x}; \xi) \rangle_{\mathbf{x}}. \quad (53)$$

For each value of ξ , the variation principle leads to the equation

$$\hat{H}(\hat{q}_e, \xi) \Psi(\mathbf{x}; \xi) = W^{a-BO}(\xi) \Psi(\mathbf{x}; \xi). \quad (54)$$

Then, it is enough that $\hat{H}(\hat{q}_e, \xi)$ be bounded from below and self-adjoint to get a complete electronic spectrum $\{W_k^{a-BO}(\xi)\}$. This statement is fully valid for the a-BO framework. Now, let us look for some characteristics.

Consider the case where two stationary geometries, $\xi^{(i)}$ and $\xi^{(j)}$, are obtained with the help of algorithms based on Eq. (54) and such that $\xi^{(i)} \neq \xi^{(j)}$. A comparison with Eq. (45) would show that

$$\lim_{\xi \rightarrow \xi^{(i)}} W_i^{\text{a-BO}}(\xi) \text{ will be } \lim_{\xi \rightarrow \xi^{(i)}} W_i^{\text{a-BO}}(\xi) = U[\Omega_i; \xi^{(i)}]. \quad (55)$$

Consequently,

$$\lim_{\xi \rightarrow \xi^{(i)}} \Psi(\mathbf{x}; \xi) = \Phi_i(\mathbf{x}; \xi^{(i)}). \quad (56)$$

This result is important taking into account that Eq. (54) is not an eigenvalue equation because it parametrically depends upon the nuclear configuration. Eq. (56) ensures that at a fixed stationary nuclear configuration, Eq. (55) at $\xi = \xi^{(i)}$ is self-adjoint yielding an electronic spectra tied to that geometry.

Note that $\Phi_i(\mathbf{x}; \xi^{(i)})$ must be equal to the diabatic basis function $\Phi_i(\mathbf{x})$. We keep the same symbol because $\Phi_i(\mathbf{x}; \xi^{(i)})$ and $\Phi_i(\mathbf{x})$ are characterized by the same NP. They are actually solutions to the same Hamiltonian.

5.1.2. a-BO potential energy functions

For the exact quantum theory, the eigenvalue cannot change with the nuclear configuration space points. Starting from $\Phi_i(\mathbf{x}; \xi^{(i)})$ when the nuclear configuration is moved away, $\xi^{(i)}$, the quantum label should be invariant. This must be true because $\Phi_i(\mathbf{x}; \xi)$ is characterized by the NP that is identified with the i -label; however, the energy eigenvalue changes.

Thus, the functional $W_i^{\text{a-BO}}(\xi)$ must be used with the constraint of NP invariance to construct a framework compatible with exact QM. In such a case, one would have the inequalities: $W_i^{\text{a-BO}}(\xi) \leq U[\Omega_i; \xi]$.

According to the present theory, the abstract BO energy functional yields a lower bound to the pure diabatic functional.

The set of eigenvalues for a given attractor geometry $W_i^{\text{a-BO}}(\xi^{(k)})$ are ordered so that a comparison is possible with those belonging to a different attractor that is already ordered $W_j^{\text{a-BO}}(\xi^{(k+1)})$. Assume that the lowest energy attractor is $k=0$ so that

$$W_{i=0}^{\text{a-BO}}(\xi^{(0)}) \leq W_{j=0}^{\text{a-BO}}(\xi^{(1)}) \leq \dots \leq W_{j=0}^{\text{a-BO}}(\xi^{(k)}) \leq W_{j=0}^{\text{a-BO}}(\xi^{(k+1)}) \leq \dots \quad (57)$$

The order shown by eigenvalues is obviously different when any two attractors compared for the electronic basis functions show characteristic NPs independently from the external nuclear potential. Thus, the eigenvalue $W_{i \neq 0}^{\text{a-BO}}(\xi^{(0)})$ can be mapped to the lowest eigenvalue of a particular attractor, say $k+1$. Thus the lowest energy state maps as $W_{i=0}^{\text{a-BO}}(\xi^{(k+1)}) \Leftrightarrow W_{i \neq 0}^{\text{a-BO}}(\xi^{(0)})$ and similarly takes $W_{i=0}^{\text{a-BO}}(\xi^{(k+1)})$ that can be mapped onto the excited state in the attractor $\xi^{(0)}$, for example, $W_{i \neq 0}^{\text{a-BO}}(\xi^{(0)})$, the measure being the NPs so that with NP conserved: $W_{i \neq 0}^{\text{a-BO}}(\xi^{(0)}) \Leftrightarrow W_{i=0}^{\text{a-BO}}(\xi^{(k+1)})$. Joining with straight lines if the attractors have different geometry these

lines would cross. For systems where two different eigenfunctions show the same attractor geometry, both are eigenstates for the same semiclassical Hamiltonian. This situation suggests a check of gradients on the excited states to sense directions of change.

At this point, it is worth noticing that where you use a computing algorithm that forces a mixing of states in a neighborhood of a crossing, the change would appear smooth and with at least one negative curvature (saddle point). For example, one-determinant functions, characteristic of the Hartree–Fock model, do produce such a type of profile. While the saddle point might be a computing artifact, its location is very useful as a sensor signaling a mixing of states that must be properly handled.

The energy crossing of two node-constrained a-BO states can be accidental; it has no physical consequences. The linear superposition of Eq. (51) can qualitatively change to produce a chemical change if and only if an external field can couple the states as it was discussed in the preceding sections.

The node-constrained a-BO is a natural framework where k -states reactivity mechanism frameworks can be developed to study chemical reactions mechanism with a methodology as near as it is possible to a rigorous quantum mechanical approach (see Sections 5.2 and 6).

To sum up, the a-BO class I scheme can deliver a quantum state depending on electronic and nuclear configuration that will have a structure similar to Eq. (51), namely, a linear superposition over the diabatic basis set multiplied by amplitudes that depend upon the nuclear configuration. Take $\mathbf{A} = \mathbf{0}$ and rewrite Eq. (51) as follows:

$$\Phi(\mathbf{x};\xi) = c_0(\xi)\Omega_0(\mathbf{x}) + c_2(\xi)\Omega_2(\mathbf{x}) + c_3(\xi)\Omega_3(\mathbf{x}) + \dots$$

In a finite basis, $\Phi(\mathbf{x};\mathbf{X})$ stands for $\Phi^{\text{a-BO}}(\mathbf{x};\xi)$. The limit given by Eq. (56) connects the a-BO scheme to our GED scheme in a clear manner.

The quantum state $\Phi^{\text{a-BO}}(\mathbf{x};\xi)$ differs radically from the standard BO scheme.

5.2. Class II models

From its inception by Schrödinger [21], the wave function for a 1-system intended to describe the particles making up for the material system. A charge density at a point in real space is proportional to $\Psi^*(\mathbf{x}',\mathbf{X}',t') \Psi(\mathbf{x}',\mathbf{X}',t')$ at time t' and the probability language describes this product as the probability of finding electron 1 at $\mathbf{x}_1'$, electron 2 at $\mathbf{x}_2'$, till electron n at $\mathbf{x}_n'$, and nucleus 1 at $\mathbf{X}_1'$ until m at $\mathbf{X}_m'$. This descriptive language would be compatible with the abstract one if an isomorphism were established between both types of spaces. If we leave both space to differ only in their descriptive properties and the full domains coincide otherwise, then nothing new emerges out of them. The interpretation of the wave function becomes a matter of social agreement. The large numbers of interpretations over-viewed by Laloé [23] show the difficulties a particle model encounters.

The particle representation of wave functions intends to describe electrons and nuclei via the configuration space understood as the set of particle position vectors with respect to an I-frame. For 1-systems with more than one nucleus, the electron configuration space is made a function of the nuclei positions thereby leading to electronic basis sets changing in nuclear configuration space. Formally, there is an implicit change: $\mathbf{x}' \rightarrow \mathbf{x}'(\mathbf{X})$ (or $\mathbf{x}'(\xi)$) that would introduce a foreign element to the quantum mechanical scheme. Such model implicitly uses at least a number of I_k -frames while the 1-system must use only one. Models of such kind are described as class II models.

The abstract BO approach and the GED schemes can be used to construct class II schemes. One would get standard BO scheme as a result in the first case. The difference between class I and II is fundamental because the electronic configuration space in the latter becomes tied to the nuclear space, namely, $\mathbf{x} \rightarrow \mathbf{x}(\mathbf{X})$; for instance by introducing the atoms-in-molecules way of constructing base states. This possibility is examined below (see also Section 6).

In class II models, one introduces a number of I_m -frames covering the total number of nuclei. Cluster subsets belong to this class of systems albeit the number of I-frames required would depend upon physical situations to be examined.

Class II systems for which the number of I-frames equals the number of nuclei are akin to molecular systems.

5.2.1. Class II GED scheme

To get the class II model, first, take the exact quantum mechanical ansatz $U[\Omega_j]$ and transform into a semiclassical one by replacing $\langle \mathbf{X} \rangle_{j(0)}$ by the fixed geometry $\mathbf{X}_{j(0)} = \mathbf{X}^{(j)}$ so that the functional $U[\Omega_j; \mathbf{X}^{(j)}]$ corresponds to a configuration nuclear space isomorphic to nuclear position vectors in real space, and designate it simply as ξ : $U[\Omega_j; \xi]$. The diabatic electronic basis function $\Omega_j(\mathbf{x})$ is now evaluated in the electronic configuration space.

The variational principle applied to $U[\Omega_j; \xi]$ with the constraint to be evaluated at the equilibrium geometry $\xi^{(j)}$ leads to the Schrödinger-like equation:

$$\left\{ \hat{H}_e(\mathbf{x}') + V_{Ne}(\mathbf{x}', \xi^{(j)}) + V_{NN}(\xi^{(j)}) \right\} \Omega_j(\mathbf{x}') = U[\Omega_j; \xi^{(j)}] \Omega_j(\mathbf{x}'). \quad (58)$$

Because $\xi^{(j)}$ is a fixed quantity, $U[\Omega_j; \xi^{(j)}]$ is a well-defined energy eigenvalue. Thus, if the j -th electronic basis function can be approximated by $\Omega_j(\mathbf{x}')$, the model so obtained is a diabatic representation.

For all electronic BSs showing a nuclear geometry $\xi^{(j)}$ corresponding to the 1-system structure, an equation similar to Eq. (58) would hold. The spectra appear to be bounded from below.

5.2.2. BO approach

Applying a procedure similar to the one used to get a class II GED [Eq. (58)] in the abstract BO scheme, we obtain the BO equations:

$$\hat{H}(\mathbf{x}';\xi)\Psi(\mathbf{x}';\xi) = W^{\text{BO}}(\xi)\Psi(\mathbf{x}';\xi). \quad (59)$$

The primed variables indicate that one might be using a multiple I-frame model.

As we discussed already for the abstract model, at the stationary geometry, the lowest electronic eigenvalue defines a fixed Hamiltonian that coincides with the one for the GED scheme. In the limit one gets the result

$$\lim: \xi \rightarrow \xi^{(i)} \quad \text{then} \quad \Psi(\mathbf{x}';\xi) \rightarrow \Psi(\mathbf{x}';\xi^{(i)}) = \Omega_i(\mathbf{x}'). \quad (60)$$

This results from a comparison of Eqs (59) and (58). Implicit in this result is the strict equality:

$$\Psi(\mathbf{x}';\xi^{(i)}) = \Psi_i(\mathbf{x}';\xi^{(i)}) = \Omega_i(\mathbf{x}'). \quad (61)$$

Only at the stationary geometry, one should interpret the lowest root as a quantum number. In solutions obtained at arbitrary geometry, for example, ξ' and ξ'' say $\Psi_i(\mathbf{x}';\xi')$ and $\Psi_i(\mathbf{x}';\xi'')$ the label i can be related to mathematical functions with totally different NPs. The reason for this situation is given by the algorithm implicit association with the electronic configuration space to nuclear arguments: $\mathbf{x}' \rightarrow \mathbf{x}'(\xi')$. This latter is a translation of the model assigning electronic functions to each nucleus. If we move it as one changes nuclear geometry, no theory will predict what might be happening.

In this perspective, standard BO model can be expressed by wave functions presenting the form $\Psi(\mathbf{x}'(\xi);\xi)$. This is equivalent to use atomic orbitals planted at the nuclei (see Section 6).

If we keep invariant the electronic configuration space, it is interesting to relate both schemes at arbitrary nuclear configurations. This can be done if we assume that all stationary diabatic or adiabatic nuclear structures have been calculated. Then, as we mentioned already,

$$\Psi(\mathbf{x}';\xi) = \sum_k C_k(\xi;\Psi)\Omega_k(\mathbf{x}'). \quad (62)$$

The structure of this equation must be clearly understood. The term $C_k(\xi;\Psi)\Omega_k(\mathbf{x}')$ contains an already fixed element, the basis set $\Omega_k(\mathbf{x}')$, and the variable one that shows a dependence on the nuclear configuration space and stands for a sort of projection of the quantum state $\Psi(\mathbf{x}';\xi)$. The quantum state is independent of the domain you select for the electronic configuration space. The amplitudes are obtained from Eq. (59) at the selected point of the PCB. A secular equation of dimension larger than the one shown in Eq. (7) is obtained.

As a matter of principle, this formal solution does not by itself change the amplitudes thereby leading to a quantum mechanical description of the chemical process. If one selects an algorithm choosing the lowest energy eigenvalue along the RC, a change will be sensed that is produced by the algorithm, of course. This part of the problem will be discussed in the following section. However, to sense the nature of the puzzling situation, we must remind the meaning of the adiabatic concept. This simply means that the energy spectra can change in absolute value but crossings are not allowed. Therefore, starting from a quantum state in a neighborhood of reactants by introducing changes in the PCB geometry, the wave function for products cannot be accessible from reactant states. As we have seen, approaching the product attractor geometry, the ordering of eigenvalues will change and at the product state the ordering has changed against the adiabatic motto. It is not enough to state that one is always on a ground state structure because the character of NP has changed. To say that electrons follow the nuclei is not a quantum mechanical statement. The puzzle arises from the actual calculations of the function that magically produces the change. In Section 6 below, we take up an analysis to clear up some aspects of this conundrum.

6. THE AO ANSATZ: NODAL PATTERNS

The method of planting atomic-like orbitals or special functions (Gaussians) at the position of the nuclear charges was born with quantum chemistry [24] and during all its existence has been a blessing and a curse.

A blessing the atomic orbitals were because the algorithms, Hartree–Fock (LCAO-MO) and Heitler–London (HL) [25,26], opened royal paths to accurate numerical calculations of molecular systems. Pioneering calculations of the hydrogen molecule at the birth of QM gave a clear hint that descriptions of chemical bond and reaction processes could be handled quantitatively.

A curse the atomic orbitals were because we never got to understand abstract and fundamental aspects of molecular QM that have emerged later on, let alone the daunting work required to construct BSs for 1-systems with $n > 1$. The implicit mathematical form can be opened to simply read $\mathbf{x}(\xi)$. The electronic configuration space is changing with the positions of the atomic centers.

In the AO-framework, there are two blends of many-electron functions that have caught attention from the beginning, namely, valence bond (VB) and molecular orbital (MO) methods. You may consult Ref. [24] and the challenging paper by Clementi and Corongiu [25]. Full computing technologies have evolved to overcome limitations shown by these seminal schemes. Multiconfiguration, coupled clusters, and many other fine

methods have been developed. Yet these methods heavily rely on particle model that bring images of electron distribution that are not akin to the basis and wave functions as treated here but are expectation values of density operators. The methodology is sometimes biased by pictures such as the BO adiabatic one: electrons following nuclear motion. The latter is obviously built in as the AO is planted at nuclei and is displaced with them.

We will formally use VB and/or MO schemes to illustrate the main points concerning NPs. For an overview of many important methods, see Ref. [26].

6.1. Nodal patterns

Independently from the particular way BSs are calculated, they should show NPs characterizing them. Thus, given a 1-system, the ground electronic state has the least node numbers. Excited electronic states add up nodes as energy increases.

The semiclassical scheme permits use of the nuclear (N) center to discuss NPs with the help of chemical graphs. For two N-centers without bonding lines, there is (at least) a nodal plane separating them. The set of nodal planes characterizes the chemical graph; in other words, there must be antibonding interactions there. One can think of the system shape as the one minimizing the antibonding interaction (repulsion). Once it is deformed, work against the antibonding field would set up repulsions. Another role has been pointed out by Aparicio et al. [27].

The NP idea is simple to implement. The number and type of nodal planes must be conserved if a given state is to serve as a BS. This would be a typical diabatic state. In terms of MO ansatz, the number and quality of unoccupied MO must be conserved if the BS is to keep identity.

For a two-I-frame system, real space collects them both so that they can be separated at infinite large distance. Obviously, direct products of basis functions are not sufficient if the 1-system representation must be explicitly taken into account. The 1-system may show a bond state at the place of a nodal plane for the aggregate. To link with fragment states, the global basis function must have a nodal plane between any two centers belonging to different I-frame systems. The assignment of degrees of freedoms (electrons as it were) will break standard rules for dissociation states; here lies a problem that can be handled with adequate multiconfiguration procedures.

More generally, in real space any two PCB centers, each one belonging to a different I-frame system, must show up a nodal plane with the normal vector located along the direction relating both PCB centers if they are to be handled as a semiclassical quantum system. There will be as many nodal planes as pairs of PCB centers connecting both I-frame systems. Both fragments appear to be “antibonding” to use a language common to most quantum chemists. The D-PEs should reflect these NPs.

6.1.1. Nodal pattern conservation: MO methods

Quantum chemistry: the simplest MO scheme constructs 1-electron states as linear superpositions of atomic orbital or mathematical functions center at nuclei. Without much detail, we have the symmetric and antisymmetric pair of MO. The standard procedure is to use the symmetric MO because it yields the lowest energy. No quarrel with this. Let us come back to the scattering case. The question is fulfillment of the nodal character because the states are prepared at infinite (very large) distance in real space and then include them with the 1-system states. In this case, we ought to employ the antibonding orbital all the way up. The potential energy of course goes up compared to the separated pair. No standard package does this as a natural choice. One has to be careful once computing of two or more I-frame systems in real space because they must be prepared as a semiclassical quantum mechanical one and not in a supermolecule view. This results from the specific algorithm $\mathbf{x}(\xi)$ one is using.

NP conservation forces a full control of relevant MOs. They are relevant not because of energy but due to symmetry, including local symmetry. Next section illustrates this point.

6.1.2. Isomerism and nodal patterns: ethylene

Ethylene ground state has two virtually irreducible electronic structures where nodal planes would appear at a $\pi/2$ angle. This means that there is a choice that can be made by selecting the nodal plane, for instance, perpendicular to the (1,3)-plane when the 3-axis is chosen along the C—C vector. One could have chosen the (2,3)-plane as well. In a representation of molecules as objects, the choice is either/or, disjunctive. For a quantum mechanical representation in terms of quantum states, there cannot be a disjunctive choice. The result is fairly illustrative of the novelty QM may bring to chemistry.

Let us analyze this issue step by step within the class I semiclassical framework. Start with the two diabatic BSs. The external PCB differentiate in real space these states, one lies on the (1,3)-lane and the other on the (2,3)-plane. The ground electronic structure of each BSs is spin singlet (closed shell).

The sigma PCB framework is planar and must be located at either plane as describe above for the ground state. Observe that here there is no symmetry operation on the PCB structure allowing a direct electronic mapping, an example of such operation would be a rotation by $\pi/2$ of the whole PCB. Because the PCB acts as an object in real space, its rotation does not entail the rotation of the diabatic basis function for which energy was a minimum. The D-PE surface shows energy well above the stationary one after $\pi/2$ rotation. Now, how do we know that this operation is not a symmetry operation? Perform the equivalent operation by rotating the frame in the inverse sense, the base functions correspond to this initial state. The energy of the system cannot depend upon such rotation, which implies that no

differences in energy would be evident. This result contradicts the previous one that is presumed to be equivalent. One concludes that such a type of rotation is not a symmetry operation in the diabatic basis, actually one gets two Marcus-like profiles.

If we label the hydrogen atoms, looked along the 3-axis, they are in an eclipsed position: 1-1' and 2-2'. The upper CH₂ group labels are 1 and 2, for the lower group 1' and 2'. The distance (1-1') is shorter than (1-2'). The $\pi/2$ -rotation just discussed does not change the internal labeling and the PCB-labeled distances do not change either.

However, the PCB permits to define an RC. This is a device allowing a connection between stationary geometries determined by *different* electronic BSs. For this case, a disrotatory displacement of one CH₂-fragment with respect to the other would relate the geometry with a change in the internal distances. Now, distances (1,1') and (2,2') are changed into distances (1,2') and (2,1'). Such a replacement is comparable to a *cis-trans* change if the *geometric positions* were somehow distinguishable.

Here pops up the fundamental difference a class I GED scheme with respect to standard class II schemes built on AO ansatz. The RC or any other coordinate set built with the PCB cannot change the electronic BSs. On the other hand, linear superpositions over the relevant BSs do change as a function of the RC. There is a problem in front of us: (i) nature of the relevant BSs and (ii) coupling mechanisms.

Controlling the PCB permits eliciting BSs once geometry optimization is carried out. Notwithstanding, the nature of the electronic structure in class I schemes cannot be altered by the changes of PCB. This is difficult to understand if one sticks to the class II or III semiclassical schemes with the AO ansatz: $\mathbf{x}(\xi)$.

The geometric change along the RC permits relating arrangements *cis* with *trans*: rotate by $\pi/2$ in a clockwise direction the upper CH₂ group and $\pi/2$ anticlockwise the lower CH₂ group and we get the geometry of the *trans*-“conformer.” But the diabatic electronic structure cannot and does not change. Invert the rotation directions to complete the D-PES. Calculate with the diabatic basis function orthogonal to the previous one. Energetically the corresponding states will cross at an angle $\pi/4$.

At $\pi/4$, there are two nodal planes, one for each CH₂ group with the normal vectors making a $\pi/2$ angle; rotating in the opposite direction there are two nodal planes at $-\pi/4$. For this geometry, there is a triplet electronic state as ground state. Also, there is an excited spin-singlet state based on the same set of orbitals. The initial double bond is gone which is well-known textbook information [24]. The difference might be in the nodal planes description.

There is a third spin-triplet state. Use the PCB to dig out the electronic structure. We know from simple MO theory that the π -double bond is “broken.” The space part must be antisymmetric because the spin component is symmetric under permutation.

Besides the displacement of the sigma framework between planes (3,1) and (3,2), the *cis-trans*-isomerism in ethylene put in action four diabatic PESs. Three spin-singlet structures and a spin triplet. Two ground state singlet states cross well above the energy of the triplet and associated singlet.

Which is the electronic mechanism corresponding to a *cis-trans* isomerism? Because in first order a triplet with a singlet states constructed on different orbitals do not interact even introducing a spin-orbit (S—O) coupling, the excited singlet state must share orbitals with the triplet; these states do interact with S—O coupling.

The energy threshold is located at the crossing of the GS-singlet with the triplet, and the excited state permits the opening of the triplet state. We use the qualitative picture discussed around secular Eq. (7). State 2 is the triplet, state 3 is the excited state, and state 1 the *cis*-conformer. Excitation with EM radiation (infrared) until getting at about the crossing energy level is required. Quantum mechanical evolution via S—O interaction to get amplitudes different from zero at the triplet is the next step. The channel toward the *trans*-conformer opens at the very moment amplitude is set up at the triplet. A coherent quantum state assisted by the excited singlet explains the opening of the product channel. The remaining part leading to relaxation at the *trans*-channel is qualitatively understandable.

An important point must be emphasized: the S—O coupling may be very small but what is relevant is the flux of amplitudes at resonance. There is no need to generate an effective potential energy surface. A chemical reaction, according to the present theory, is a qualified quantum mechanical process. The PE surfaces are tools to help calculations and help visualizing things. A chemical reaction is not a wandering over such mathematical objects, albeit the picturesque description may catch the imagination.

We have given a partial answer to the query (i), namely, there are at least four diabatic BSs, and to query (ii), there is need for two interaction operators – the standard EM coupling between singlet states and S—O between excited singlet and parent triplet.

One may wonder whether there is something for pure chemists along mechanistic pictures. There is one. Let us give some clues.

The electronic structure of $\pm\pi/4$ rotated systems has a spin triplet as ground state and orbital angular momentum $L=2$, it is a Δ -state. Look from the 3-direction the upper nodal plane normal makes with the lower nodal plane normal at a $\pi/2$ angle. In a projection, they look like a “d-orbital.” In fact, because the dis-rotation can also be done with the opposite sign, there is a virtual “d-orbital” at each center. This is a qualitative picture that may help sensing the complexity of the electronic structure.

The amplitude different from zero at the triplet state is mediated by a second excited singlet state. But the key is the production of nonzero amplitude at the BS showing a broken bond. The passage to the second ground state

singlet, the isomer, is done similarly, the triplet being commonly shared. The relevant BSs amount to five if the triplet is shared, six otherwise.

This triplet state may be the root state (ground state) in a process designed to “break” the single C—C bond. For that there is need of a triplet state, where such a bond is no longer in act, and a parent-excited singlet state. The spin multiplicity will increase to $S=2$. This state would correspond to two triplet methylene radicals referred to one-I-frame, while a chemical reaction where each one is described with its own I-frame would correspond to a biradical (bimolecular) reaction.

6.1.3. Scattering and entangled states

For bimolecular and termolecular reactions, many-I-frames quantum systems allow for reacting beams description (diffusion collision) leading to a one-I-frame product quantum state possibly via activated complexes. The total number of electrons and nuclei is conserved, only quantum states change.

The many-I-frames systems have classical physics edges producing some peculiarities in the setup of computing schemes. One QM aspect appears at the level of BSs, namely, those belonging to one-I-frame and those to many-I-frame systems coexist. Thus, the basis set would include both types even if the many-I-frame case has definite classical elements to the extent I-frames’ origins are located in real space. The problem for a quantum description is that one-I-frame and many-I-frames are noncommensurable unless we do something to put on common descriptive levels.

A simple example would help presentation: Two hydrogen atoms are prepared for a scattering experiment. The problem is a calculation of possible quantum states after interaction. To the quantum states of this two-I-frame system, one should have in mind the one-I-frame system $|H_2\rangle$ with its electronic quantum states; this latter includes $|H_2^+\rangle \otimes |\text{continuum 1-e-state}\rangle$. The two-I-frame system has an irreducible classical physic element. They stand for two non-interacting subsystems. The system can be prepared in an infinite number of internal quantum states located anywhere in a laboratory. For all practical cases, the configuration space implicitly depends upon where the I-frame is located; thus, the one-I-frame system description must be adapted to this situation.

Now select the common origin according to the scattering geometric setup and refer the electronic configuration space of the many-I-frames is shifted so that a semiclassical model is adopted; consider the j -th I-frame fragment, the electronic configuration space $\mathbf{r}$ is referred now with respect to the new global origin to get $\mathbf{x}(\mathbf{R}_j) = \mathbf{R}_j + \mathbf{r}$. The electronic degrees of freedom correspond to the j -th system’s number of electrons. The complete electronic configuration space appears partitioned:

$$(\mathbf{x}_1, \dots, \mathbf{x}_{k1}, \mathbf{x}_{k1+1}, \dots, \mathbf{x}_{k1+k2}, \dots, \mathbf{x}_{k1+k2+1}, \dots, \mathbf{x}_{k1+k2+km}) \Leftrightarrow [\mathbf{x}(\mathbf{R}_1), \mathbf{x}(\mathbf{R}_2), \dots, \mathbf{x}(\mathbf{R}_m)].$$

In this case, there are m -I-frames independent from each other but ordered in accord with the one chosen for the one-I-frame system, the sum total

$k_1+k_2+k_m$ of degrees of freedom tuned to the one-I-frame system. From the perspective of the latter, the configuration space for the independent m -I-frames looks as a class II or class III semiclassical model, but we have both levels referred to one-I-frame.

There is an important caveat: the one-I-frame system must be handled as semiclassical in so far nuclear configuration space is concerned to suture with the asymptotic states. For the one-I-frame system, there might be bonding situations (GED attractors) one can relate to asymptotic state fragments. Now, when constructing the asymptotic basis functions commensurate to the one-I-frame semiclassical system, enforce nodal planes between those nuclear centers belonging to different fragments, this trick would do the job. This procedure is well adapted to the linear superposition representation of the global quantum state, do not let the program fill the orbitals using energy criterion only. The bonding states, if any, are always there as base states for the one-I-frame system, so the focus is not on objects but on quantum states.

For dihydrogen, let us take the hydrogen atom ground electronic state $^2S_{1/2}$. Spin states can be chosen as simple product $\alpha\alpha, \beta\beta, \beta\alpha$, or $\alpha\beta$ because beam sources are located in real space. Ordering imparted by the beams is implicit in the product order, and this one is determined by the experimenter who chose beam directions. At laboratory space, the beams cross at a point selected as origin for a third I-frame. Reciprocal space vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ indicate the direction of the beam I-frames, for example, in a head-on approach with $\mathbf{k}_2 = -\mathbf{k}_1$.

Before interaction, there are four possible simple products spin states an experimenter may prepare:

$$\begin{aligned} &|^2S_{1/2}; \mathbf{k}_1\rangle|^2S_{1/2}; \mathbf{k}_2\rangle|\alpha\rangle|\alpha\rangle, |^2S_{1/2}; \mathbf{k}_1\rangle|^2S_{1/2}; \mathbf{k}_2\rangle|\beta\rangle|\beta\rangle \\ &|^2S_{1/2}; \mathbf{k}_1\rangle|^2S_{1/2}; \mathbf{k}_2\rangle|\alpha\rangle|\beta\rangle, |^2S_{1/2}; \mathbf{k}_1\rangle|^2S_{1/2}; \mathbf{k}_2\rangle|\beta\rangle|\alpha\rangle. \end{aligned} \quad (63)$$

The spin state can be chosen at will between these alternatives. The spin quantization axis is the same for both beams. Note that one can locally change this condition with external magnetic fields and gradients. If no interaction is present, in a classic perspective, the internal quantum states of the beams are unchanged. That the fragment system has not yet interacted is shown by the fact that for the total spin operators, $\hat{S}^2$ and $\hat{S}_3$, these basis functions are eigenfunctions of $\hat{S}_3$ but not $\hat{S}^2$.

For the most elementary case, the following quantum base states can be constructed in the direct product basis set with obvious notations (subindex indicates the beam):

$$\begin{aligned} &|1s_1(1)\rangle|\alpha\rangle \otimes |1s_2(2)\rangle|\alpha\rangle, |1s_1(1)\rangle|\beta\rangle \otimes |1s_2(2)\rangle|\beta\rangle \\ &|1s_1(1)\rangle|\alpha\rangle \otimes |1s_2(2)\rangle|\beta\rangle, |1s_1(1)\rangle|\beta\rangle \otimes |1s_2(2)\rangle|\alpha\rangle \\ &|1s_2(1)\rangle|\alpha\rangle \otimes |1s_1(2)\rangle|\beta\rangle, |1s_2(1)\rangle|\beta\rangle \otimes |1s_1(2)\rangle|\alpha\rangle \\ &|1s_2(1)\rangle|\alpha\rangle \otimes |1s_1(2)\rangle|\alpha\rangle, |1s_2(1)\rangle|\beta\rangle \otimes |1s_1(2)\rangle|\beta\rangle. \end{aligned} \quad (64)$$

Arrange these elements as a fixed 1×6 row vector. Let the initial quantum state be the column vector $[1 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0]$, namely, two alpha spin ground state H-atoms. Note that you can make a different choice (e.g., $[0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 1]$). If, at the interaction center, there is no spin-flipping external field, the quantum state is unaltered. The detectors put along beam directions will signal α -states for our first choice. For the quantum state $[0 \ 1 \ 0 \ 0 \ 0 \ 0 \ 0]$, detectors will signal β -states. In fact, we have used this representation because permutation symmetry has not been allowed for. Including it one would have written the basis set as separate factors:

$$\text{Space basis set } (|1s_1(1)\rangle|1s_2(2)\rangle, |1s_2(1)\rangle|1s_1(2)\rangle) \quad (65)$$

$$\text{Spin basis set } (|\alpha\rangle|\alpha\rangle, |\beta\rangle|\beta\rangle, |\alpha\rangle|\beta\rangle, |\beta\rangle|\alpha\rangle). \quad (66)$$

Observe what space permutation could have done at configuration label, namely, $|1s_1(2)\rangle|1s_2(1)\rangle$ instead of $|1s_2(1)\rangle|1s_1(2)\rangle$. It is understood that for beam states $|\mathbf{k}_1\rangle$ and $|\mathbf{k}_2\rangle$, the sum $\mathbf{k}_1 + \mathbf{k}_2$ is conserved so that individual terms can change by interaction with $\mathbf{k}'_1 + \mathbf{k}'_2$ that equals the initial sum. The change of beam labels is permitted.

Quantum interaction produces a profound change to the initial beam states. The rules valid for the one-I-frame system must be applied to the system of outgoing beams: permutation symmetry for fermion states.

With the above basis sets, the space antisymmetric state fulfills the node constraint: from Eq. (64), one gets $(1/2)^{1/2}[0 \ 0 \ 1 \ -1 \ 0 \ 0]$ that is antisymmetric under permutation:

$$\left(\frac{1}{2}\right)^{1/2} (|1s_1(1)\rangle|1s_2(2)\rangle - |1s_2(1)\rangle|1s_1(2)\rangle). \quad (67)$$

For fermion states, the spin state must be symmetric under beam label permutation, Eq. (65):

$$\left(\frac{1}{2}\right)^{1/2} \begin{bmatrix} 1 & 1 \end{bmatrix} = \left(\frac{1}{2}\right)^{1/2} (|\alpha\rangle|\beta\rangle + |\beta\rangle|\alpha\rangle). \quad (68)$$

The base state satisfying the conditions imposed to two independent beam states is to become an entangled state: space entangled and spin entangled [Eqs (67) and (68)].

Entangled states are one of the fundamental novelties introduced by QM. The particular case of an antisymmetric spin state $(|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle)$ must combine with a symmetric product of space function:

$$\frac{|1s_1(1)\rangle|1s_2(2)\rangle + |1s_2(1)\rangle|1s_1(2)\rangle}{\sqrt{2}} \frac{|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle}{\sqrt{2}}. \quad (69)$$

This state is rejected because no nodal plane between the space function is present. A fundamental bonding state belongs to the bound system as a true one-I-frame case.

The rule is that incorporation of two asymptotic states (fragments) into the one-I-frame system requires the construction of at least spin-entangled states involving spin base states from the different fragments with a space term introducing nodal planes between the fragments.

It remains to find a mechanism to put amplitude over the ground electronic state of the one-I-frame system: $|1\rangle = |H_2^1\Sigma_g^+; v'\rangle$, where v' stands for a vibration base state. The asymptotic states are represented by Eqs (67) and (68), $|2\rangle = |\Psi(S=1, M_S=0)\rangle$, and a third state $|3\rangle = |H_2^1\Sigma_u^+\rangle$. Thus, $C_1|1, v'\rangle + C_2|2\rangle + C_3|3\rangle$ for the interaction of two hydrogen atom having $M_S=0$, $C_1=C_3=0$, and $C_2=1$, there must be an operator mixing states $|2\rangle$ and $|3\rangle$ to get a spin-singlet amplitude and another operator that opens a nonzero amplitude at $|1\rangle$, thereby helping to set up amplitude at the molecular product.

The case discussed above is oversimplified. The point is that the electronic spectra of the global system which is coupled by external fields provide the basic elements to construct a computing algorithm. A coupling operator with an external EM vector potential and a spin-orbit operator would do the job. The difficulty in getting amplitude at the ground state $|H_2^1\Sigma_g^+; v'=0\rangle$ resides in the symmetry of the nuclear system.

If we remember the initial nonentangled state, once quantum interaction has taken place, the result is an entangled state for which there is no way to write it as a simple product again. Quantum correlations are unavoidable. This is a quantum physical law.

Retain one important aspect: one would require three electronic states to change amplitudes from asymptotic states (bond broken in chemical language) into the bonding base state, the antibonding showing a nodal plane. This count will be used in what follows.

6.2. Mapping a chemical reaction D-PES

Hilbert space does not include object description, only quantum states. Let us consider again the set of chemical graphs: for example, $|H_2CO\rangle$, $|H_2CO, n\pi^*, S=1\rangle$, $|H_2CO, n\pi^*, S=0\rangle$, $|H_2\rangle|CO\rangle$, $|H_2O\rangle|C\rangle$, and $|HCO\rangle|H\rangle$. The composition of the 1-system is invariant, but in laboratory space there can be aggregates or molecules as indicated by the basis kets.

The simple 1-system is represented here by three states $|H_2CO\rangle$, $|H_2CO, n\pi^*, S=1\rangle$, and $|H_2CO, n\pi^*, S=0\rangle$. We will discuss the cases $|H_2\rangle + |CO\rangle$ and $|H_2:CO\rangle$ that correspond to the semiclassical model. The basic approximate configuration of CO is given by $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$ and dihydrogen $(\sigma_g 1s)^2$. To include 1-system states, the commensurate combined states must show antibonding states signaled with $\dot{\cdot}$. There are two C:H

antibonding states or two nodal planes separating C from H. Of course, there are two more nodal planes between O and H. If we replace a bonding state for an antibonding one in H_2 and replace the H:C by bonding configurations, we prefigure the 1-system state $|H_2CO\rangle$ with a geometry far from the equilibrium one. How do we couple such states? We have some elements from the preceding case, but before that let us examine some elementary situations.

Select 3-direction along the C—O axis and an origin near C to fix ideas. There are two planes (1,3) and (2,3) perpendicular to each other. The 3-axis intercepts at the middle of H—H axis so that one can put the motif H—H on either of these two planes. In fact, this motif may occupy any position on the plane perpendicular to 3-axis. As for ethylene, two equivalent planes may contain the motif HHCO. A rotation symmetry around 3-axis is present for the independent molecules CO and H_2 . Rotating HH by an angle $\pi/2$ around 3-axis, the “molecular motif” changes from one plane into the other. Let us “break” the π -bond of CO to get a triplet state by using angle $\pi/4$ for the carbon center gets a nodal plane with one electron, do the same (virtual) to the O-center in a disrotatory manner, $-\pi/4$ to put a nodal plane, their normal vectors form a $\pi/2$ angle. Thus, a triplet state can be formed along a (virtual) RC. For the hydrogen molecule we have seen in the preceding section on scattering that an asymptotic triplet spin state [(cf. Eq. (68)] in conjunction with an excited singlet state is required to couple the singlet spin entangled with separated hydrogen atoms.

To theoretically prepare the configuration space required to set up a reactive linear superposition, we need at least $3+3+3+3$ states as three bonds enter the chemical game; the count is one H—H, two C—H, and one C—O entanglement to reshuffle. This is a minimal configuration space that would allow for a deeper understanding of this chemical reaction mechanism.

A description can be given based on more elementary terms. Consider two states where you have control over the NP. Take a simple case where the (H)OMO in NP(2) ($H-H::CO$) would appear as (L)UMO for NP(1)($H:HC-O$). The H—H bonding appears as antibonding in NP(1) while the two CH antibonding in NP(2) are displaced by two H—C bonding. At crossing you suspect they have the same energy so that you cannot have an answer if you use a standard package. If these states (orbitals) were the only differentiation, you may force the calculation to fill the HF space fulfilling NP conservation. Of course, you were monitoring the (L)UMO in NP(1) that after crossing would move down in energy below the (H)OMO in NP(1), all other things being equal. You would have obtained the nearest to diabatic potential energy curves by forcing the orbital filling not with energy but taking the nodal plane symmetry. The reaction we have studied, $H_2 + CO$ leading to formic aldehyde (H_2CO), can be described this way and eventually calculated. In H_2CO , there is an antibonding between the hydrogen centers while in the reactant there is a bonding situation. The C in

CO must have nodal planes with the hydrogen centers and a supermolecule (one-I-frame system) calculation will show the antibonding character as a function of the RC. The crossing energy is well above the energy of the first electronic excited state ($n\pi^*$) of H_2CO . The transition state is about this energy [13]. Most interestingly, one of the hydrogen centers and the oxygen presents an interaction leading to an asymmetry in the transition state to appear; as a matter of fact, this interaction relates to $\text{H}-\text{C}-\text{O}-\text{H}$ attractor (unpublished results). Because the energy of reactant and product are almost equal, the energy required to bring the hydrogen molecule in a vicinity of carbon monoxide must work against the repulsive antibonding states. This permits understanding the high activation energy of about 80 Kcal/mol. With this energy, the system approaches the excited state of H_2CO .

The principle of NP conservation concerns enforcing of symmetry while calculating D-PES. This may help in planning complex computations. Applying the quantum mechanical linear superposition principle leads to a more detailed view of chemical change and energy funneling. This latter is trivially understandable.

The BO wave function takes on a definite dependence on the geometry of the PCB. However, to get the right basis functions, we have to construct the geometry that render optimal the energy functional. At that point, you get also a GED basis function as we discussed in Section 5.2.2 [Eqs (60) and (61)]. Keep that wave function and all integrals for further use (see also Section 6.3.2).

6.3. Generalized many-state reactivity framework

The chemical reaction mechanism discussed above sets up the basic premises for a G-MS (generalized many-state) reactivity framework. In a basis set of chemical graphs, the linear combination from Eq. (51) must be extended to a number of basis that are required to couple reactant to product states and use the semiclassical model for the nuclear configuration space $\mathbf{X}$:

$$\Phi(\mathbf{x};\mathbf{X},\mathbf{A}) = c_0(\mathbf{A};\mathbf{X})\Omega_0(\mathbf{X}) + c_1(\mathbf{A};\mathbf{X})\Omega_2(\mathbf{X}) + c_2(\mathbf{A};\mathbf{X})\Omega_3(\mathbf{X}) + \dots \quad (70)$$

A first estimate of basis function required to study a given mechanism is a function of the number of bond made (k_{BM}) plus the number of broken bonds (k_{BB}), so to speak. The minimal number for two-electron state bonds is $3(k_{\text{BM}} + k_{\text{BB}})$.

6.3.1. Hydrogen peroxide nitrite case

Let us examine the two-state reactivity mechanism for the rearrangement of hydrogen peroxynitrite to nitric acid reported by Contreras et al. [28]. These authors found a spin-triplet reactive intermediate $^3\text{HOONO}^*$ on a two-state reactivity (2-SR) potential energy surface. The biradical was postulated as a possible activated species responsible for the powerful oxidant activity [28].

There are three stationary geometries: spin-singlet reactant ($^1\text{HOONO}$) and product ($^1\text{HNO}_3$) and the spin-triplet intermediate ($^3\text{HOONO}^*$). The triplet was found with the help of the reactant potential energy surface, which is the reason to call the method as 2-SR.

For the GED scheme, this is four-state reactivity scheme. The triplet state cannot interact with reactant and product states because their basis orbitals are different.

The triplet originates in σ to σ^* excitation (HOMO-LUMO), which implies that it is the singlet excited state with the same orbitals that may mediate the interaction of reactant singlet state with the intermediate triplet state. This is a key point to understand spin-orbit interactions. In view of the floppy structure due to the presence of other electronic states related to local spin rearrangements, the initial diradical $\text{HO}^\bullet-\text{O}-\text{NO}$ may be found shifted to $\text{O}-\text{N}^\bullet(\text{OH})\text{O}$ in the triplet state. Here, it will be the σ to σ^* from the bonding $\text{N}-\text{OH}$ in the fragment $\text{O}-\text{N}(\text{OH})\text{O}$ with the triplet and singlet states that will prompt for an opening of the product channel. All in all, the simplest quantum mechanical description would require six BSs. Using graphs as labels we would have

$$\begin{aligned} &|{}^1(\text{HO}-\text{ONO})\rangle, |{}^1(\text{HO}^\bullet-\text{O}-\text{NO})\rangle, |{}^1(\text{HO}^\bullet-\text{O}-\text{NO})\rangle \\ &|{}^3(\text{O}-\text{N}^\bullet(\text{OH})\text{O})\rangle, |{}^3(\text{O}-\text{N}^\bullet(\text{OH})\text{O})\rangle, |{}^1(\text{O}-\text{N}(-\text{OH})\text{O})\rangle. \end{aligned}$$

This is the number obtained with the general rule given above: $3(1+1)$. One broken bond and one antibonding turn into a bonding, thus requiring six base states as a minimum.

The changes of nodal planes indicate the type of LUMOS that are necessary to get a quantum mechanical representation. In this case, it is quite apparent.

Observe, however, again that the expression bond breaking or forming refers to the quantum state where the amplitudes for these states would be changing. It is not a molecular mechanics (object) change. Therefore, if during a dynamic process you set up to probe a spectrum rooted at a particular BS, whenever the amplitude there takes on values different from zero, you may experimentally detect finite response – this without being able to “separate” the “compound” originating the spectrum. You will be confronted with a fundamental quantum mechanical system sustained by the material system of your choice.

6.3.2. $\text{H}_2 + \text{CO}$, OCH_2 , HCOH , $\text{H} + \text{HCO}$, and $\text{C} + \text{H}_2\text{O}$ cases

The sixteen electrons and nuclear atomic number vector $\mathbf{Z} = (8,6,1,1)$ presents a number of reaction channels that can be described in terms of a G-MS reactivity framework. Observe that by changing the nuclear background into $\mathbf{Z} = (6,6,1,1,1,1)$, one gets ethylene while $\mathbf{Z} = (8,8)$ corresponds to dioxygen. The chemical nature is determined by the set of atomic numbers. In a diabatic scheme, the same types of NP characterize the electronic basis

functions. The PCB selects those patterns via different energies, for example, ground state of O_2 is a spin triplet while for ethylene it is in an excited state.

The generic $Z = (8,6,1,1)$ plus 16 electrons may sustain several diabatic BSs that enter into a G-MS reactivity framework. The headline underlies some of them. For the time being, leave aside $C + \text{water}$ channel and focus on two asymptotic states, $H_2 + CO$ and $H + HCO$ asymptotic and formic aldehyde (OCH_2) and $HCOH$ attractors.

For the reaction $H_2 + CO$ leading to formic aldehyde (OCH_2) in a chemical description, there are two bonds making ($H-C$ twice) and one bond breaking ($H-H$); each one of these elements requires three basis functions, namely, the bonding state plus a singlet and triplet states constructed on the same angular momentum basis. Moreover, there is a change from a two-I-frame system to one I-frame system. Thus, in preparing the theoretical analysis, before actual computations, one has to include the role of nodal planes that we will loosely refer to as “antibonding.” We graphically design nodal planes with $\cdot$ symbol inside the basis ket. Thus, $|H_2\cdot CO\rangle$ is a diabatic base state referred to the same one-I-frame as the normal attractors, for example, $|OCH_2\rangle$ and $|HCOH\rangle$, the potential is repulsive for diabatic states and goes to zero as the distance increases. Inside an attractor state, there are nodal structures between all nonbonded nuclei. Thus, for OCH_2 , there are antibonding states between $H\cdot H$ and $H\cdot O$ twice, while for $HCOH$, one gets $(C)H\cdot O$, $H\cdot H$, and $C\cdot H(O)$. From the analysis leading to inequalities in Eq. (57), we know that the attractors are ranged in energy and may yield D-PES. These constitute the bricks for the construction of G-MS reactivity schemes.

Now, some qualitative guidelines are obtained from our BSs. We know that the energy of the ground state $|OCH_2\rangle$ and the asymptotic state $|H-H\rangle \otimes |CO\rangle$ are nearly equal. The result may be surprising because one $H-H$ bond in the asymptotic state is replaced by two $C-H$ bonds in $|OCH_2\rangle$. In the latter state, the distances in the stationary geometry are short between the centers related by $\cdot$ interaction, namely, $H\cdot H$ and $H\cdot O$ twice, the latter two repulsive interactions may well compensate the excess in bonding, thereby leading to almost equal energy states. This result says very little were it not for the fact that activation energy is found to be about 80 kcal mol^{-1} in a vicinity of the first electronic excited state $|OCH_2, n \rightarrow \pi^*\rangle$. Let us see some factors that might be contributing to this activation: (i) the approach between the fragments follows a repulsive diabatic potential energy; (ii) hydrogen must be excited internally, vibration-rotation degrees of freedom; and (iii) CO must also be activated. Factor i is new in the standard quantum chemical context. In a two-I-frame picture, part of relative kinetic energy will be spent in approaching fragments. Factor ii would tend to increase the HH distance to get the antibonding state lower and the bonding higher in the energy scale until a crossing is obtained. This would be a natural occurrence because the attractor state has an internal $H\cdot H$ interaction. Thus another portion of excitation energy will be consumed

by internal hydrogen “stretching” interaction; however, such elongation is not the cause of H-H scission, the diabatic BS does not change with this operation. Factor iii would complete the energy requirement to get the system in a nuclear configuration domain where the diabatic quantum BSs would control the internal dynamics of nuclear fluctuations.

The quantum state is the linear superposition of the diabatic BSs or of a-BO submitted to symmetry constraints. In the semiclassical regime, the nuclei can be seen as classic object or in a quantum perspective where each nucleus is trapped in an attractor-like potential resultant from the linear superposition. At the transition configurations, the BSs $|H_2:CO\rangle$, $|OCH_2\rangle$, $|OCH_2, n \rightarrow \pi^*\rangle$, $|HCOH\rangle$, $|HCO:H\rangle$, and so on are driving the nuclear state. This can be translated into a picture where the attractor $|HCOH\rangle$ by participating with a finite amplitude would produce a transition geometry with hydrogen atoms showing an asymmetric arrangement, one of them nearest the oxygen nucleus the other near the carbon atom. Such is the result obtained with Hartree-Fock methods [13]. Thus, if one were to follow in a classical molecular dynamics simulation with the set of diabatic potential energy associated with the present set of basis function, one would see an hydrogen atom displaying a rather strange behavior: it will appear to move away from the C-center toward the oxygen one, and because one would expect a small amplitude at $|HCO:H\rangle$, wandering over large regions can be expected as forces from all base states add up loosening the standard local bonding picture.

A mechanism of the kind described above is far from simple transition state theory possibilities. The G-MS reactivity approach formulated in the quantum linear superposition approach may offer new vistas on chemical reaction mechanism and reactivity.

Finally, a three-state approach with model D-PE surfaces has been explored by Arteca and coworkers [8–10,29,30]. A new feature is the introduction of a phase diagram where all possible potential energy surface topologies (consistent with three-state systems in two linear RCs) are matched with actual model parameters. By varying the coupling strengths between diabatic states, they classify regions of this phase diagram in terms of electronic and structural similarities. One interesting finding is that some regions comprise models whose reaction paths have geometries that belong to the attractor (catchment) region of the reactant, yet are electronically akin to the diabatic transition state or product.

For the analysis of classical photochemical cases, see Ref. [31] that eventually can be cast in terms of the present scheme.

7. ALGORITHMS: COMMENTS AND PROPOSAL

In handling the problem of separation of electronic from nuclear degrees of freedom, a path differing from standard approaches is taken. We have examined, from first principle theory, whether searching different regions

of a nuclear configuration space could change quantum numbers. The answer was negative. Then, an effort was made to bridge abstract to real space quantum formalisms. This first entails use of abstract mathematical spaces to project quantum states as well as BSs. Here pops up a fundamental difference with traditional approaches. The latter assumes each point in configuration space there is to indicate the position of a particle. Consequently, wave functions would describe particle dynamics, this with or without the quantum adjective.

The fundamental stance we use is that QM is about quantum states sustained by specific material systems. You would not ask where the particles are because this question addresses a noncommensurate issue. They are in laboratory space while quantum state belong to Hilbert space. A Coulomb Hamiltonian specifies material parameters. Thereafter, focus is about time evolution of quantum states once a pertinent basis set is defined. The material system is invariant and sustains quantum evolution. Nowhere is found a basis function whose quantum numbers could be changed *only* by exploring different regions of nuclear configuration space. We have shown that via quantum numbers a separation model of diabatic type can be implemented: the so-called GED scheme. An abstract BO scheme is obtained via the linear superposition principle where the amplitudes depend parametrically on the nuclear configuration. Interestingly, to produce a change in the amplitudes, external fields coupling diabatic BSs are required in agreement with general quantum theory.

Because the scheme can be used equally well with a nuclear configuration space defined in real space, the introduction of RCs is made possible. Moreover, because a RC relates (but not change) BSs attractor geometry with different symmetries (quantum numbers), this auxiliary tool cannot be a symmetry operation of the system. This geometric property is a natural result of the present approach.

7.1. Nodal patterns algorithm

Decomposing a 1-system into aggregates each described with one I-frame and fixed number of electrons and nuclei so that the total sum recomposes an initial 1-system permits further analysis of laboratory situations. Introducing the concept of NPs, the analysis of quantum states incorporating BSs from the 1-systems and its fragments is greatly simplified. For now, the fragments' quantum state must show a definite NP separating from each other relative to the 1-system state. This idea helps correcting electronic calculations between I-frame systems that could for instance have a bonded state in the global system. The calculation of diabatic PE must be made with conservation of the NP selected as initial state. Such a type of computation leads to clean intersections by signature conserving PE surfaces. The artifact effects produced by the atomic-orbital model can at least be controlled.

Consider two different geometry attractors, the set of eigenvalues for a given attractor geometry that are the same for abstract BO and GED. The same result holds for class II models if the same computing algorithm is used; also class III models would show this property only at the stationary geometry:

$$\text{Attractor } k: W_{i=0}^{\text{a-BO}}(\xi^{(k)}) = W_{i=0}^{\text{a-GED}}(\xi^{(k)}); W_i^{\text{BO}}(\xi^{(k)}) \leq W_i^{\text{GED}}(\xi^{(k)}) \quad (71a)$$

$$\text{Attractor } kk: W_j^{\text{a-BO}}(\xi^{(kk)}) = W_j^{\text{a-GED}}(\xi^{(kk)}); W_j^{\text{BO}}(\xi^{(kk)}) \leq W_j^{\text{GED}}(\xi^{(kk)}). \quad (71b)$$

The eigenfunctions for a given attractor appear in a given order but the criterion to classify them, when the I-frame is the same for all, is the pattern of nodal points, planes, and so on. For the second attractor, using this criterion, the order imposed by the energy eigenvalues is shambled when the NP criterion is used to correlate states from different attractors; this is one origin for crossings.

Implicit in this argument is the fact that the solutions obtained with the functional forms are made with complete electronic basis sets when one moves from the abstract to the semiclassical models.

7.2. Diabatic (ghost) orbital algorithm

The use of electronic basis functions center at the nuclei in real space can generate artifacts. The ansatz changes the nature of the electronic configuration space, $\mathbf{x}(\xi)$, and for nuclei displacement far away, the local geometric stationary arrangement may force dissociation situations. Such algorithm may permit to go about changing the quantum numbers of the geometry stationary electronic basis functions. This is part of the curse; let us see the blessing aspect.

7.2.1. Back to ethylene D-PES

Consider ethylene two irreducible NP basis function [29]; ground state to begin with something simple. Take the a-BO wave function from Eq. (54) calculated at the stationary geometry of *cis*-conformer $\Psi_{i=0}(\mathbf{x}; \xi = \text{cis})$ and the one for the *trans*-conformer $\Psi_{j=0}(\mathbf{x}; \xi = \text{trans})$. Remember that the attractor geometry is located on two orthogonal planes.

The spectrum of electronic states calculated from Eq. (54) with $\Psi_{i=0}(\mathbf{x}; \xi = \text{cis})$ is complete. This property ensures that the basis function showing the NP of the *trans*-conformer must be in the list. This is true for a complete electronic space, the same for all attractors.

Now, for methods where atomic orbitals help us in performing calculations, how does a change of quantum number become possible? The answer is that the atomic basis set changes the rules of the game via an algorithm $\mathbf{x}(\xi)$. In the a-BO scheme, one cannot change a quantum number by

changing nuclear configurations, but for functions of the type $\Psi_{i=0}(\mathbf{x}(\xi); \xi)$ it does. The index $i=0$ indicates that the lowest root is always chosen but it is not related to the distribution of nodal planes.

To rescue the computationally adapted a-BO and/or a-GED schemes, it is necessary to have a fixed electronic configuration space. In practical terms, orbital distributions that cover all the attractor symmetries provide a model to proceed with quasidiabatic computations. So, if you put ghost orbitals (“Banquo”) completing the correct set for both conformers and save relevant density matrices (or the orbital amplitudes), you will at least get results over a fixed electronic configuration space.

The enhanced atomic basis set is maintained fixed now. Calculate the BSs and, for instance, identify in the *cis*-geometry the excited energy level for the *trans*-conformer: $W_{i=trans}^{a-BO}(\xi) = \langle \Psi_{i=trans}(\mathbf{x}; \xi) | \hat{H}(\mathbf{x}, \xi) | \Psi_{i=trans}(\mathbf{x}; \xi) \rangle_{\mathbf{x}}$ calculated at $\xi = cis$. In the energy scale, $W_{i=trans}^{a-BO}(\xi_{cis})$ is located very high up. Pick up the one among $W_{i=trans}^{a-BO}(\xi_{cis})$ with the lowest energy. The NP for $\Psi_{i=trans}(\mathbf{x}; \xi_{cis})$ and $\Psi_{i=trans}(\mathbf{x}; \xi_{trans})$ must be the same. $W_{i=trans}^{a-BO}(\xi_{trans})$ is the energy at the bottom of the *trans*-attractor, but you are up in energy now. The Hellmann–Feynman force calculated along the RC in the direction of the *trans*-basin will enforce a change of PCB geometry from ξ_{cis} toward ξ_{trans} . This is not magic because one is using the NP characteristic of the *trans*-attractor. The numerical result is a diabatic PE surface for the *trans*-conformer albeit one starts from the *cis*-geometry. See Ref. [29] that would complement the present analysis.

For the a-BO scheme with imposed NP conservation, one would get $\Psi_{i=trans}(\mathbf{x}; \xi_{cis} \rightarrow trans)$ the limit being $\Psi_{i=0}(\mathbf{x}; \xi = trans)$, at least if you have the correct ghost basis set. Energy goes down steeply until getting at the attractor minimum. By interchanging the initial point, a similar analysis can be done to get two D-PES. They cross at the disrotatory angle of $\pi/4$. These two D-PESs represent a type of Marcus potentials. Now you can go back to Section 6.1.3. Change in your input spin multiplicity and calculate the spin triplet. With the stationary geometry for the spin triplet, explore the parent singlet and you have computed the basic elements to start up a generalized-many-states reactivity study for ethylene (cf. Section 6.3).

Once all the diabatic states are at hand, the time evolution of the system is ensured by couplings to external sources [29].

7.2.2. Ghost (diabatic) basis for $H_2 + CO$ reaction

This system offers some interesting aspects relating to ethylene reactivity that will help us understand the geometry of the transition state we once numerically determined [13].

In the 1-system channel, OCH_2 , there is a methylene fragment: $-CH_2$. According to our rule on RC, the electronic base states are two nodal planes containing π -nodes. One plane cutting the H–H distance while fixing a CO π -node, and at $\pi/2$ a second plane that includes the whole sigma structure

and a second CO π -node. It goes without saying that the HH system sustains an antibonding interaction, $\text{H}:\text{H}$.

Now comes a novelty. There is another two-I-frame state: $|\text{C}\rangle|\text{OH}_2\rangle$. This adds a nodal plane ($\cdot$) when included in the 1-system space: $|\text{C}:\text{OH}_2\rangle$. The virtual and planar OH_2 can be put in the same plane as the methylene fragment. And we have reconstituted the basic elements of ethylene. To get a BS with one broken CO bond, take the $\pi/4$ disrotatory RC displacement; put ghost orbital to simulate water appropriately. You will find a triplet state. Complete the space with the related excited singlet state to construct a quantum mechanical description of the chemical process.

The transition state calculated with standard BO procedures showed geometry with broken symmetry when compared to C_{2v} group of product channel [13]. One of the H pointed toward oxygen, the second was nearer to the C. In a linear combination with ghost orbitals, it is quite natural to see that the geometry will reflect some specific linear superposition that would contain BSs such as $|\text{H}-\text{C}-\text{O}-\text{H}\rangle$. Thus, even in calculating standard saddle-point structures, one may use present type of qualitative analysis to figure out basis electronic states that might be relevant.

An accurate calculation along the lines discussed above requires implementation of a procedure where the atomic basis set remains fixed while nuclei's positive charge can be moved. The atomic basis set that is displaced with the nuclei is referred to as *adiabatic* AO basis. While the AO functions planted in real space at the position in which each one of the attractors will be referred to as *diabatic* AO basis set (D-AO). The number of D-AO required to span all geometry attractors if all relative distances change is equal to the number of orbital used to calculate a given state multiplied by the number of attractors. If there are relative distances that do not change one may select an input **Z**-matrix (geometry) that takes advantage of the invariant distances or one can use Cartesian coordinates.

The D-AO configuration represents all attractors at a time. The external potential set up by the nuclei gets to a stationary value depending on which BS is used to calculate the energy average value. To do this, the corresponding density matrices must be stored. The collection of basis functions contains

$$|\text{OCH}_2\rangle, |\text{OC}:\text{H}_2\rangle, |\text{H}-\text{C}-\text{O}-\text{H}\rangle, |\text{OCH}:\text{H}\rangle, |\text{C}:\text{OH}_2\rangle, |\text{OCH}_2, n \rightarrow \pi^*\rangle, \dots$$

As discussed above, the amplitudes that might be significantly different from zero at the bottleneck region are $|\text{OCH}_2\rangle$, $|\text{OC}:\text{H}_2\rangle$, $|\text{H}-\text{C}-\text{O}-\text{H}\rangle$, $|\text{OCH}:\text{H}\rangle$, and $|\text{OCH}_2, n \rightarrow \pi^*\rangle$. So far, the nuclei dynamics is not yet involved. One way to do this is to calculate the vibration states for the auxiliary diabatic potential energy in order to attain a quantum mechanical level of description. Thus, nuclear positions fade away. Energy levels substitute the classical mechanical picture. This aspect is emphasized in

Sections 4.2 and 4.4. But one can also prepare a molecular dynamics simulation of the mass-endowed PCB. If one takes one H-nucleus and calculates the force acting on it, the result will be an average force where each attractor contributes with weight $|C_k(\xi)|^2$ that multiplies the Hellmann–Feynman force on the nuclei at ξ . The resultant picture would be an H-atom wandering over the nuclear configuration region covered by the attractors involved in the linear superposition; the second hydrogen would appear more trapped.

Thus, if one has amplitude at $|\text{H}-\text{C}-\text{O}-\text{H}\rangle$, the TS cannot show a C_{2v} symmetry. Simple transition state theory may have difficulties to yield a mechanistic description. The reason is simple to see. If passage over a simple barrier were the reaction mechanism, then one would expect zero amplitude at $|\text{H}-\text{C}-\text{O}-\text{H}\rangle$, but amplitudes over this state are experimentally detectable as product.

7.3. Standard BO and diabaticization procedures

The parametric dependence on the nuclear geometry of the standard s-BO scheme is, according the preceding analyses, basically due to planting atomic functions right on top their positions and makes them follow nuclear displacements. This dependence can be called algorithmic. It does not entail a foundation for quantum molecular frameworks.

Let us hint at some important problems the algorithm raises. Take the nuclei-fix electronic operator with notation $\hat{H}_e(\mathbf{x}|\mathbf{X})$ that includes nuclei–nuclei repulsion, one usually picks up the nuclear kinetic energy operator $\hat{T}(\mathbf{X})$ (see e.g. [32]) so that the total electronuclear Hamiltonian is written as

$$\hat{H}(\mathbf{x},\mathbf{X}) = \hat{T}(\mathbf{X}) + \hat{H}_e(\mathbf{x}|\mathbf{X}). \quad (72)$$

This procedure we have all used. However, there is a problem. First note the symbol $\mathbf{X}$ appearing in $\hat{T}$ is not commensurate to the one in $\hat{H}_e(\mathbf{x}|\mathbf{X})$. We all know that the best one can do is to get a type of Hamiltonian like the one appearing in Eq. (6) where we call the nuclear kinetic energy operator as $\hat{K}_N$. This is referred to variables in relation to the attractor set up by the electronic basis function.

Equation (72) would be correct if the electronic energy functional in the functional equation $\hat{H}_e(\mathbf{x}|\mathbf{X})\Psi(\mathbf{x};\mathbf{X}) = E(\mathbf{X})\Psi(\mathbf{x};\mathbf{X})$ yielded $E(\mathbf{X})$ as *true* eigenvalues and not as functionals. The analysis carried out both for the abstract BO and class III models shows that such premise is not fulfilled. The nuclear spectra are tied to specific attractors and appear as fluctuation modes (vibration). The approach is basically an algorithm to guide computing studies of stationary geometry cases. And, in this sense, it is extremely useful.

Without entering the dispute on the nonexistence of strictly diabatic molecular electronic bases, see Ref. [33] and references therein, we can point out two things: (i) an algorithm cannot be used to prove or disprove

another algorithm and (ii) at geometric attractors we have shown that all blends of BO and our blend of diabatic electronic states converge. Using D-AO basis set, the electronic state is invariant to any displacement of PCB.

We believe that there is a misplaced dispute here due to lack of theoretical understanding of abstract QM tenets. Something has crept in the formalism that destroys its direct belonging to abstract QM. This is the parametric dependence of the electronic configuration space: $\mathbf{x} \rightarrow \mathbf{x}(\mathbf{X})$.

As the present work emphasizes, the nuclear position dependence of electronic wave functions is fundamentally due to the AO planted at nuclei algorithm not to a general underlying principle. This does not mean that the algorithm itself is not useful. Note that to this class of algorithm belong the generalized James-Coolidge functions where the basis functions are expressed in elliptic coordinates [25,26].

The diabatic schemes unify BO to GED models at an abstract level and permit understanding some of the limitations of current algorithms. At the same time, these schemes offer some help to produce potential energy functions under symmetry control. The introduction of the principle of NP invariance would help in having a minimal control over what is going on in our computations when semiclassical real space system is included into the global 1-system to form an extended set with asymptotic states.

Yet, it is of interest to examine standard BO procedures within the AO ansatz. For, even if it is an algorithm, the results there from obtained are of interest. In particular, conical intersections that signal regions where the quantum state might be rapidly changing due to changes of overlaps between standard AOs. In other words, the algorithm $\mathbf{x} \rightarrow \mathbf{x}(\mathbf{X})$ may introduce some diabolical surprises. It is the mechanical displacement of nuclear centers that create the change. This is not a pure quantum mechanical effect.

Moreover, the use of such information in the present context is totally different. This type of zones would indicate aperture of reactive channels, changes of amplitudes over the active attractor states, without the need to jump over high barriers. One should focus on the quantum mechanical aspects rather the classical wanderings over surfaces. One should emphasize the linear superposition over electronic configurations rather than the structural mechanical picture.

With all these elements at hand, one can easily see that Brattsev theorem [34], see also Epstein [35,36], is not valid to the extent that the formulation used corresponds to a particular algorithm as it has been extensively discussed in this work.

Be it an algorithm or an approximation, the BO scheme and beyond is being used to study time-dependent processes [37]. To the extent the AO ansatz underlies computing, one should be careful and control the nature of the BSs that allow for the time-dependent formalism to be implemented.

We leave these matters without further elaboration. Work along these and related lines would contribute to a better understanding of energy

funneling mechanism, electron transfer phenomena, and so on. To the extent we understand the nature of our models, computational quantum chemistry can help exploring more and more complex systems where electronuclear separability does not work the way we are used to.

7.4. How far from exact representations are GED-BO schemes?

One problem faced by semiclassical models resides in the passage from an abstract space to real space when handling nuclear degrees of freedom.

Due to the AO orbital ansatz, nuclear displacements in real space induce radical changes of the electronic space thereby fragmenting the electronic configuration. The algorithm is given a form affecting the electronic configuration space that now should read as $\mathbf{x}(\mathbf{X})$. The passage from abstract $\mathbf{x}$ to $\mathbf{x}(\mathbf{X})$ is a decision taken within the scientific society; it is not a physical process. This situation adds a dimension when an answer is to be given to headline's question: a-GED and a-BO schemes represent approximations to an exact Schrödinger equation obtained via the separation algorithm $\Omega_j(\mathbf{x}) \Gamma_{j(m)}(\mathbf{X})$ (cf. Section 4.4). On the contrary, s-BO and those methods using an ansatz $\mathbf{x}(\mathbf{X})$ that by itself induces separation of asymptotic channels are not approximations yet they provide very useful computation algorithms.

We have proposed, for some cases, the use of diabatic (ghost) electronic basis set distributions that remain invariant or at least one can continuously control the symmetries. Formally, one picks up a set $(\mathbf{x}(\mathbf{X}^{(0)}), \mathbf{x}(\mathbf{X}^{(1)}), \dots, \mathbf{x}(\mathbf{X}^{(i)}))$ representing one-electron basis orbitals localized at attractors position. Thus, they provide a fixed electronic configuration space. Remember the ethylene case. Schemes of this kind are fully diabatic.

Having imposed reasonable symmetry constraints, one ends up with discrete, ordered sets of attractors all calculated on equal footing. Each one would now yield a complete set of vibration spectra containing all elements related by the fundamental symmetries the problem might have in that attractor.

The relationships given in Eqs (71a) and (71b) are valid for the GED scheme and we assume that they are valid for the computed functionals.

Let us assume that we have obtained a complete set of attractors with their spectra. Order them by using the lowest (ground state) level of each attractor. Each BS is repeated an infinity of times, continuously relating the points generated by one and the same diabatic electronic function leading to D-PES. The best picture would be a set of Marcus-like PE surfaces. Also, if one keeps invariant the NPs, a-BO scheme would yield sets of lower bounds to the D-PE surfaces. Note that for a one-I-frame system, no asymptotic solutions are obtained due to general quantum mechanical boundary conditions on the electronic functions. Nuclear dynamics is handled as usual either as a classical dynamics problem or as a quantum dynamical one. Each D-PE traps the nuclear system that can be seen as a set of atom fluctuations from the stationary geometry, each atom trajectory can be evaluated.

Another way is to solve a nuclear Schrödinger equation to get collective nuclear fluctuations (normal modes). This is well-known stuff.

Folding the spectra of all attractors, means to pick up the ground state for each attractor and collect the vibration levels, one would obtain an approximation to the spectra of the exact Hamiltonian. This can be done, as a matter of principle, because the nodal plane pattern is invariant and one can use it to search for the pattern one is interested in. Then one should find the intersection of the ground state with the attractor of interest, the vibronic states found in the energy slice between the intersection and the energy of the ground state with the geometry of the attractor under scrutiny are interspersed; now fold them according to the electronic quantum number. One will have a diagram with vertical vibronic energy ladders corresponding to the given electronic base state. The union of these sets is a model for the spectra that can be obtained by solving the time-independent Schrödinger Eq. (40):

$$\mathbf{E}'_{j,j(m)} = \langle \phi_{j,j(m)}(\mathbf{x}, \mathbf{X}) | \hat{H}(\mathbf{x}, \mathbf{X}) | \phi_{j,j(m)}(\mathbf{x}, \mathbf{X}) \rangle. \quad (73)$$

Now, use a RC (a classical object) to fold the spectra at the attractor positions. A sort of *Jablonski* diagram (see Ref. [38] page 552–553) would emerge that would include all relevant vibronic states.

The procedure discussed above actually defines an approximation to the exact spectra. Thus, each type of attractor symmetry (equilibrium nuclear configuration) is consistent with the symmetry imposed by the diabatic electronic basis function.

The spectra used to construct, in principle, quantum states with Eq. (1) can be retrieved in an approximate manner from the semiclassical procedures we have just analyzed. But there is a plus to all this, namely, a structural picture has emerged based on sound diabatic theory.

From the analysis leading to Eq. (73), it is apparent that s-BO cannot be an approximation to the exact Schrödinger equation due to the AO ansatz, $\mathbf{x}(\mathbf{X})$. The a-BO and the other blend introduced here as linear superpositions do present approximations to the quantum state of the electronuclear system, and this, provided we do not abuse the AO ansatz by controlling invariance of NPs. The corresponding time evolution is just a type of wave packet dynamics overcoming the mechanical particle picture.

The linear superposition understood by Fidler and the author [5] and shown in the appendix of this work means that as soon as amplitudes develop at a given BS, the spectra rooted at this state is susceptible to show up. Thus, in a process where these amplitudes are changing, a time varying spectra will develop under measurement with appropriate radiation frequencies.

The great challenge corresponds to the representation of situations where the number of I-frames involved in laboratory preparations must be correlated to the 1-system represented by one-I-frame sustaining the total

material system states. The many-I-frame states appear as asymptotic states that have to be included with the one-I-frame attractors to be able to describe dissociating processes as well as reactive collisions.

As shown in Section 6.1.3, one has to introduce appropriate algorithms $\mathbf{x}(\mathbf{X})$ forcing asymptotic states into a one-I-frame presentation.

7.5. The Jahn–Teller effect and linear superposition principle

The Jahn–Teller effect [39] was experimentally well identified for the first time by Bleaney and Bowers. They found a radical change of the spectrum in some cupric ion salts at low temperatures. The change from one spectrum to the other occurred over a rather wide temperature range. They reported the possibility to see two different spectra simultaneously. The spectral change is reversible with temperature. The experimental results were discussed in light of the Jahn–Teller theorem [40].

Jahn–Teller effect is defined in semiclassical frameworks [41,42]. Nonadiabaticity effects are assumed to mix adiabatic electronic states by nuclear displacements: a vibronic mixing. This is especially relevant in presence of degenerate or close-in energy electronic states [42–46].

The issue here is the following. The GED-BO electronuclear separation by quantum numbers does not have a simple mechanism to describe the Jahn–Teller effect the way it is currently being done [42–46]. This does not mean that the models used so far are not adequate. The special theory focuses on the calculation of energy levels for a one-electron Schrödinger equation under special external potentials. The latter imposes specific symmetry to the electronic states coupled to vibration modes [41].

Here, one case is shortly examined to show the way Jahn–Teller effect would appear in the present context.

- (1) There is a vibronic spectrum obtained as we pointed out above by folding the spectra to specific attractors (geometry element). The elements required to discuss the analog of a Jahn–Teller process can easily be set up with the help, for instance, of Jablonski-type diagrams.
- (2) Assume existence of a degenerate electronic state for a high symmetry attractor together with a lower symmetry attractor below the degenerate excited state.
- (3) We can think of preparing a quantum state with amplitudes at both the degenerate basis and the near degenerate vibronic states belonging to the low symmetry attractor that produce a model for a metastable state. The dominating amplitudes correspond to the degenerate electronic attractor. Note that in presence of an external EM field (temperature different from zero), the system may be coupled (weakly) to any vibronic state belonging to other attractors. For a class of quantum states fulfilling the conditions just addressed, you can probe the

spectral response from the degenerate subsystem and you will “see” the spectra associated with the high symmetry attractor perturbed by an external potential (crystal) of lower symmetry.

- (4) Cool the system. The physical system may start to relax toward the ground state of the low symmetry attractor. Probing the quantum state as it changes one may see the superposition of spectra. Once the quantum state shows amplitudes dominated by the lower energy attractor, the spectra that can be probed belongs to the one identifying this attractor.
- (5) Heat it back. The vibration activation sets up until coming to the resonance region that overlaps with the electronic degenerate state. The whole is being reversible.

Actually, we have rephrased Bleany and Bowers salts behavior. The Jahn–Teller effect is a pure spectroscopic vibronic effect. The only thing that is needed to make this model work is the coupling between the vibronic states. The mechanism is provided by the external EM field that put the system in an excited electronic state in the first place. Geometric deformations are ensured whenever the electronic attractors do have different attractor geometry.

The time evolution of the initial quantum state is ensured in a manner similar to those invoked for other physical processes.

For the present approach, there is no special nuclear coordinate that would prompt for the splitting or a propagation leading to a change of geometry. Of course, if the standard AO-based algorithm were used to carry out the study, all the effects discussed in the literature would be “reactivated.”

8. DISCUSSION

We have gone a long way in discussing paths from abstract QM down to computing algorithms. Specialized discussions have already been presented at different places above. Here, some key points are highlighted.

- (1) The concept of 1-system whose quantum states are projected to one I-frame permits focusing on algorithms where the electronic states play central roles. Unimolecular processes can all be described in this context.
- (2) The inclusion of asymptotic, noninteracting m -I-frame subsystems (fragments with respect to the one-I-frame system) requires a two-step procedure, first basis sets for the fragments that are independently worked out, second, all fragment I-frames are referred to the one used in the one-I-frame system. Thus, for example, at very low temperatures, a Bose–Einstein condensate (BEC) can be formed [8,9,29,47] by changing the amplitudes between the fully coherent atom state and other states of weakly interacting atoms: that is, from a one-I-frame state to multiple-I-frame state. The nodal planes between pairs

of I-frames systems ensure weak repulsive forces and intermolecular interactions ensure weak attractions.

- (3) Relating geometric features in real space to abstract quantum mechanical spectral elements is one of the most spectacular results obtained with the separation via quantum numbers procedure followed here. In a strict quantum state description of spectral region where changes of quantum states may happen, the state of affairs may look dull. The geometric aspect adds two important features. On the one hand, a connection with real space is open. On the other hand, phenomena such as Jahn–Teller effects, and similar, can be appraised in its full quantum mechanical nature and, concomitantly, geometric elements become a natural way to describe such situations.

The framework presented in this chapter permits simulations of relatively complex situations. Arteca and coworkers have used model representations of the diabatic PE surfaces mimicking chemical reactions [8,9,29,30].

- (4) The presentation of a chemical process is a clean quantum mechanical time evolution as soon as external sources are switched on [15]. Spectral regions where resonance takes place act as energy funnels if the system is unfolded along a RC. Then, one could describe energy flowing through molecular structures once the semiclassical view is “activated.”
- (5) Crespo et al. [48] tested the *diabatic*-AO (ghost) algorithm to study D-PE and s-BO-PE for H + H and H₂ systems. Several basis sets up to aug-cc-pV6Z were tested in conjunction with multiconfiguration methods. A diabatic PE for H₂(¹S_g⁺) state was calculated for the first time. The potential would cross all excited states PE found below the free-electron limit. The diabatic algorithm was used to help characterize a low-energy spin-triplet state.
- (6) Arteca and the author have studied the diabatic potential energy description of ammonia isomerism (umbrella inversion) [49]. This is a problem having some similarities to ethylene isomerism. The ghost functions consist of floating Gaussians placed on fixed (optimized) grids defined by stationary geometries.
- (7) The concept of basis function and quantum state have been cleanly separated: the former constitute elements of a row vector with fixed order; the latter are complex numbers arranged in a column vector, the position corresponds to the quantum base state in the row vector. One can follow time-dependent changes without problems. In general, a pattern of nonzero amplitudes serves to characterize a quantum state; the spectral response is well defined.
- (8) D-PES were used to generalize two- and three-state reactivity scheme. A detailed analysis showed the role of excited triplet and singlet states rooted in the same angular momentum base functions. This is a feature rooted in the present theory.

- (9) Arteca et al. with simple harmonic models have covered many aspects of chemical reactivity, see for instance [8,30] and references therein.
- (10) Within the BO scheme to describe molecular systems, the nuclei move on a single potential energy surface set up by an average of the electronic Hamiltonian operator with an electronic wave function [50]. In this chapter, it is found that the parametric dependence of the electronic wave function on nuclear positions is due to location of atomic-orbital algorithm that changes the structure of the electronic configuration space. For this reason, we do not call the BO as an approximation to the electronic Hamiltonian. It is an algorithm that has shown its enormous usefulness. Conical intersections are as diabolical as ever but now they would affect the algorithm rather than the physics. The methodology developed to study such behavior continues to be extremely useful [51].
- (11) The concepts of bond breaking and bond forming have been challenged by a deny of classical mechanical pictures: a classic dictum, “there must be objects if the world is to have an unalterable form” [52], ought to be changed into “there must be quantum states if the world is to show processes changing it.” The quantum mechanical mechanisms required for producing amplitude changes open perspectives and possibilities to understand stability in terms of lifetimes originated at resonant states channeling passages to new attractors and/or different asymptotic behavior; nothing is unalterable. The fundamentals are summarized in the generalized many states reactivity theory of Section 6.3. As the theory pushes the boundaries of normality, as it were, the reader is invited to carefully examine the challenging essay by Hoffman and Hopf [53].

To sum up, in general, the potential energy surfaces appear as extremely useful tools that would help constructing spectral elements required to understand chemical mechanisms. But, remember, a chemical reaction does not “occur” on a potential energy surface. This is only a tool directing our attention to critical points where the linear superpositions may tell us something more about the rate and mechanism [8] controlled by neighboring spectral features but that can be spatially far from the presumed local active site.*

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*In a recent letter from Prof. Morokuma and coworkers [56], they have released a theoretical study on photo dissociation dynamics of formaldehyde. The results reported give support to the theoretical view developed here.

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APPENDIX

All along the present paper, QM has sounded differently when compared to the orthodox view. And this is actually so. Here, we summarize the axioms that in fact in two key ways differ from what we are used to.

The principle difference between textbooks and the present view of QM concerns the nature of elements constituting Hilbert space. Given a material system, the mathematical structure of QM would address all possible quantum states sustained by such system. QM is not about description of particles themselves.

The mathematical structure is fundamentally the same as standard QM as you find out in textbooks with the statistical probabilistic interpretation erased.

A.1. Axioms of quantum mechanics

Now we write down the axioms compatible with the present approach. They depart only for those statements concerning measurements otherwise they are fairly well accepted in modern QM.

Axiom 1: At a given time t_0 , the physical state of a given system is defined entirely by a vector $|\Psi(t_0)\rangle$ belonging to the linear vector space over the complex numbers field $\mathbb{C}$, namely, the system's Hilbert space H . The vectors are normalized to one or to a Dirac distribution.

Note that *it is not* the physical system as an object that is represented by a vector in Hilbert space but its quantum state. For example, an aggregate of n -electrons and m -nuclei displays infinity of quantum states that can be spectroscopically identified in many chemical guises depending upon external manipulations.

Axiom 2: To every measurable quantity A corresponds a linear self-adjoint (hermitean) operator $\hat{A}$ defined in H .

A self-adjoint operator implies existence of a complete set of eigenvalues and eigenvectors:

$$\hat{A}|a_i\rangle = a_i|a_i\rangle \quad \text{for } i = 0, 1, \dots \quad (\text{A1})$$

The business of workers in QM is to construct the operators and solve these types of problems first.

The complete and denumerable set $\{|a_i\rangle\}$ serves as a base for representing a quantum state $|\Psi(t)\rangle$ as a linear superposition:

$$|\Psi(t)\rangle = \sum_i \langle a_i | \Psi(t) \rangle |a_i\rangle = \sum_i C_i(\Psi(t)) |a_i\rangle. \quad (\text{A2})$$

It is essential to make the difference between quantum states and base states. Arranging the amplitudes as a column vector and the base set as a row vector, in this case, both have infinite dimension, and the quantum state is given by the column vector. The base set as a row remains invariant as a quantum state changes. Thus, the quantum state (column vector) of a system that shows spectral response from only one root state is $(0 \dots 0_{k-1} \ 1_k \ 0_{k+1} \dots)$ where we have assigned the root state to the k -th eigenfunction [cf. Eq. (2)].

**Axiom 3: Quantum states are measurable, and the response to external measuring probes is expressed as spectra that is a function over the set of eigenvalues of the associated operator $\hat{A}$, namely, the spectral response of the (measurable) physical quantity A .*

In this sense, the numerical value of a measurable physical quantity A is expressed via the spectrum of $\hat{A}$.

**Axiom 4: The measurement of the spectral response rooted at the eigenstate $|\alpha_i\rangle$ for the quantum state $|\Psi\rangle$ will show a relative intensity I_i given by*

$$I_i = |\langle a_i | \Psi \rangle|^2. \quad (\text{A3})$$

Balmer's series were among the first spectral response involving level $n = 2$ as root to the sequence $n = 3, 4$, and so on of the material system known as hydrogen. Energy differences expressed as a spectrum are the key elements sensed by measuring probes.

Linear superpositions represent coherent states. The case represented in Axiom 4 corresponds to a measurement in intensity regime. In this case, the system is reduced to a decoherent state due to the local nature of probing devices. Here, each term with nonzero amplitude can contribute to the global spectra with weight I_i .

A measurement in amplitude would target the complete linear superposition. A response to a probe will reflect the set of initial amplitudes. For probes having all spectral possibilities, only transitions rooted at base state having nonzero amplitudes at initial time can be sensed. Axiom 3 states just this property.

Axioms with a star prefix differ from the standard probabilistic model. For a complete set of commuting hermitean operators, the joint eigenstates provide a base set to represent quantum states as linear superpositions. The spectra elicit characteristic responses to external interaction. They are

invariant properties of a given material system. A quantum state is given by the set of complex amplitudes appearing in the linear superposition. When put in interaction with a measuring system, amplitude changes in time would elicit physical and chemical processes undergone by the material system.

The axioms presented above are related to a theory of measurement different from the standard one. This latter has been presented in the literature [5]. There an experimenter must be able to prepare the measuring and measured quantum states, this is a key point.

First, any material system may show a spectral response to external probes. This condition applies to the 1-system case as well. This makes a difference for a measurement theory because a spectral family implies pairs of energy eigenvalues one of them having nonzero amplitude in the quantum state (root base state). It is the difference that marks the energy in laboratory space. Here, there seems to be a problem: the spectra of a given system would contain an infinite number of "excitations" as the energy spectrum can be formed from a infinity of base states. But, such is not the case because *only root base states having nonzero amplitude in the linear superposition can put up a response to a probe*. Normalization to unity permits defining relative intensity responses and the ensemble concept may help understanding modulation in intensity, but it is not a fundamental element. The observables, to the extent they can be recorded, are the spectral lines not the energy levels. The amplitudes modulate the relative intensities that are measurable too; transition amplitudes are incorporated into resulting amplitudes cooperating to the intensity of specific lines.

The probe may be selected so that only a fraction of the spectra is probed. Observe that a quantum system can interact in a quantum mechanical fashion only, namely, via spectral response. Here lies the bottom line to quantization of material systems. As an I-frame, the system behaves classically, but then the space involved is no longer Hilbert space but laboratory (real) space.

A quantum measuring device can only measure a quantum state not the object (1-system). The material system as object can be detected, thereby revealing events in real space. I-frames actually are real space elements. The double-slit experiment serves illustrative purposes in this respect. The quantum state of the material system (one electron) is prepared (to simplify) as a plane wave. There is a screen with two holes conveniently separated and having exactly the same qualities, they act as source of interaction with the same quantum state. This sameness is one of the keys to get coherent superposition of the states scattered at each hole. The quantum state after scattering by the holes is a linear superposition including the in-going state. An interference pattern is obtained that subsumes all possibilities the quantum mechanical system may show; understanding is disclosing such possibilities at the theoretical level (Hilbert space). At the

laboratory level, detection and registering are operations that express themselves in real space. Energy is exchanged between the sensitive register device and the quantum system that is to be measured. These factual features cannot disclose possibilities in Hilbert space; the role of QM is fundamental. The material system sustains the quantum state; energy exchange takes place at a location. To the question which way does it take the material system? the answer would be this question does not belong to QM, it is a classical mechanics problem. A particle passing through a slit in a diaphragm is not relevant. What is relevant is the sameness of the quantum state impinging on the screen and the identity of the scattering centers. The quantum state associated with the situation is all what one can calculate in QM.

Understanding here is the projection of all possibilities that QM correctly delivers. Knowledge as correct representation of the real world is not receivable [54]. Because QM is about quantum states and not objects provides a reason why one can construct theories of chemical reactions without populations involved in statistical mechanics.

In femtochemistry, one starts seeing the response of a given base state as soon as the amplitude there becomes different from zero, and the energy available in the probe can be exchanged with the material system sustaining the measured quantum state. The material system is an invariant; it is right there. What we are able to sense is the time-dependent change of amplitudes via intensity response.

For standard (orthodox), QM it is necessary to predict the emergence of a single result in a single realization of an experiment [23]. This requirement leads to a special postulate: the reduction of the state vector. In the present approach, the requirement is overcome. The quantum state can be probed either as a whole or by activating a response from any base (root) state provided amplitude found there is different from zero [5]. To set up a response, interactions with external systems are needed. An important result is obtained: change of the state vector due to interaction is nothing like a reduction of the state vector. This was one of the basic tenets of standard QM that now becomes superfluous. QM weirdness fades away as it is the concept of quantum state and not of particles that occupies the center stage.

The energy exchange between the quantum system and the screen is made by localized quanta. It corresponds to an event registered by a screen situated beyond the diffracting screen (system) in real space. Can one predict an event within QM? The answer is no. QM does not predict real space events. However, it is obvious that the material system by sustaining the quantum state is the carrier via the corresponding I-frame. The energy exchange is determined by the change of internal quantum state, unless you are measuring impacts on the screen. In the latter case, it is the quantum state involving the I-frame which is put in evidence.

The identification of a given quantum state boils down to get the set of nonzero amplitudes with their labels. There can be a spectral activation if and only if the amplitude at the relevant root state, that is, the one where the spectrum originates, happens to be different from zero. For those energy levels that can put up a relative intensity, select a subset that might be sufficient to put labels (partially) identifying the system although the detailed quantum state is not (fully) determined. Energy must be exchanged between measured and measuring systems. A many-world view [5,55] just fades away. The measuring system has to pay the energy bill.

The spectral response description differs from standard interpretations and can be considered as an element of a third “interpretation” of QM. The gathering of probe and measuring system constitutes a detector that functions as a unit. A larger unit follows after including the measured system. Quantum base states labels cannot be erased, amplitudes do. Entangled states for instance complete the global system; they must be counted by one and not be mixed up with the asymptotic base states.

Focusing on fact’s discovery alone will fatally obscure the Hilbert space dimension disclosure of possibilities. The linear superposition principle just permits calculations of accessibility to such possibilities the material system may show in real space.

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CHAPTER 3

Exact Signal–Noise Separation by Froissart Doublets in Fast Padé Transform for Magnetic Resonance Spectroscopy

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1. INTRODUCTION

A powerful and invaluable complement to anatomical diagnostics, magnetic resonance spectroscopy (MRS) provides biochemical information about viability and overall functionality of the scanned tissue. This latter information is not available directly from time signals, or equivalently, free induction decays (FIDs) encoded from patients via MRS. Rather time signals need to be spectrally analyzed by considering the quantification problem. By solving this problem, one can reconstruct the complex-valued frequencies and the corresponding amplitudes. These spectral parameters are the only elements of the fundamental harmonics that constitute the studied time signal. Each harmonic (transient) has its resonant frequency, relaxation time, intensity, and phase that completely characterize the underlying normal-mode damped oscillations in the signal. Such four real-valued parameters can be identified directly from the reconstructed complex frequencies and amplitudes, thus yielding the peak areas of the associated resonance profiles in the related spectrum. Here, the most clinically relevant quantities are metabolite concentrations that can also be extracted from the time signal, since they are proportional to the retrieved peak areas.

The present work tackles one of the most challenging numerical aspects for solving the quantification problem in MRS. The primary goal is to investigate whether it could be feasible to carry out a rigorous computation within finite arithmetics to reconstruct exactly all the machine accurate input spectral parameters of every resonance from a synthesized noiseless time signal. A positive outcome from this most stringent testing would prove that the estimator chosen for such a reconstruction is exceptionally stable and robust against round-off errors from computations. Estimators that do not meet these highest standards imposed on spectral analysis with ideal input data could hardly have any systematic reliability for processing insufficiently accurate data corrupted with noise as encoded customarily via

MRS. We also consider simulated time signals embedded in random Gaussian distributed noise of the level comparable to the weakest resonances in the corresponding spectrum. Among many methods that can be used with varying success as parametric estimators [1–76], the present choice for this high-resolution task in MRS is the fast Padé transform (FPT) [77–95].

In theory, all the sought spectral parameters (complex frequencies and amplitudes) can unequivocally be reconstructed from a given input time signal by using the FPT. Being a response or system function, as expressed by the unique ratio of two polynomials, the FPT is known as the most frequently used estimator in vastly different research fields. Moreover, the present computations demonstrate that the FPT can achieve the so-called spectral convergence, which represents the exponential convergence rate as a function of the signal length for a fixed bandwidth. Such an extraordinary feature equips the FPT with the exemplary high-resolution capabilities that are, in fact, theoretically unlimited. This is illustrated in the present study by the exact reconstruction (within machine accuracy) of all the spectral parameters from an input time signal consisting of 25 harmonics, that is, complex damped exponentials, including those for tightly overlapped and nearly degenerate resonances whose chemical shifts differ by an exceedingly small fraction of only 10^{-11} ppm. Moreover, without exhausting even a quarter of the full signal length, the FPT is shown to retrieve exactly all the input spectral parameters defined with 12 digits of accuracy and hence the robustness of the FPT even against round-off errors. Specifically, we demonstrate that when the FPT is close to the convergence region, an unprecedented phase transition occurs, since literally two additional signal points are sufficient to reach the full 12-digit accuracy with the exponentially fast rate of convergence. This is the critical proof-of-principle for the high-resolution power of the FPT for machine accurate input data. Furthermore, it is proven that the FPT is also a highly reliable method for quantifying noise-corrupted time signals reminiscent of those encoded via MRS in clinical neurodiagnostics and other related problem areas in medicine. All of the conclusions reached in this review about the performance of the FPT hold also true in, for example, analytical chemistry when using the ion cyclotron resonance mass spectroscopy (ICR-MS) or nuclear magnetic resonance (NMR) spectroscopy, as well as in several applied sciences and technologies that employ signal processing for data analysis [77].

2. RATIONAL RESPONSE FUNCTION TO GENERIC EXTERNAL PERTURBATIONS

By definition, quantification in MRS coincides with the well-known harmonic inversion problem in quantum theory of resonances and spectroscopy [84]. Therefore, the general quantum-mechanical relaxation formalism

can advantageously be exploited to solve the quantification problem in MRS. Presently, we use the quantum-mechanical parametric signal processing through the frequency-dependent Green function $G(\omega)$. This approach, when implemented algorithmically via the FPT, is capable of reconstructing exactly all the spectral parameters [77–91]. The FPT generates the frequency spectrum as the unique quotient of two polynomials:

$$G_{L,K}(\omega) \propto \frac{P_L(\omega)}{Q_K(\omega)}. \quad (1)$$

Here, the two subscript labels L and K of the Green function indicate the degrees of the numerator and the denominator polynomial, respectively. Depending on the relationship between the polynomial degrees L and K , these quotients are called the off-diagonal ($L \neq K$) and the diagonal ($L = K$) versions of the FPT. The special case $L = K - 1$ of the off-diagonal FPT is called the para-diagonal FPT. The para-diagonal and the diagonal FPT are used most frequently in applications.

The off-diagonal FPT is useful to describe spectra that have a rolling background contribution as in MRS. This is because the quotient P_L/Q_K for $L > K$ can always be expressed as a sum of a polynomial B_{L-K} and the diagonal FPT, which is the quotient A_K/Q_K :

$$G_{L,K}(\omega) \propto \frac{P_L(\omega)}{Q_K(\omega)} = B_{L-K}(\omega) + \frac{A_K(\omega)}{Q_K(\omega)}, \quad (2)$$

where ω is the angular frequency, $\omega = 2\pi\nu \equiv 2\pi f$, with ν or f being the usual linear frequency. Here, the polynomial B_{L-K} describes the background, whereas the new diagonal quotient A_K/Q_K describes the polar structures of the spectrum, that is, its resonances. The mathematical form (1) of a rational quantum response function to some external perturbations or excitations is dictated by the intrinsically quantum origin of FIDs from MRS, as well as by the resolvent form (an operator-valued Padé approximant (PA)) of the Green operator, which is the generator of the dynamics of the studied system [77].

The rational form of a general response function $R(\omega)$, that is, the system function, in many interdisciplinary fields also follows from a standard relationship between the input $I(\omega)$ and the output $O(\omega)$ data:

$$\text{Output} = \text{Response} \times \text{Input}, \quad O(\omega) = R(\omega)I(\omega). \quad (3)$$

Thus for a generic system, $R(\omega)$ must be a rational algebraic function expressed as a quotient of the output and the input data:

$$\text{Response} = \frac{\text{Output}}{\text{Input}}, \quad R(\omega) = \frac{O(\omega)}{I(\omega)}. \quad (4)$$

Clearly, the simplest form of the response function is the quotient of two polynomials $O_L(\omega)$ and $I_K(\omega)$, in which case $R(\omega)$ is specified as $R_{L,K}(\omega)$:

$$R_{L,K}(\omega) \propto \frac{O_L(\omega)}{I_K(\omega)}, \quad (5)$$

as in the FPT with reference to (1). However, simplicity is not the only reason that leads us to such a rational polynomial for the response function. More importantly, this latter functional form is implied by the physics of the response mechanism of any investigated system to external perturbations. Specifically, a system excited by an external field is set into an oscillatory type of motion that is described mathematically by a differential equation of a definite order. A similar differential equation also governs the intrinsic state of the system even without any external perturbation. The algebraically equivalent structures of these differential equations are their characteristic or secular polynomials. The degree of a given characteristic polynomial is equal to the order of the associated differential equation. Solving a differential equation is equivalent to finding all the roots of the corresponding characteristic polynomial. The physical meaning of the roots of the characteristic polynomial $Q_K(\omega)$ for the input data is that they represent the fundamental frequencies $\{\omega_k\}$ ($1 \leq k \leq K$) of the intrinsic oscillations of the considered system. Here, K is the total number the fundamental attenuated harmonics described by the complex frequencies $\{\omega_k\}$ and the corresponding complex amplitudes $\{d_k\}$.

Therefore, under most general circumstances in any research field, including MRS, the adequate physical considerations invariably lead to a polynomial quotient, as in the FPT, for the response function, which is called a frequency spectrum in signal processing. This is expected, since the formalism of the Green function is entirely equivalent to the Schrödinger equation through which quantum physics becomes applicable to any system including living organisms. However, while direct solutions of the Schrödinger equations are feasible only for the simplest systems of a very limited practical utility, the Green functions can be computed for any physical system irrespective of its complicated structures as long as, for example, the autocorrelation functions or, equivalently, time signal points are available. Precisely, such time signals are encountered in MRS and in many other fields [77]. Therefore, the quantum-mechanical formalism of the Green functions implemented via, for example, the FPT can be used to spectrally analyze such in vivo time signals, as has been previously reported in Refs. [85,86,90,91].

3. THE EXACT SOLUTION FOR THE GENERAL HARMONIC INVERSION PROBLEM

Naturally, the adequacy of any modeling of a studied phenomenon depends critically on the proper description of the underlying physical process.

Section 2 clearly indicates that the FPT is the method of choice for solving the quantification problem in MRS and beyond. Overall, both physics and mathematics lend support to this contention: physics – because MRS gives time signals stemming from damped harmonic oscillators that are equivalent to quantum-mechanical autocorrelation functions (for these time signals, in fact, the FPT is the exact filter) [77]; mathematics – because the exact spectrum for such time signals is a polynomial quotient. Crucially, whenever a function to be modeled is itself a ratio of two polynomials, as is the case with the exact Green function, the FPT represents, by definition, the exact theory and hence the optimality of the FPT for signal processing.

The FPT encompasses two equivalent versions of the Green functions $G^{(+)}$ and $G^{(-)}$, with the incoming and the outgoing boundary conditions, inside and outside the unit circle in the complex plane of the harmonic variable z , and they are denoted by the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$, respectively. The $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$ coincide, respectively, with the causal and anticausal Padé- z transforms that are used extensively in mathematical statistics and the engineering literature on signal processing [77]. The present study applies the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$ to time signals from MRS to prove explicitly that both variants of the FPT are capable of solving exactly the typical quantification problem in MRS, as in Refs. [77–95].

From the computational point of view, the FPT is an extremely efficient signal processor, which is a fast algorithm in the sense of the standard fast Fourier transform (FFT). This can be achieved in the FPT by using the Euclid algorithm implemented with the corresponding continued fractions (CFs) [31,32]. In such a case, the FPT requires $N(\log_2 N)^2$ multiplications, and this is comparable to the customary $N \log_2 N$ multiplications in the FFT.

Regarding applications within MRS especially relevant for clinical diagnostics, there is the unique possibility within the FPT for achieving unequivocal resolution of tightly overlapped resonances [78,82,83]. This is amply demonstrated in the present work on a synthesized time signal reminiscent of those encountered in MRS at the magnetic field strength 1.5 T and short echo time of about 20 ms when encoding is carried out from the brain of a healthy volunteer, as in Ref. [96]. The present study has two special emphases in the most stringent testing of the overall performance of the FPT for synthesized data from MRS: (i) stability and robustness against algorithmic round-off errors in computations aimed at machine accurate reconstructions for noiseless machine accurate input time signals and (ii) optimal reliability for high-resolution quantifications of time signals corrupted with random Gaussian distributed noise.

4. DELAYED TIME SERIES

In studies of the time evolution of a given system, one most frequently starts from an initial state Φ_0 prepared at the instant $t_0 = 0$, which corresponds to $n = 0$.

Here, n counts the discrete time $t \equiv t_n = n\tau$ ($n = 0, 1, 2, \dots$), where τ is the sampling time (also called the dwell time). One of the important characteristics of a given time signal is its total duration $T = N\tau$, which is also known as the total acquisition time. According to the Schrödinger picture of quantum mechanics, for a given Φ_0 , the state Φ_n is obtained from $\Phi_n = \hat{U}\Phi_0$. The time signal $\{c_n\}$ ($0 \leq n \leq N-1$) of length N is equivalent to the quantum-mechanical autocorrelation function $c_n = (\Phi_0 | \hat{U}^n | \Phi_0)$, where $\hat{U} = \hat{U}(\tau)$ is the evolution operator, $\hat{U} = \exp(-i\tau\hat{\Omega})$, with $\hat{\Omega}$ being the system's dynamical operator, which is the Hamiltonian $\hat{H}$ in quantum mechanics. Throughout, the symmetric inner product is used $(f|g) = (g|f)$, that is, with no complex conjugation of either function. The choice $t_0 = 0$ implies that the first element of the so-called data (or Hankel) matrix $\mathbf{H}_n(c_0) \equiv \{c_{i+j}\}$ is the signal point $c_0 = (\Phi_0 | \Phi_0) \neq 0$. Otherwise, the general element $c_{ij} = c_{i+j}$ of the matrix $\mathbf{H}_n(c_0)$ is the overlap between the two Schrödinger (Krylov) states $c_{i+j} = (\Phi_j | \Phi_i) = (\Phi_0 | \hat{U}^{i+j} | \Phi_0) \equiv U_{ij}^{(0)}$. Of course, the matrix that eventually provides the sought spectrum is not $\mathbf{H}_n(c_0)$, but rather $\mathbf{H}_n(c_1)$, which is the evolution matrix. The general element of the matrix $\mathbf{H}_n(c_1)$ is given by $c_{i+j+1} = (\Phi_j | \hat{U} | \Phi_i) \equiv U_{ij}^{(1)}$.

In many situations of practical interest, it is important to consider a nonzero initial time, $t_0 \neq 0$. In this review, in addition to $t_0 = 0$, we shall also consider the delayed time signals with the nonzero initial time $t_s = s\tau$ ($0 \leq s < N-1$). An appropriate mathematical model for the delayed time signal $\{c_{n+s}\}$ ($0 \leq n \leq N-1$, $0 \leq s < N-1$) is a sum of damped complex exponentials:

$$c_{n+s} = \sum_{k=1}^K d_k e^{-i(n+s)\omega_k\tau} = \sum_{k=1}^K d_k^{(s)} u_k^n, \quad (6)$$

$$d_k^{(s)} = d_k u_k^s, \quad d_k \equiv d_k^{(0)}, \quad u = e^{-i\omega\tau}, \quad u_k = e^{-i\omega_k\tau}, \quad (7)$$

where ω_k and $d_k^{(s)}$ are the fundamental angular frequencies and amplitudes, respectively. It is seen from here that the spectral analysis of nondelayed $\{c_n\}$ and delayed time signals $\{c_{n+s}\}$ ($s \neq 0$) can be performed on the same footing, where:

$$c_n = \sum_{k=1}^K d_k e^{-in\omega_k\tau} = \sum_{k=1}^K d_k u_k^n. \quad (8)$$

Both $\mathbf{H}_n(c_0)$ and $\mathbf{H}_n(c_1)$ are the special cases of the general delayed Hankel matrix $\mathbf{H}_n(c_s) = \{c_{n+m+s}\} \equiv \mathbf{U}_n^{(s)}$, which reads as:

$$\mathbf{H}_n(c_s) = \mathbf{U}_n^{(s)} = \begin{pmatrix} c_s & c_{s+1} & c_{s+2} & \cdots & c_{s+n-1} \\ c_{s+1} & c_{s+2} & c_{s+3} & \cdots & c_{s+n} \\ c_{s+2} & c_{s+3} & c_{s+4} & \cdots & c_{s+n+1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ c_{s+n-1} & c_{s+n} & c_{s+n+1} & \cdots & c_{s+2n-2} \end{pmatrix}, \quad (9)$$

where $\mathbf{U}_n^{(s)} = \{U_{ij}^{(s)}\}_{i,j=0}^{n-1}$ and the corresponding delayed Hankel determinant is:

$$\mathbf{H}_n(c_s) = \det \mathbf{H}_n(c_s) = \begin{vmatrix} c_s & c_{s+1} & c_{s+2} & \cdots & c_{s+n-1} \\ c_{s+1} & c_{s+2} & c_{s+3} & \cdots & c_{s+n} \\ c_{s+2} & c_{s+3} & c_{s+4} & \cdots & c_{s+n+1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ c_{s+n-1} & c_{s+n} & c_{s+n+1} & \cdots & c_{s+2n-2} \end{vmatrix}. \quad (10)$$

The “argument” c_s in the small parentheses in $\mathbf{H}_n(c_s)$ denotes the leading element from the first row and first column in the matrix (9). For $s=0$ and $s=1$, the Hankel matrices $\mathbf{H}_n(c_0)$ and $\mathbf{H}_n(c_1)$ become the overlap matrix $\mathbf{S}_n = \mathbf{U}_n^{(0)}$ and the evolution or relaxation matrix $\mathbf{U}_n = \mathbf{U}_n^{(1)}$ in the Schrödinger basis set $\{|\Phi_n\rangle\}$.

5. DELAYED GREEN FUNCTION

A nonzero initial time $t_s \neq 0$ in lieu of $t_0=0$ can also be considered in spectral methods that are based upon the Green function, such as the state-space formulation of the FPT. Here, the delayed Green operator is the delayed resolvent defined by:

$$\hat{R}^{(s)}(u) \equiv (\hat{1}u - \hat{U})^{-1} \hat{U}^s = \sum_{n=0}^{\infty} \hat{U}^{n+s}(\tau) u^{-n-1}. \quad (11)$$

The corresponding delayed Green function $G^{(s)}(u)$ is introduced as the usual matrix element $\langle \Phi_0 | \hat{R}^{(s)}(u) | \Phi_0 \rangle$, which together with Eq. (11) becomes:

$$G^{(s)}(u) = \langle \Phi_0 | \hat{R}^{(s)}(u) | \Phi_0 \rangle = \sum_{n=0}^{\infty} c_{n+s} u^{-n-1}. \quad (12)$$

This is a direct extension of the conventional nondelayed Green function:

$$G(u) = \sum_{n=0}^{\infty} c_n u^{-n-1}, \quad (13)$$

where $G^{(0)}(u) \equiv G(u)$. The delayed counterpart of the usual Green function emerges naturally in signal processing when the infinite time interval $[0, \infty]$ is split into two parts according to $[0, \infty] = [0, s-1] + [s, \infty]$. In such a case, it follows from Eq. (13) that:

$$\begin{aligned} G(u) &= \sum_{n=0}^{s-1} c_n u^{-n-1} + u^{-s} \sum_{n=0}^{\infty} c_{n+s} u^{-n-1} \\ &= \sum_{n=0}^{s-1} c_n u^{-n-1} + u^{-s} G^{(s)}(u), \end{aligned} \quad (14)$$

where $\Sigma_{n=0}^{-1} \equiv 0$. This gives a relationship between the two exact Green functions $G^{(s)}(u)$ and $G^{(0)}(u)$ that correspond to the case with and without the delay, that is, $s \neq 0$ and $s = 0$, respectively. We see from Eq. (13) that the delayed spectrum $G^{(s)}(u)$ is multiplied by the term u^{-s} to compensate for the time evolution of the system from $t_0 = 0$ to $t_s \neq 0$.

Substituting Eq. (6) in the rhs of Eq. (11), it follows:

$$\begin{aligned} \sum_{n=0}^{\infty} c_{n+s} u^{-n-1} &= \sum_{n=0}^{\infty} \left\{ \sum_{k=1}^K d_k^{(s)} u_k^n \right\} u^{-n-1} \\ \sum_{k=1}^K d_k^{(s)} u^{-1} \left\{ \sum_{n=0}^{\infty} (u_k/u)^n \right\} &= \sum_{k=1}^K d_k^{(s)} u^{-1} (1 - u_k/u)^{-1}, \end{aligned}$$

where the geometric series $\Sigma_{n=0}^{\infty} x^n = 1/(1-x)$ is employed, so that:

$$\sum_{n=0}^{\infty} c_{n+s} u^{-n-1} = \sum_{k=1}^K \frac{d_k^{(s)}}{u - u_k}. \quad (15)$$

This is the most important feature of the mathematical model (6). The lhs of Eq. (15) represents the *exact* delayed spectrum associated with the delayed signal (6). This exactness is due to the presence of an infinite sum, that is, a series of signal points. It is precisely here that the model (6) displays its distinct power by using no approximation whatsoever to reduce the *infinite* sum over the signal points $\Sigma_{n=0}^{\infty} c_{n+s} u^{-n-1}$ to the finite sum over the reconstructed signal's parameters $\Sigma_{k=1}^K d_k^{(s)} / (u - u_k)$. Of course, in practice, only a finite number of signal points is customarily available, so that the exact spectrum $\Sigma_{n=0}^{\infty} c_{n+s} u^{-n-1}$ cannot be obtained. Nevertheless, in such a case, the finite geometric sum $\Sigma_{n=0}^{N-1} x^n = (1 - x^N)/(1 - x)$ can be used to obtain the following exact result for the truncated spectrum:

$$\sum_{n=0}^{N-1} c_{n+s} u^{-n-1} = \sum_{k=1}^K d_k^{(s)} \frac{1 - (u_k/u)^N}{u - u_k}. \quad (16)$$

This result tends to Eq. (15) as $N \rightarrow \infty$ if $|u_k/u| < 1$ ($1 \leq k \leq K$). In the response functions (15) and (16) corresponding, respectively, to the infinite ($N = \infty$) and finite ($N < \infty$) signal length, the exact delayed spectrum for the model (4.1) is given by rational functions. The two rational functions from the rhs of (15) and (16) are the polynomial quotients that are the PAs for the input sums $\Sigma_{n=0}^{\infty} c_{n+s} u^{-n-1}$ and $\Sigma_{n=0}^{N-1} c_{n+s} u^{-n-1}$, respectively. Thus, for any processing method used to reconstruct the spectral parameters $\{u_k, d_k^{(s)}\}$ from the input signal of the form (6), the resulting spectrum will invariably be the PA, as the unique ratio of two polynomials for the given power series expansion (e.g., the Green function and the like). Hence, there can be hardly any doubt

as to which signal processor is optimal for parametric estimations of spectra due to the time signal (6).

6. THE KEY PRIOR KNOWLEDGE: INTERNAL STRUCTURE OF TIME SIGNALS

By definition, the PA becomes the exact theory if the input function is a rational function given as a quotient of two polynomials (a rational polynomial). Here, the exactness overrides the requested optimality, and therefore, the PA has no competitor for studying input functions that are themselves defined as rational polynomials. However, the input function in signal processing is *not* a ratio of two polynomials, but rather a single sum $\sum_n c_n + s u^{-n-1}$ for which no processor is exact. The only way to salvage the situation and eventually still arrive at an exact theory of this latter spectrum is to invoke the appropriate prior information, for example, the existence of a harmonic structure of the signal, as in Eq. (6). In such a case, without any further approximation, the single sum $\sum_n c_n + s u^{-n-1}$ from the original input becomes exactly equivalent to a rational polynomial (15) or (16), for which the Padé approximation is again the exact theory.

To elaborate the general issue of prior information, the minimal knowledge needed in advance would be an assumption that the time signal *has a structure*. For example, by solely plotting a given signal, a practitioner who is experienced with time sequences could qualitatively discern certain oscillatory patterns pointing at a harmonic-type structure. Such structures often become more pronounced by viewing the corresponding derivative of the time signal. Of course, the Fourier shape spectrum in the frequency domain would give a more definitive indication of an underlying structure through a clearer display of a number of peaks. In this way, the otherwise generic structure would become more specific, indicating the resonant nature of the spectrum.

However, the Fourier method does not capitalize on this critical finding from its own analysis and, therefore, in the end it is left with the envelope spectrum alone. The lack of ability to exploit the structure of the processed signal is reflected directly in the so-called “Fourier uncertainty principle.” According to this principle, for a fixed total acquisition time T , or equivalently, a given full signal length N at a fixed bandwidth, the corresponding Fourier spectrum cannot offer an angular frequency resolution better than the Fourier bound $2\pi/T$. The first drawback of such a principle is in an immediate implication that, irrespective of their intrinsic nature, all the signals of the same acquisition time T have the same frequency resolution $2\pi/T$. Stated equivalently, all Fourier spectra due to all time signals of the same length N will have the same resolution. Specifically, prior to both measurements and processing, the Fourier method predefines the

frequencies at which all the spectra exist and these are the frequencies from the Fourier grid $2\pi k/T$ ($k = 0, 1, \dots, N-1$). This fact rules out the chance for interpolation or extrapolation. Without an interpolation feature, the Fourier method is restricted to the predetermined minimal separation $\omega_{\min} = 2\pi/T$ between any two adjacent frequencies. Moreover, without an extrapolation property, the Fourier approach has no predictive power. Instead of extrapolation, the Fourier analysis usually resorts to zero filling (zero padding) beyond N or to using the signal's periodic extensions $c_{n+N} = c_n$. For genuinely nonperiodic signals encountered in most circumstances, neither of these two latter recipes invoke any extrapolation, let alone new information.

The first step in an attempt to simultaneously circumvent all the listed basic limitations of the Fourier method is to acknowledge the fact that each signal does indeed possess its own inner structure. The second step would follow afterward with the aim of unfolding the hidden structure which can be parametrized. The third, quantitative step is to find the spectral characteristics by reconstructing the resonance parameters $\{u_k, d_k^{(s)}\}$ from the signal. This opens the door to parametric estimations of spectra as opposed to shape processing by Fourier. In particular, the fact that the signal has an internal structure via, for example, a number of constituent harmonics $\{d_k^{(s)} u_k^n\}$, clearly offers the possibility for resolution improvement beyond the Fourier bound $2\pi/T$. For parametric processors, the total acquisition time T of the signal ceases to be a prerequisite for definition of the spectral resolution. Therefore, parametric estimations of spectra can indeed lower the Fourier bound $2\pi/T$, which automatically leads to an improved resolution beyond the prescription of the Fourier uncertainty principle. What made the Fourier uncertainty principle obsolete in the realm of parametric processing is a milder restriction imposed by “the informational principle.” This latter principle states that no more information could possibly be obtained from a spectrum in the frequency domain than what has been encoded originally in the time domain. This indispensable conservation of information translates into an algebraic condition that requires a minimum of $2K$ signal points to reconstruct all the spectral parameters $\{u_k, d_k^{(s)}\}$ ($1 \leq k \leq K$). Such a condition is guided by the demand that the underlying system of linear equations must be at least determined (the number of equations equal to the number of the unknown parameters). In practice, the experimentally measured time signals are usually corrupted with noise whose presence could be partially mitigated by solving a corresponding overdetermined system in which the number of signal points exceeds the number $2K$ of the sought parameters $\{u_k, d_k^{(s)}\}$.

The delayed signal $\{c_{n+s}\}$ stems from a physical system which has already evolved from $t_0 = 0$ to $t_s \neq 0$ before starting to count the time. In this case, the spectral analysis is concerned with the delayed Hankel matrix $\mathbf{H}_n(c_s) = \{c_{i+j+s}\}$, with the first element being $c_s = (\Phi_0 | \hat{U}^s | \Phi_0) \neq 0$. In the FFT,

such a delay effect in the signal is conceived merely as skipping the first s points $\{c_r\}$ ($0 \leq r \leq s-1$) from the whole signal $\{c_n\}$ ($0 \leq n \leq N-1$). However, the ensuing FFT spectra are known to be of unacceptably poor quality that cannot be corrected for the skipped data. Therefore, it is important to design signal processors that can handle data matrices $\{c_{i+j+s}\}$ that describe the evolution of the investigated system from a nonzero initial time $t_s = s\tau \neq 0$.

The problem of spectral analysis of data records with delayed time series is of great importance in many applications that rely upon signal processing methods. Naturally, theoretical developments always favor the analysis of the general delayed Hankel matrix $\mathbf{H}_n(c_s)$, since the corresponding counterparts $\mathbf{H}_n(c_0)$ and $\mathbf{H}_n(c_1)$ from signal processing are merely two particular cases of the former data taken at $s=0$ and $s=1$, respectively. Of course, a general approach based upon $\mathbf{H}_n(c_s)$ is likely to offer certain potential advantages over a particular one given by the evolution matrix $\mathbf{H}_n(c_1)$, especially in the practical domain of creating more fruitful algorithms. This will be partially documented in the present review. It will be shown that the mere introduction of a nonzero initial time $t_s \neq 0$ has far-reaching consequences for spectral analysis, even if we are actually interested in keeping the whole signal $\{c_n\}$ ($0 \leq n \leq N-1$) of total length N . For example, processing the evolution matrix $\mathbf{H}_n(c_1)$ ordinarily requires matrix diagonalizations or, equivalently, rooting the corresponding characteristic equation to obtain the spectral parameters $\{u_k, d_k\}$ of the signal (8). In sharp contrast to this, both of these latter procedures can be bypassed altogether when $\mathbf{H}_n(c_s)$ is used with any fixed integer $s > 0$ and not just $s=1$ as in the evolution matrix $\mathbf{H}_n(c_1)$. The sought spectral parameters $\{u_k, d_k\}$ will follow directly from convergence of the appropriate “delayed” CF coefficients as the values of number s are systematically increased [77].

As opposed to the FFT, the space methods such as the FPT from the Schrödinger picture of quantum mechanics can spectrally analyze data matrices with an arbitrary initial time t_s . These estimators rely upon the evolution operator $\hat{U}$, which generates the state Φ_s at the delayed moment t_s via the prescription $\Phi_s = \hat{U}^s \Phi_0$, as already mentioned. Here, the delay is achieved by starting the analysis from Φ_s rather than from Φ_0 , which refers to $s=0$. Evolution of the system in the time interval $[t_0, t_s]$ of nonzero length must be properly taken into consideration. This correction is readily adjusted in the state-space methods via multiplication of the vector Φ_0 by the required operator $\hat{U}^{-s} = \exp(is\hat{\Omega}\tau)$, which would cancel out the evolution effect accumulated in the state vector in the time interval $t \in [0, t_s]$. In other words, if the first s signal points are skipped, all the matrix elements in the state-space version of the FPT must be modified by the counteracting operator $\exp(is\hat{\Omega}\tau)$. Therefore, in such signal processors, taking the instant $t_s \neq 0$ instead of $t_0=0$ for the initial time will not cause any difficulty.

The state-space methods perform spectral analysis by diagonalizing¹ the data matrix $\mathbf{H}_n(c_s)$ for any integer s precisely in the same fashion as for $\mathbf{H}_n(c_0)$ and $\mathbf{H}_n(c_1)$. Moreover, there is a very important advantage in diagonalizing the delayed evolution matrix $\mathbf{H}_n(c_s) = \mathbf{U}_n^{(s)} = \{U_{ij}^{(s)}\}$ relative to $\mathbf{H}_n(c_1)$, where the general element $U_{ij}^{(s)}$ stems from the s th power of $\hat{U}$ via $U_{ij}^{(s)} = (\Phi_j | \hat{U}^s | \Phi_i)$. This advantage is in the possibility of identifying spurious roots. To achieve such a goal, one could diagonalize the matrix $\mathbf{U}_n^{(s)}$, not only for the primary case of interest ($s=1$), but also for $s=2$, for example, and compare the obtained eigenfrequencies. The matching frequencies for different values of s would be retained as physical (genuine), whereas those frequencies that change when going from $s=1$ to $s=2$ should be rejected as unphysical (spurious). Likewise, in the non-state-space variant of the FPT, one could employ different powers s of the evolution operator $\hat{U}$ that are, in fact, implicit in the para-diagonal elements $[(n+s-1)/n]_G(u)$ of the Padé table² associated with the delayed counterpart $G^{(s)}(u)$ of the Green function $G(u)$ from Eq. (13). Here, we would select several values of s to distinguish between physical and spurious eigenroots of the denominator polynomials, which are the same as the mentioned characteristic polynomials. Those roots that are stable/unstable for different s are conceived as physical/unphysical, respectively. These are some of the practical advantages to which we alluded earlier that give support to considering the initial times t_s different from the customary one, $t_0=0$.

7. THE RUTISHAUSER QUOTIENT–DIFFERENCE RECURSIVE ALGORITHM

A general CF is another way of writing the PA as a staircase with descending quotients. There are several equivalent symbolic notations in use for a given CF and two of them are given by:

$$\frac{A_1}{B_1 + \frac{A_2}{B_2 + \frac{A_3}{B_3 + \ddots}}} \equiv \frac{A_1}{B_1} + \frac{A_2}{B_2} + \frac{A_3}{B_3} + \dots \quad (17)$$

The lhs of (17) is a natural way of writing the staircase-shaped CF, but for frequent use, the rhs of the same equation is more economical as it takes less space. It should be observed that the plus signs on the rhs of (17) are *lowered* to remind us of a “step-down” process in forming the CF. In other words,

¹As an alternative to diagonalization of the data matrix, the standard FPT can resort to rooting the corresponding characteristic equations.

²The symbol $[m/n](x)$ is the standard notation for the polynomial quotient $P_m(x)/Q_n(x)$ that represents the PA to the Maclaurin series expansion of a given function $f(x)$.

the rhs of (17) could also be equivalently written using the ordinary plus signs as $A_1/(B_1 + A_2/(B_2 + A_3/(B_3 + \dots)))$.

The infinite- and the m th-order delayed CF to the time series (12) are, respectively, defined as [77]:

$$G^{\text{CF}(s)}(u) = \frac{a_1^{(s)}}{u} - \frac{a_2^{(s)}}{1} - \frac{a_3^{(s)}}{u} - \dots - \frac{a_{2r}^{(s)}}{1} - \frac{a_{2r+1}^{(s)}}{u} - \dots \quad (18)$$

$$G_m^{\text{CF}(s)}(u) = \frac{a_1^{(s)}}{u} - \frac{a_2^{(s)}}{1} - \frac{a_3^{(s)}}{u} - \dots - \frac{a_{2m}^{(s)}}{1} - \frac{a_{2m+1}^{(s)}}{u} \quad (19)$$

where $a_n^{(s)}$ are the expansion coefficients. All the elements of the set $\{a_n^{(s)}\}$ can be found from the equality between the expansion coefficients of the series of the rhs of (18) developed in powers of u^{-1} and the signal points $\{c_{n+s}\}$ from Eq. (12). The analysis is similar to the one from Ref. [84] for nondelayed time signals and Green functions when $s=0$. Therefore, it suffices to give some of the main results that will be needed in the subsequent analysis:

$$a_{2n}^{(s)} = \frac{H_n(c_{s+1})H_{n-1}(c_s)}{H_{n-1}(c_{s+1})H_n(c_s)}; \quad a_{2n+1}^{(s)} = \frac{H_{n-1}(c_{s+1})H_{n+1}(c_s)}{H_n(c_s)H_n(c_{s+1})}, \quad (20)$$

$$\alpha_n^{(s)} = a_{2n+1}^{(s)} + a_{2n+2}^{(s)}; \quad [\beta_n^{(s)}]^2 = a_{2n}^{(s)}a_{2n+1}^{(s)} \quad (n \geq 1), \quad (21)$$

where the Hankel determinant $H_n(c_s)$ is defined by Eq. (10). Here, $\alpha_n^{(s)}$ and $[\beta_n^{(s)}]^2$ are the Lanczos coupling constants in the nearest neighbor approximation [77]. The first three Lanczos parameters computed from Eq. (21) are:

$$\alpha_0^{(s)} = \frac{c_{s+1}}{c_s}; \quad \alpha_1^{(s)} = \frac{c_s^2 c_{s+3} - 2c_s c_{s+1} c_{s+2} + c_{s+1}^3}{c_s(c_s c_{s+2} - c_{s+1}^2)}, \quad (22)$$

$$[\beta_1^{(s)}]^2 = \frac{c_s c_{s+2} - c_{s+1}^2}{c_s^2}. \quad (23)$$

Using Eqs. (20) and (21), a recursive algorithm can be derived for computations of all the coefficients $\{a_n^{(s)}\}$. To this end, we shall interchangeably use the following alternative notation:

$$a_{2n}^{(s)} \equiv q_n^{(s)}, \quad a_{2n+1}^{(s)} \equiv e_n^{(s)}. \quad (24)$$

Then, the product of $q_n^{(s)}$ and $e_n^{(s)}$ becomes:

$$\begin{aligned} q_n^{(s)} e_n^{(s)} &= \frac{H_{n-1}(c_s)H_n(c_{s+1})}{H_{n-1}(c_{s+1})H_n(c_s)} \frac{H_{n-1}(c_{s+1})H_{n+1}(c_s)}{H_n(c_s)H_n(c_{s+1})} \\ \therefore q_n^{(s)} e_n^{(s)} &= \frac{H_{n-1}(c_s)H_{n+1}(c_s)}{H_n^2(c_s)}. \end{aligned} \quad (25)$$

In a similar way, we can evaluate the product of $q_{n+1}^{(s)}$ and $e_n^{(s)}$ as:

$$\begin{aligned}
 q_{n+1}^{(s)} e_n^{(s)} &= \frac{H_n(c_s) H_{n+1}(c_{s+1})}{H_n(c_{s+1}) H_{n+1}(c_s)} \frac{H_{n-1}(c_{s+1}) H_{n+1}(c_s)}{H_n(c_s) H_n(c_{s+1})} \\
 &= \frac{H_{n-1}(c_{s+1}) H_{n+1}(c_{s+1})}{H_n(c_{s+1}) H_n(c_{s+1})} \\
 &= \frac{H_{n-1}(c_{s+1}) H_n(c_{s+2})}{H_{n-1}(c_{s+2}) H_n(c_{s+1})} \frac{H_{n-1}(c_{s+2}) H_{n+1}(c_{s+1})}{H_n(c_{s+2}) H_n(c_{s+1})} \\
 &= q_n^{(s+1)} e_n^{(s+1)}, \\
 \therefore q_{n+1}^{(s)} e_n^{(s)} &= q_n^{(s+1)} e_n^{(s+1)}, \quad s \geq 0.
 \end{aligned} \tag{26}$$

Using the following well-known identity among Hankel determinants:

$$[H_n(c_s)]^2 = H_n(c_{s-1}) H_n(c_{s+1}) - H_{n+1}(c_{s-1}) H_{n-1}(c_{s+1}), \tag{27}$$

we can calculate the sum of $q_n^{(s+1)}$ and $e_{n-1}^{(s+1)}$:

$$\begin{aligned}
 q_n^{(s+1)} + e_{n-1}^{(s+1)} &= \frac{H_{n-1}(c_{s+1}) H_n(c_{s+2})}{H_{n-1}(c_{s+2}) H_n(c_{s+1})} + \frac{H_{n-2}(c_{s+2}) H_n(c_{s+1})}{H_{n-1}(c_{s+1}) H_{n-1}(c_{s+2})} \\
 &= [H_{n-1}(c_{s+2}) H_{n-1}(c_{s+1}) H_n(c_{s+1})]^{-1} \\
 &\quad \times [H_{n-1}^2(c_{s+1}) H_n(c_{s+2}) + H_{n-2}(c_{s+2}) H_n^2(c_{s+1})] \\
 &= [H_{n-1}(c_{s+2}) H_{n-1}(c_{s+1}) H_n(c_{s+1}) H_n(c_s)]^{-1} \\
 &\quad \times \{H_{n-1}^2(c_{s+1}) [H_n(c_s) H_n(c_{s+2})] \\
 &\quad + [H_n(c_s) H_{n-2}(c_{s+2})] H_n^2(c_{s+1})\} \\
 &= [H_{n-1}(c_{s+2}) H_{n-1}(c_{s+1}) H_n(c_{s+1}) H_n(c_s)]^{-1} \\
 &\quad \times \{H_{n-1}^2(c_{s+1}) [H_n^2(c_{s+1}) + H_{n+1}(c_s) H_{n-1}(c_{s+2})] \\
 &\quad + H_n^2(c_{s+1}) [H_{n-1}(c_s) H_{n-1}(c_{s+2}) - H_{n-1}^2(c_{s+1})]\} \\
 &= \frac{H_{n-1}^2(c_{s+1}) H_{n+1}(c_s) H_{n-1}(c_{s+2})}{H_{n-1}(c_{s+2}) H_{n-1}(c_{s+1}) H_n(c_{s+1}) H_n(c_s)} \\
 &\quad + \frac{H_n^2(c_{s+1}) H_{n-1}(c_s) H_{n-1}(c_{s+2})}{H_{n-1}(c_{s+2}) H_{n-1}(c_{s+1}) H_n(c_{s+1}) H_n(c_s)} \\
 &= \frac{H_{n-1}(c_s) H_n(c_{s+1})}{H_{n-1}(c_{s+1}) H_n(c_s)} + \frac{H_{n-1}(c_{s+1}) H_{n+1}(c_s)}{H_n(c_s) H_n(c_{s+1})} \\
 &= q_n^{(s)} + e_n^{(s)}, \\
 \therefore q_n^{(s)} + e_n^{(s)} &= q_n^{(s+1)} + e_{n-1}^{(s+1)}.
 \end{aligned} \tag{28}$$

The derived relationships (26) and (28) for the delayed CF coefficients are recognized as the Rutishauser quotient–difference (QD) algorithm [10]:

$$\left. \begin{aligned} e_n^{(s)} &= e_{n-1}^{(s+1)} + q_n^{(s+1)} - q_n^{(s)} \\ q_{n+1}^{(s)} &= q_n^{(s+1)} \frac{e_n^{(s+1)}}{e_n^{(s)}} \\ e_0^{(s)} &= 0 \quad (s \geq 1), \quad q_1^{(s)} = \frac{c_{s+1}}{c_s} \quad (s \geq 0) \end{aligned} \right\}. \quad (29)$$

From here, the first few coefficients are readily deduced in the form

$$\begin{aligned} q_1^{(s)} &= \frac{c_{s+1}}{c_s}, \\ e_1^{(s)} &= \frac{c_s c_{s+2} - c_{s+1}^2}{c_s c_{s+1}}, \\ q_2^{(s)} &= \frac{c_s (c_{s+1} c_{s+3} - c_{s+2}^2)}{c_{s+1} (c_s c_{s+2} - c_{s+1}^2)}, \\ e_2^{(s)} &= \frac{c_{s+1} (c_s c_{s+2} c_{s+4} - c_{s+1}^2 c_{s+4} - c_{s+2}^3 - c_s c_{s+3}^2 + 2 c_{s+1} c_{s+2} c_{s+3})}{(c_s c_{s+2} - c_{s+1}^2) (c_{s+1} c_{s+3} - c_{s+2}^2)}. \end{aligned} \quad (30)$$

As seen from Eq. (29), the vectors $q_n^{(s)}$ and $e_n^{(s)}$ are generated by interchangeably forming their quotients and differences and hence the name “quotient–difference” for this algorithm. The QD algorithm is one of the most extensively used tools in the field of numerical analysis. The vectors $q_n^{(s)}$ and $e_n^{(s)}$ form a two-dimensional table as a double array of a lozenge form which can be depicted for $s = 0, 1, 2, \dots$, as:

$$\begin{array}{ccccccc} & & q_1^{(0)} & & & & \\ e_0^{(1)} & & & e_1^{(0)} & & & \\ & q_1^{(1)} & & & q_2^{(0)} & & \\ e_0^{(2)} & & e_1^{(1)} & & & e_2^{(0)} & \\ & q_1^{(2)} & & q_2^{(1)} & & \ddots & \\ e_0^{(3)} & & e_1^{(2)} & & e_2^{(1)} & & \\ \vdots & q_1^{(3)} & & q_2^{(2)} & & \ddots & \\ & \vdots & e_1^{(3)} & \vdots & e_2^{(2)} & & \\ & & \vdots & & \vdots & \ddots & \end{array} \quad (31)$$

where the first column is filled with zeros $e_0^{(0)}=0$. We see from the array (31) that the subscript (n) and superscript (s) denote a column and a counter-diagonal, respectively. The columns of the arrays $q_n^{(s)}$ and $e_n^{(s)}$ are interleaved. The starting values are $e_0^{(s)}=0$ ($s=1, 2, \dots$) and $q_1^{(s)}=c_{s+1}/c_s$ ($s=0, 1, 2, \dots$). Further arrays $q_n^{(s)}$ and $e_n^{(s)}$ are generated through two intertwined recursions of quantities that are located at the vertices (corners) of the lozenge in the array (31). The column containing only the vectors $e_n^{(s)}$ are derived via the differences $e_n^{(s)}=q_n^{(s+1)}-q_n^{(s)}+e_{n-1}^{(s+1)}$ ($n=1, 2, \dots$ and $s=0, 1, 2, \dots$). Likewise, the columns with the arrays $q_n^{(s)}$ are constructed by means of the quotients $q_n^{(s)}=q_{n-1}^{(s+1)}e_{n-1}^{(s+1)}/e_{n-1}^{(s)}$ ($n=2, 3, \dots$ and $s=0, 1, 2, \dots$). This is the whole procedure by which the QD algorithm generates one column at a time by alternatively forming the quotients and differences of the q - and e -quantities via the recursive relations from Eq. (29).

8. THE GORDON PRODUCT–DIFFERENCE RECURSIVE ALGORITHM

The Lanczos algorithm is known to experience numerical difficulties such as loss of orthogonality among the elements of the Lanczos basis set $\{\psi_n\}$. This can, in turn, severely deteriorate the required accuracy of the coupling parameters that are generated during the construction of the state vectors $\{\psi_n\}$. Since the Lanczos coupling constants are of paramount importance for spectral analysis, it is imperative to search for more stable algorithms than the Lanczos recursion for state vectors $\{\psi_n\}$, but still rely upon the signal points $\{c_n\}$ as the only input data. Since the main goal is to obtain the couplings, it is natural to try to alleviate any unnecessary computations for this purpose, and especially to avoid the construction of state vectors $\{\psi_n\}$ whose orthogonality could be destroyed during the Lanczos recursion. Fortunately, there are at least two recursive algorithms that fulfill the two said requirements by securing the reliance solely upon the signal points and by simultaneously avoiding the Lanczos state vectors altogether. One of them is Rutishauser's QD algorithm [10] and the other is Gordon's [12] product–difference (PD) algorithm. Both of them can compute the complete set of the coupling constants $\{\alpha_n^{(s)}, \beta_n^{(s)}\}$ for arbitrarily large values of n . This is important especially in view of a statement from *Numerical Recipes* [37] claiming that computing these coupling parameters generated by, for example, the power moments $\{\mu_n\}$ (equivalent to $\{c_n\}$) must be considered as useless due to their ill-conditioning. However, such a claim does not apply to the power moments generated by the QD and PD algorithms [10,12].

In order to write the general prescription for the PD algorithm, we first introduce an auxiliary matrix $\lambda^{(s)} = \{\lambda_{n,m}^{(s)}\}$ with zero-valued elements below the main counter-diagonal:

$$\lambda^{(s)} = \begin{pmatrix} \lambda_{1,1}^{(s)} & \lambda_{1,2}^{(s)} & \lambda_{1,3}^{(s)} & \cdots & \lambda_{1,n-2}^{(s)} & \lambda_{1,n-1}^{(s)} & \lambda_{1,n}^{(s)} \\ \lambda_{2,1}^{(s)} & \lambda_{2,2}^{(s)} & \lambda_{2,3}^{(s)} & \cdots & \lambda_{2,n-2}^{(s)} & \lambda_{2,n-1}^{(s)} & 0 \\ \lambda_{3,1}^{(s)} & \lambda_{3,2}^{(s)} & \lambda_{3,3}^{(s)} & \cdots & \lambda_{3,n-2}^{(s)} & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ \lambda_{n-2,1}^{(s)} & \lambda_{n-2,2}^{(s)} & \lambda_{n-2,3}^{(s)} & \cdots & 0 & 0 & 0 \\ \lambda_{n-1,1}^{(s)} & \lambda_{n-1,2}^{(s)} & 0 & \cdots & 0 & 0 & 0 \\ \lambda_{n,1}^{(s)} & 0 & 0 & \cdots & 0 & 0 & 0 \end{pmatrix}. \quad (32)$$

The first column of this matrix is initialized to zero except for the element $\lambda_{1,1}^{(s)}$, which is set to unity, whereas the second column is filled with the signal points with the alternating sign according to:

$$\lambda^{(s)} = \begin{pmatrix} 1 & c_s & c_{s+1} & \cdots & \lambda_{1,n-2}^{(s)} & \lambda_{1,n-1}^{(s)} & \lambda_{1,n}^{(s)} \\ 0 & -c_{s+1} & -c_{s+2} & \cdots & \lambda_{2,n-2}^{(s)} & \lambda_{2,n-1}^{(s)} & 0 \\ 0 & c_{s+2} & c_{s+3} & \cdots & \lambda_{3,n-2}^{(s)} & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & (-1)^{n-1}c_{n+s-3} & (-1)^{n-1}c_{n+s-2} & \cdots & 0 & 0 & 0 \\ 0 & (-1)^n c_{n+s-2} & 0 & \cdots & 0 & 0 & 0 \\ 0 & 0 & 0 & \cdots & 0 & 0 & 0 \end{pmatrix}. \quad (33)$$

Here, the general matrix element $\lambda_{n,m}^{(s)}$ is defined by:

$$\lambda_{n,m}^{(s)} \equiv - \begin{vmatrix} \lambda_{1,m-2}^{(s)} & \lambda_{1,m-1}^{(s)} \\ \lambda_{n+1,m-2}^{(s)} & \lambda_{n+1,m-1}^{(s)} \end{vmatrix}. \quad (34)$$

This can be rewritten as a simple recursion:

$$\lambda_{n,m}^{(s)} = \lambda_{1,m-1}^{(s)} \lambda_{n+1,m-2}^{(s)} - \lambda_{1,m-2}^{(s)} \lambda_{n+1,m-1}^{(s)}, \quad (35)$$

with the initialization:

$$\lambda_{n,1}^{(s)} = \delta_{n,1}, \quad \lambda_{n,2}^{(s)} = (-1)^{n+1} c_{n+s-1}, \quad \lambda_{n,3}^{(s)} = (-1)^{n-1} c_{n+s}, \quad (36)$$

where $\delta_{n,1}$ is the Kronecker symbol ($\delta_{n,m}=1$ for $n=m$ and $\delta_{n,m}=0$ for $n \neq m$). Once the arrays $\{\lambda_{i,j}^{(s)}\}$ are generated, we can compute all the coefficients $\{a_n^{(s)}\}$ of the delayed CFs (18) by using the following expression:

$$a_n^{(s)} = \frac{\lambda_{1,n+1}^{(s)}}{\lambda_{1,n-1}^{(s)} \lambda_{1,n}^{(s)}} \quad (n=1, 2, 3, \dots). \quad (37)$$

Substituting Eq. (37) into Eq. (24), it follows:

$$q_n^{(s)} = \frac{\lambda_{1,2n+1}^{(s)}}{\lambda_{1,2n-1}^{(s)} \lambda_{1,2n}^{(s)}}, \quad e_n^{(s)} = \frac{\lambda_{1,2n+2}^{(s)}}{\lambda_{1,2n}^{(s)} \lambda_{1,2n+1}^{(s)}} \quad (38)$$

Finally, the Lanczos coupling parameters $\{\alpha_n^{(s)}, [\beta_n^{(s)}]^2\}$ are obtained by substituting the string $\{a_n^{(s)}\}$ in Eq. (21). The explicit dependence of the pair $\{\alpha_n^{(s)}, [\beta_n^{(s)}]^2\}$ upon the auxiliary elements $\{\lambda_{1,n}^{(s)}\}$ follows from Eqs. (21) and (37) as:

$$\alpha_n^{(s)} = \frac{[\lambda_{1,2n+2}^{(s)}]^2 + \lambda_{1,2n}^{(s)} \lambda_{1,2n+3}^{(s)}}{\lambda_{1,2n}^{(s)} \lambda_{1,2n+1}^{(s)} \lambda_{1,2n+2}^{(s)}}, \quad [\beta_n^{(s)}]^2 = \frac{\lambda_{1,2n+2}^{(s)}}{\lambda_{1,2n-1}^{(s)} [\lambda_{1,2n}^{(s)}]^2}. \quad (39)$$

We see that the recursion (34) on the vectors $\{\lambda_{n,m}^{(s)}\}$ involves only their products and differences, but no divisions and hence the name “product-difference” algorithm. The PD algorithm for nondelayed signals or moments ($s=0$) has originally been introduced by Gordon [12]. The extension of the PD algorithm to delayed time signals or moments $\{c_{n+s}\} = \{\mu_{n+s}\}$ was given by Belkić [77]. As seen from Eq. (37), the PD algorithm performs the division only once at the end of the computations to arrive straight at the delayed CF coefficients $\{a_n^{(s)}\}$. For this reason, the PD algorithm is error-free for signal points $\{c_{n+s}\}$ that are integers. Such integer data matrices $\{c_{n+s}\}$ are measured experimentally in MRS, NMR, ICR-MS, and so on. The same infinite-order precision (no round-off errors) is achievable within the PD algorithm for autocorrelation functions $\{c_n\}$ or power moments $\{\mu_{n+s}\}$ given as rational numbers. In many cases of physical interest (e.g., systems exposed to external fields), the role of signal points is played by expansion coefficients that are obtained exactly as rational numbers from the quantum-mechanical perturbation theory. Here, one would operate directly with rational numbers by means of symbolic language programming, such as MAPLE and the like [45–47]. The computational complexity of the PD algorithm for the CF coefficients $\{a_m^{(s)}\}$ ($1 \leq m \leq n$) is of the order of n^2 multiplications. By comparison, a direct computation of the Hankel determinant $H_n(c_s)$ of the dimension n entering the definition (20) for $\{a_n^{(s)}\}$ requires, within the Cramer rule, some formidable $n!$ multiplications that would preclude any meaningful application for large n .

We saw in Section 7 that the QD algorithm (29) for the auxiliary double array $\{q_n^{(s)}, e_n^{(s)}\}$ carries out divisions in each iteration. In a finite-precision arithmetic, this could lead to round-off errors that might cause the QD algorithm to break down for noninteger signal points. However, if the input data $\{c_{n+s}\}$ are nonzero integers, then divisions would produce rational numbers during the QD recursion. This would be innocuous leading to error-free results, provided that the infinite-precision arithmetic with rational numbers is employed via MAPLE [45–47], for example.

It is also possible to show that the vectors $\{\lambda_{1,m}^{(s)}\}$ can advantageously be combined to produce Hankel determinants of arbitrary orders. To this end, using Eq. (34), we have generated the first several vectors $\{\lambda_{n,m}^{(s)}\}$ and their particular values yield the following relationships in terms of the Hankel determinants $\{H_n(c_s)\}$ [84]:

$$\begin{aligned} H_2(c_s) &= \frac{\lambda_{1,4}^{(s)}}{\prod_{m=1}^2 \lambda_{1,m}^{(s)}} H_1(c_s), \\ H_3(c_s) &= \frac{\lambda_{1,6}^{(s)}}{\prod_{m=1}^4 \lambda_{1,m}^{(s)}} H_2(c_s), \\ H_4(c_s) &= \frac{\lambda_{1,8}^{(s)}}{\prod_{m=1}^6 \lambda_{1,m}^{(s)}} H_3(c_s), \text{ etc,} \\ \therefore H_n(c_s) &= \frac{\lambda_{1,2n}^{(s)}}{\lambda_{2n-2}^{(s)}} H_{n-1}(c_s), \quad \lambda_n^{(s)} = \prod_{m=1}^n \lambda_{1,m}^{(s)}. \end{aligned} \quad (40)$$

The recursion (40) can be trivially solved by iterations with the explicit result:

$$H_n(c_s) = c_s \prod_{m=2}^n \frac{\lambda_{1,2m}^{(s)}}{\lambda_{2m-2}^{(s)}}, \quad H_1(c_s) = c_s \quad (n=2, 3, \dots). \quad (41)$$

This completes the demonstration that the general-order Hankel determinant $H_n(c_s)$ can be easily obtained from the recursively precomputed string $\{\lambda_{1,m}^{(s)}\}$. We have verified explicitly that, for example, the particular results for $H_2(c_s)$, $H_3(c_s)$, and $H_4(c_s)$ can be reproduced from Eq. (41). A remarkable feature of the expression (41) is that it effectively carries out only the computation of the simplest 2×2 determinant from Eq. (34). For integer data $\{c_{n+s}\}$, the determinant $H_n(c_s)$ is also an integer number, say $N_n^{(s)}$. In such a case, the expression (41) for $H_n(c_s)$ would evidently be a rational number. However, by construction (40), the numerator in (41) is, in fact, equal to $\prod_{m=2}^n \lambda_{1,2m}^{(s)} = N_n^{(s)} \prod_{m=2}^n \lambda_{2m-2}^{(s)}$ so that $H_n(c_s) = N_n^{(s)}$, as it should be. To achieve this in practice, integer algebra could be used in which the

generated integers $\{\lambda_{ij}^{(s)}\}$ should be kept in their composite intermediate forms without carrying out the final multiplications in Eq. (41). This would allow the exact cancellation of the denominator $\prod_{m=2}^n \lambda_{2m-2}^{(s)}$ by the corresponding part of the numerator in $H_n(c_s)$ from Eq. (41) to yield the exact result in the integer form $H_n(c_s) = N_n^{(s)}$.

The generalization of the PD algorithm from its original nondelayed variant of Gordon [12] to the delayed version of Belkić [77] is particularly advantageous regarding the eigenvalues $\{u_k\}$. Namely, having only the nondelayed CF coefficients $\{a_n\} \equiv \{a_n^{(0)}\}$ as in Ref. [12], the eigenvalues $\{u_k\}$ can be obtained either by rooting the characteristic polynomial $Q_k(u) = 0$ or by solving the eigenproblem for the corresponding Jacobi matrix [77]. However, the delayed CF coefficients $\{a_n^{(s)}\}$ can bypass altogether these two latter standard procedures and provide an alternative way of obtaining the eigenvalues of data matrices from the following limiting procedure:

$$u_k = \lim_{s \rightarrow \infty} a_{2k}^{(s)} = \lim_{s \rightarrow \infty} \frac{\lambda_{1,2k+1}^{(s)}}{\lambda_{1,2k-1}^{(s)} \lambda_{1,2k}^{(s)}}. \quad (42)$$

For the purpose of checking, it is also useful to consider the same limit $s \rightarrow \infty$ in the string $\{a_{2n+1}^{(s)}\}$ with the result:

$$\lim_{s \rightarrow \infty} a_{2k+1}^{(s)} = \lim_{s \rightarrow \infty} \frac{\lambda_{1,2k+2}^{(s)}}{\lambda_{1,2k}^{(s)} \lambda_{1,2k+1}^{(s)}} = 0. \quad (43)$$

The accuracy of the results for the eigenvalues $\{u_k\}$ computed in this way using the delayed PD algorithm can be checked against the formula $u_k = \lim_{s \rightarrow \infty} a_{2k}^{(s)}$ by means of the analytical expression for $a_{2k}^{(s)}$. The exact closed formula for the general delayed CF coefficients $a_n^{(s)}$ has been obtained by Belkić [77] as:

$$a_{n+1}^{(s)} = \frac{c_{n+s} - \sigma_n^{(s)} \pi_{n-1}^{(s)} - \zeta_n^{(s)} \pi_{n-4}^{(s)}}{\pi_n^{(s)}}, \quad (44)$$

$$\pi_n^{(s)} = \prod_{i=1}^n a_i^{(s)}; \quad \sigma_n^{(s)} = \left[\sum_{j=2}^n a_j^{(s)} \right]^2, \quad (45)$$

$$\zeta_n^{(s)} = \sum_{j=\lceil \frac{n-1}{2} \rceil}^{n-3} a_j^{(s)} [\xi_j^{(s)}]^2; \quad \xi_j^{(s)} = \sum_{k=2}^{j+1} a_k^{(s)} \sum_{\ell=2}^{k+1} a_\ell^{(s)}, \quad (46)$$

$$\pi_n^{(s)} \equiv 0 \quad (n \leq 0), \quad \sigma_n^{(s)} \equiv 0 \quad (n \leq 3), \quad (47)$$

where the symbol $[n/2]$ represents the integer part of $n/2$. Of course, if we have the CF coefficients $\{a_n^{(s)}\}$, then the input data $\{c_{n+s}\}$ could be retrieved exactly by means of the explicit formula:

$$c_{n+s} = \pi_{n+1}^{(s)} + \sigma_n^{(s)} \pi_{n-1}^{(s)} + \zeta_n^{(s)} \pi_{n-4}^{(s)}. \quad (48)$$

Clearly, with the availability of the exact delayed CF coefficients $\{a_n^{(s)}\}$ from Eq. (44), one can immediately obtain the exact delayed CF of a fixed order as the explicit polynomial quotient, which is the corresponding PA. For example, the even-order delayed CF is the following PA:

$$G_{2n}^{\text{CF}(s)}(u) = a_1^{(s)} \frac{\tilde{P}_n^{\text{CF}(s)}(u)}{\tilde{Q}_n^{\text{CF}(s)}(u)}. \quad (49)$$

Likewise, the delayed odd-order CF, which is denoted by $G_{2n-1}^{\text{CF}(s)}(u)$, is obtained from the even-order CF by setting $a_{2n}^{(s)} \equiv 0$:

$$G_{2n-1}^{\text{CF}(s)}(u) \equiv \{G_{2n}^{\text{CF}(s)}(u)\}_{a_{2n}^{(s)}=0} \quad (n=1, 2, 3, \dots). \quad (50)$$

The polynomials $\tilde{P}_n^{\text{CF}(s)}(u)$ and $\tilde{Q}_n^{\text{CF}(s)}(u)$ from Eq. (49) can be defined through their general power series representations:

$$\tilde{P}_n^{\text{CF}(s)}(u) = \sum_{r=0}^{n-1} \tilde{p}_{n,n-r}^{(s)} u^r, \quad \tilde{Q}_n^{\text{CF}(s)}(u) = \sum_{r=0}^n \tilde{q}_{n,n-r}^{(s)} u^r. \quad (51)$$

The expansion coefficients $\tilde{p}_{n,n-r}^{(s)}$ and $\tilde{q}_{n,n-r}^{(s)}$ are available as the analytical expressions derived by Belkić [77]:

$$\tilde{p}_{n,m}^{(s)} = (-1)^{m-1} \underbrace{\sum_{r_1=3}^{2(n-m+2)} a_{r_1}^{(s)} \sum_{r_2=r_1+2}^{2(n-m+3)} a_{r_2}^{(s)} \cdots \sum_{r_{m-1}=r_{m-2}+2}^{2n} a_{r_{m-1}}^{(s)}}_{m-1 \text{ summations}}, \quad (52)$$

$$\tilde{q}_{n,m}^{(s)} = (-1)^m \underbrace{\sum_{r_1=2}^{2(n-m+1)} a_{r_1}^{(s)} \sum_{r_2=r_1+2}^{2(n-m+2)} a_{r_2}^{(s)} \sum_{r_3=r_2+2}^{2(n-m+3)} a_{r_3}^{(s)} \cdots \sum_{r_m=r_{m-1}+2}^{2n} a_{r_m}^{(s)}}_{m \text{ summations}}, \quad (53)$$

where $n \geq m$.

9. DELAYED LANCZOS CONTINUED FRACTIONS

Using Eq. (24), the infinite-order and the m th-order delayed CFs $G^{\text{CF}(s)}(u)$ and $G_m^{\text{CF}(s)}(u)$ from Eqs. (18) and (19) can, respectively, be written as:

$$G^{\text{CF}(s)}(u) = \frac{c_s}{u} - \frac{q_1^{(s)}}{1} - \frac{e_1^{(s)}}{u} - \dots - \frac{q_r^{(s)}}{1} - \frac{e_r^{(s)}}{u} - \dots, \quad (54)$$

$$G_m^{\text{CF}(s)}(u) = \frac{c_s}{u} - \frac{q_1^{(s)}}{1} - \frac{e_1^{(s)}}{u} - \dots - \frac{q_m^{(s)}}{1} - \frac{e_m^{(s)}}{u}. \quad (55)$$

Likewise, the infinite-order and the m th-order of the even part of the corresponding Lanczos continued fractions (LCFs) are defined by:

$$\begin{aligned} G_e^{\text{LCF}(s)}(u) &= \frac{c_s}{u - q_1^{(s)} - e_0^{(s)}} - \frac{q_1^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_1^{(s)}} - \dots - \frac{q_r^{(s)} e_r^{(s)}}{u - q_{r+1}^{(s)} - e_r^{(s)}} - \dots \\ &= \frac{c_s}{u - \alpha_0^{(s)}} - \frac{[\beta_1^{(s)}]^2}{u - \alpha_1^{(s)}} - \dots - \frac{[\beta_r^{(s)}]^2}{u - \alpha_r^{(s)}} - \dots \end{aligned} \quad (56)$$

$$\begin{aligned} G_{e,m}^{\text{LCF}(s)}(u) &= \frac{c_s}{u - q_1^{(s)} - e_0^{(s)}} - \frac{q_1^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_1^{(s)}} - \dots - \frac{q_m^{(s)} e_m^{(s)}}{u - q_{m+1}^{(s)} - e_m^{(s)}} \\ &= \frac{c_s}{u - \alpha_0^{(s)}} - \frac{[\beta_1^{(s)}]^2}{u - \alpha_1^{(s)}} - \dots - \frac{[\beta_m^{(s)}]^2}{u - \alpha_m^{(s)}}. \end{aligned} \quad (57)$$

To establish a general relationship between $G_{e,m}^{\text{LCF}(s)}(u)$ and $G_m^{\text{CF}(s)}(u)$, it is sufficient to extract explicitly a few of the first terms from Eqs. (54)–(57). For example, setting $m=2$ in Eq. (55) and $m=1$ in Eq. (57) gives:

$$G_2^{\text{CF}(s)}(u) = \frac{c_s}{u} - \frac{q_1^{(s)}}{1} = \frac{c_s}{u - q_1^{(s)}} = \frac{c_s}{u - \alpha_0^{(s)}}, \quad (58)$$

$$G_{e,1}^{\text{LCF}(s)}(u) = \frac{c_s}{u - q_1^{(s)}} = \frac{c_s}{u - \alpha_0^{(s)}}, \quad (59)$$

$$\therefore G_{e,1}^{\text{LCF}(s)}(u) = G_2^{\text{CF}(s)}(u). \quad (60)$$

Similarly, letting $m=4$ in Eq. (55) and $m=2$ in Eq. (57) yields:

$$\begin{aligned} G_4^{\text{CF}(s)}(u) &= \frac{c_s}{u} - \frac{q_1^{(s)}}{1} - \frac{e_1^{(s)}}{u} - \frac{q_2^{(s)}}{1} \\ &= \frac{c_s}{u - q_1^{(s)} - \frac{q_1^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_1^{(s)}}} = \frac{c_s}{u - q_1^{(s)}} - \frac{q_1^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_1^{(s)}}, \end{aligned} \quad (61)$$

$$\begin{aligned} G_{e,2}^{\text{LCF}(s)}(u) &= \frac{c_s}{u - \alpha_0^{(s)}} - \frac{[\beta_1^{(s)}]^2}{u - \alpha_1^{(s)}} = \frac{c_s}{u - q_1^{(s)}} - \frac{q_1^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_1^{(s)}} \\ &= \frac{c_s [u - \alpha_1^{(s)}]}{u^2 - [\alpha_0^{(s)} + \alpha_1^{(s)}]u + \{\alpha_0^{(s)} \alpha_1^{(s)} - [\beta_1^{(s)}]^2\}}, \end{aligned} \quad (62)$$

$$\therefore G_{e,2}^{\text{LCF}(s)}(u) = G_4^{\text{CF}(s)}(u). \quad (63)$$

The polynomial coefficients in Eq. (62) can be expressed via signal points alone as follows:

$$\alpha_1^{(s)} = \frac{c_s^2 c_{s+3} - 2c_s c_{s+1} c_{s+2} + c_{s+1}^3}{c_s (c_s c_{s+2} - c_{s+1}^2)}, \quad (64)$$

$$\alpha_0^{(s)} + \alpha_1^{(s)} = \frac{c_s c_{s+3} - c_{s+1} c_{s+2}}{c_s c_{s+2} - c_{s+1}^2}, \quad (65)$$

$$\alpha_0^{(s)} \alpha_1^{(s)} - [\beta_1^{(s)}]^2 = \frac{c_{s+2}^2 - c_{s+1} c_{s+3}}{c_{s+1}^2 - c_s c_{s+2}}. \quad (66)$$

We carried out a similar calculation for higher orders m and observed that all the particular results Eqs. (60), (63), and so on, satisfy the following general pattern:

$$G_{e,n}^{\text{LCF}(s)}(u) = G_{2n}^{\text{CF}(s)}(u). \quad (67)$$

We see that $G_{2n}^{\text{CF}(s)}(u)$ is matched by $G_{e,n}^{\text{LCF}(s)}(u)$, which is also called the contracted continued fraction $G_{e,n}^{\text{CCF}(s)}(u) = G_{2n}^{\text{CF}(s)}(u)$. The relation (67) for delayed time signals is an extension of the corresponding result for non-delayed signals from Ref. [84].

There is also the infinite-order and the m th-order odd part of Eq. (54) denoted, respectively, by $G_o^{\text{LCF}(s)}(u)$ and $G_{o,m}^{\text{LCF}(s)}(u)$. By definition:

$$G_o^{\text{LCF}(s)}(u) = \frac{c_s}{u} \times \left[1 + \frac{q_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}} - \frac{q_2^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_2^{(s)}} - \cdots - \frac{q_r^{(s)} e_{r-1}^{(s)}}{u - q_r^{(s)} - e_r^{(s)}} - \cdots \right], \quad (68)$$

$$\begin{aligned} G_{o,m}^{\text{CF}(s)}(u) &= \frac{1}{u} \\ &\times \left[c_s + \frac{c_{s+1}}{u - q_1^{(s)} - e_1^{(s)}} - \frac{q_2^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_2^{(s)}} - \cdots - \frac{q_m^{(s)} e_{m-1}^{(s)}}{u - q_m^{(s)} - e_m^{(s)}} \right], \quad (69) \\ &= \frac{1}{u} \left\{ c_s + \frac{c_{s+1}}{u - \alpha_0^{(s+1)}} - \frac{[\beta_1^{(s+1)}]^2}{u - \alpha_1^{(s+1)}} - \cdots - \frac{[\beta_{m-1}^{(s+1)}]^2}{u - \alpha_{m-1}^{(s+1)}} \right\}, \end{aligned}$$

(where $m = 1, 2, 3, \dots$). Comparing Eq. (68) with the identity:

$$\sum_{n=0}^{\infty} c_{n+s} u^{-n-1} = \frac{c_s}{u} + \frac{1}{u} \sum_{n=0}^{\infty} c_{n+s+1} u^{-n-1}, \quad (70)$$

it follows that

$$\begin{aligned} &\sum_{n=0}^{\infty} c_{n+s+1} u^{-n-1} \\ &= c_s \left[\frac{q_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}} - \frac{q_2^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_2^{(s)}} - \cdots - \frac{q_{r+1}^{(s)} e_r^{(s)}}{u - q_{r+1}^{(s)} - e_{r+1}^{(s)}} - \cdots \right] \quad (71) \\ &= c_s \left\{ \frac{q_1^{(s)}}{u - \gamma_1^{(s)}} - \frac{[\delta_1^{(s)}]^2}{u - \gamma_2^{(s)}} - \cdots - \frac{[\delta_r^{(s)}]^2}{u - \gamma_{r+1}^{(s)}} - \cdots \right\}, \end{aligned}$$

where

$$\gamma_n^{(s)} = q_n^{(s)} + e_n^{(s)}, \quad [\delta_n^{(s)}]^2 = q_{n+1}^{(s)} e_n^{(s)}. \quad (72)$$

However, using Eqs. (21) and (29), we have:

$$q_n^{(s)} + e_n^{(s)} = q_n^{(s+1)} + e_{n-1}^{(s+1)} = \alpha_{n-1}^{(s+1)}, \quad (73)$$

$$q_{n+1}^{(s)} e_n^{(s)} = q_n^{(s+1)} e_n^{(s+1)} = [\beta_n^{(s+1)}]^2, \quad (74)$$

$$\gamma_n^{(s)} = \alpha_{n-1}^{(s+1)}; \quad [\delta_n^{(s)}]^2 = [\beta_n^{(s+1)}]^2, \quad (75)$$

so that

$$\begin{aligned}
 & \sum_{n=0}^{\infty} c_{n+s+1} u^{-n-1} \\
 &= \frac{c_{s+1}}{u - q_1^{(s)} - e_1^{(s)}} - \frac{q_2^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_2^{(s)}} - \cdots - \frac{q_{r+1}^{(s)} e_r^{(s)}}{u - q_{r+1}^{(s)} - e_{r+1}^{(s)}} - \cdots \quad (76) \\
 &= \frac{c_{s+1}}{u - \alpha_0^{(s+1)}} - \frac{[\beta_1^{(s+1)}]^2}{u - \alpha_1^{(s+1)}} - \cdots - \frac{[\beta_r^{(s+1)}]^2}{u - \alpha_r^{(s+1)}} - \cdots.
 \end{aligned}$$

It is seen now that the second line of Eq. (76) coincides with the second line of Eq. (56), when s is replaced by $s+1$, as it should be. Therefore, Eq. (76) is a retrospective proof that Eq. (68) is correct. Then, returning to Eq. (69) for the odd part of $G_n^{\text{CCF}(s)}(u)$, which is $G_{e,n}^{\text{CCF}(s)}(u) = G_{e,n}^{\text{LCF}(s)}(u)$, we have for $m=1$:

$$G_{o,1}^{\text{LCF}(s)}(u) = \frac{1}{u} \left[c_s + \frac{c_{s+1}}{u - q_1^{(s)} - e_1^{(s)}} \right]. \quad (77)$$

Substituting $m=3$ in (55), it follows that:

$$\begin{aligned}
 G_3^{\text{CF}(s)}(u) &= \frac{c_s}{u} - \frac{q_1^{(s)}}{1} - \frac{e_1^{(s)}}{u} = \frac{c_s}{u - \frac{q_1^{(s)}}{1 - \frac{e_1^{(s)}}{u}}} = \frac{c_s}{u - \frac{q_1^{(s)} u}{u - e_1^{(s)}}} \\
 &= \frac{c_s}{u} + \frac{c_s}{u - \frac{q_1^{(s)} u}{u - e_1^{(s)}}} - \frac{c_s}{u} \\
 &= \frac{c_s}{u} + \left\{ \frac{c_s [u - e_1^{(s)}]}{u [u - e_1^{(s)}] - q_1^{(s)} u} - \frac{c_s}{u} \right\} \quad (78) \\
 &= \frac{c_s}{u} + \frac{c_s [u - e_1^{(s)}] - [u - q_1^{(s)} - e_1^{(s)}]}{u - q_1^{(s)} - e_1^{(s)}} \\
 &= \frac{c_s}{u} + \frac{c_s}{u} \frac{q_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}} \\
 \therefore G_3^{\text{CF}(s)}(u) &= \frac{1}{u} \left[c_s + \frac{c_{s+1}}{u - q_1^{(s)} - e_1^{(s)}} \right] = \frac{1}{u} \left[c_s + \frac{c_{s+1}}{u - \alpha_0^{(s+1)}} \right].
 \end{aligned}$$

Comparison of Eqs. (77) and (78) yields the equality:

$$G_{o,1}^{\text{LCF}(s)}(u) = G_3^{\text{CF}(s)}(u). \quad (79)$$

We also obtained the following result for $G_3^{\text{CF}(s)}(u)$:

$$G_3^{\text{CF}(s)}(u) = \frac{a_1^{(s)}}{u} \frac{u - a_3^{(s)}}{u - a_2^{(s)} - a_3^{(s)}}. \quad (80)$$

Employing Eqs. (24) and (73), we can rewrite Eq. (80) as:

$$G_3^{\text{CF}(s)}(u) = \frac{c_s}{u} \frac{u - e_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}} = \frac{c_s}{u} \frac{u - e_1^{(s)}}{u - \alpha_0^{(s+1)}}. \quad (81)$$

Furthermore, we have:

$$e_1^{(s)} = \alpha_0^{(s+1)} - \alpha_0^{(s)}, \quad (82)$$

so that Eq. (81) becomes

$$G_3^{\text{CF}(s)}(u) = \frac{c_s}{u} \frac{u - \alpha_0^{(s+1)} + \alpha_0^{(s)}}{u - \alpha_0^{(s+1)}}. \quad (83)$$

The results (78) and (81) or (83) must be identical to each other, and to check this, we calculate:

$$\begin{aligned} \frac{1}{u} \left[c_s + \frac{c_{s+1}}{u - q_1^{(s)} - e_1^{(s)}} \right] &= \frac{c_s}{u} \left[1 + \frac{q_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}} \right] \\ &= \frac{c_s}{u} \frac{u - q_1^{(s)} - e_1^{(s)} + q_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}} = \frac{c_s}{u} \frac{u - e_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)}}, \quad (84) \\ \therefore \left\{ [G_3^{\text{CF}(s)}(u)] \right\}_{\text{Eq. (78)}} &= \left\{ [G_3^{\text{CF}(s)}(u)] \right\}_{\text{Eq. (81)}} \quad (\text{QED}). \end{aligned}$$

Using Eqs. (79) and (83), we can write Eq. (77) as:

$$G_{o,1}^{\text{LCF}(s)}(u) = \frac{c_s}{u} \frac{u - \alpha_0^{(s+1)} + \alpha_0^{(s)}}{u - \alpha_0^{(s+1)}}, \quad (85)$$

$$\alpha_0^{(s+1)} = \frac{c_{s+2}}{c_{s+1}}, \quad \alpha_0^{(s+1)} - \alpha_0^{(s)} = \frac{c_s c_{s+2} - c_{s+1}^2}{c_s c_{s+1}}. \quad (86)$$

Next, we set $m = 2$ in Eq. (69) and extract the term:

$$G_{o,2}^{\text{LCF}(s)}(u) = \frac{1}{u} \left\{ c_s + \frac{c_{s+1}}{u - \alpha_0^{(s+1)}} - \frac{[\beta_1^{(s+1)}]^2}{u - \alpha_1^{(s+1)}} \right\}. \quad (87)$$

This with the help of Eq. (68) can also be written explicitly as:

$$\begin{aligned} G_{o,2}^{\text{LCF}(s)}(u) &= \frac{c_s}{u} + \frac{1}{u} \frac{c_{s+1}}{u - \alpha_0^{(s+1)} - \frac{[\beta_1^{(s+1)}]^2}{u - \alpha_1^{(s+1)}}} \\ &= \frac{c_s}{u} + \frac{1}{u} \frac{q_1^{(s)}}{u - q_1^{(s)} - e_1^{(s)} - \frac{q_2^{(s)} e_1^{(s)}}{u - q_2^{(s)} - e_2^{(s)}}}. \end{aligned} \quad (88)$$

For $m = 5$, we have from Eqs. (19) and (55):

$$\begin{aligned} G_5^{\text{CF}(s)}(u) &= \frac{c_s}{u} - \frac{q_1^{(s)}}{1} - \frac{e_1^{(s)}}{u} - \frac{q_2^{(s)}}{1} - \frac{e_2^{(s)}}{u} \\ &= \frac{a_1^{(s)}}{u} - \frac{a_2^{(s)}}{1} - \frac{a_3^{(s)}}{u} - \frac{a_4^{(s)}}{1} - \frac{a_5^{(s)}}{u}. \end{aligned} \quad (89)$$

The corresponding form of the explicit polynomial quotient from Eq. (89) is:

$$G_5^{\text{CF}(s)}(u) = \frac{c_s}{u} \frac{u^2 - [a_3^{(s)} + a_4^{(s)} + a_5^{(s)}]u + a_3^{(s)} a_5^{(s)}}{u^2 - [a_2^{(s)} + a_3^{(s)} + a_4^{(s)} + a_5^{(s)}]u + \{a_2^{(s)}[a_4^{(s)} + a_5^{(s)}] + a_3^{(s)} a_5^{(s)}\}}. \quad (90)$$

Using Eqs. (21) and (24), it can be shown that the following relations hold:

$$a_2^{(s)} + a_3^{(s)} + a_4^{(s)} + a_5^{(s)} = \alpha_0^{(s+1)} + \alpha_1^{(s+1)}, \quad (91)$$

$$a_2^{(s)}[a_4^{(s)} + a_5^{(s)}] + a_3^{(s)} a_5^{(s)} = \alpha_0^{(s+1)} \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2, \quad (92)$$

$$a_3^{(s)} a_5^{(s)} = e_1^{(s)} e_2^{(s)} = [\alpha_0^{(s+1)} - \alpha_0^{(s)}] \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2, \quad (93)$$

$$a_3^{(s)} = e_1^{(s)} = \alpha_0^{(s+1)} - \alpha_0^{(s)}, \quad (94)$$

$$a_3^{(s)} + a_4^{(s)} + a_5^{(s)} = a_3^{(s)} + \alpha_1^{(s+1)} = \alpha_0^{(s+1)} - \alpha_0^{(s)} + \alpha_1^{(s+1)}. \quad (95)$$

We can also express Eqs. (91)–(95) in terms of signal points only:

$$\alpha_0^{(s+1)} + \alpha_1^{(s+1)} = \frac{c_{s+2}c_{s+3} - c_{s+1}c_{s+4}}{c_{s+2}^2 - c_{s+1}c_{s+3}}, \quad (96)$$

$$\alpha_0^{(s+1)} \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2 = \frac{c_{s+3}^2 - c_{s+2}c_{s+4}}{c_{s+2}^2 - c_{s+1}c_{s+3}}, \quad (97)$$

$$\begin{aligned} & [\alpha_0^{(s+1)} - \alpha_0^{(s)}] \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2 \\ &= \frac{c_s c_{s+2} c_{s+4} - c_{s+1}^2 c_{s+4} + 2c_{s+1} c_{s+2} c_{s+3} - c_{s+2}^3 - c_s c_{s+3}^2}{c_s (c_{s+1} c_{s+3} - c_{s+2}^2)}, \end{aligned} \quad (98)$$

$$\begin{aligned} & \alpha_0^{(s+1)} - \alpha_0^{(s)} + \alpha_1^{(s+1)} \\ &= \frac{c_{s+1} c_{s+2}^2 - c_{s+1}^2 c_{s+3} - c_s c_{s+2} c_{s+3} + c_s c_{s+1} c_{s+4}}{c_s (c_{s+1} c_{s+3} - c_{s+2}^2)}. \end{aligned} \quad (99)$$

Substituting Eqs. (91)–(95) in Eq. (90) finally gives:

$$\begin{aligned} G_5^{\text{CF}(s)}(u) &= \frac{c_s}{u} \\ &\times \frac{u^2 - [\alpha_0^{(s+1)} - \alpha_0^{(s)} + \alpha_1^{(s+1)}]u + \{[\alpha_0^{(s+1)} - \alpha_0^{(s)}] \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2\}}{u^2 - [\alpha_0^{(s+1)} + \alpha_1^{(s+1)}]u + \{\alpha_0^{(s+1)} \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2\}}. \end{aligned} \quad (100)$$

On the other hand, we can transform Eq. (88) as follows:

$$\begin{aligned} & \frac{u}{c_s} G_{0,2}^{\text{LCF}(s)}(u) \\ &= 1 + \frac{q_1^{(s)}}{u - \alpha_0^{(s+1)} - \frac{[\beta_1^{(s+1)}]^2}{u - \alpha_1^{(s+1)}}} = 1 + \frac{\alpha_0^{(s)}}{u - \alpha_0^{(s+1)} - \frac{[\beta_1^{(s+1)}]^2}{u - \alpha_1^{(s+1)}}} \\ &= \frac{[u - \alpha_0^{(s+1)}][u - \alpha_1^{(s+1)}] - [\beta_1^{(s+1)}]^2 + \alpha_0^{(s)}[u - \alpha_1^{(s+1)}]}{[u - \alpha_0^{(s+1)}][u - \alpha_1^{(s+1)}] - [\beta_1^{(s+1)}]^2} \\ &= \frac{u^2 - [\alpha_0^{(s+1)} - \alpha_0^{(s)} + \alpha_1^{(s+1)}]u + \{[\alpha_0^{(s+1)} - \alpha_0^{(s)}] \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2\}}{u^2 - [\alpha_0^{(s+1)} + \alpha_1^{(s+1)}]u + \{\alpha_0^{(s+1)} \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2\}}, \end{aligned}$$

so that

$$G_{o,2}^{\text{LCF}(s)}(u) = \frac{c_s}{u} \times \frac{u^2 - [\alpha_0^{(s+1)} - \alpha_0^{(s)} + \alpha_1^{(s+1)}]u + \{[\alpha_0^{(s+1)} - \alpha_0^{(s)}]\alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2\}}{u^2 - [\alpha_0^{(s+1)} + \alpha_1^{(s+1)}]u + \{\alpha_0^{(s+1)}\alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2\}}. \quad (101)$$

An inspection of Eqs. (100) and (101) gives the identity:

$$G_{o,2}^{\text{LCF}(s)}(u) = G_5^{\text{CF}(s)}(u). \quad (102)$$

We continued this type of calculation for higher orders and verified that all these particular results, such as Eqs. (79), (102), and so on, conform with the general relationship:

$$G_{o,n}^{\text{LCF}(s)}(u) = G_{2n+1}^{\text{CF}(s)}(u). \quad (103)$$

Thus, we see from Eqs. (67) and (103) that the even and odd parts of the delayed Lanczos approximants $G_{e,n}^{\text{LCF}(s)}(u)$ and $G_{o,n}^{\text{LCF}(s)}(u)$ of order n ($n=1,2,3,\dots$) are equal to the delayed CFs $G_{2n}^{\text{CF}(s)}(u)$ and $G_{2n+1}^{\text{CF}(s)}(u)$ of orders $2n$ and $2n+1$, respectively.

10. DELAYED PADÉ-LANCZOS APPROXIMANT

The delayed Padé–Lanczos approximant (PLA) is defined as:

$$G_{L,K}^{\text{PLA}(s)}(u) = \frac{c_s}{\beta_1^{(s)}} \frac{P_L^{(s)}(u)}{Q_K^{(s)}(u)}. \quad (104)$$

The para-diagonal case $L=K$ of Eq. (104) will hereafter be denoted by:

$$G_{n,n}^{\text{PLA}(s)}(u) \equiv G_n^{\text{PLA}(s)}(u), \quad G_n^{\text{PLA}(s)}(u) = \frac{c_s}{\beta_1^{(s)}} \frac{P_n^{(s)}(u)}{Q_n^{(s)}(u)}. \quad (105)$$

Here, $Q_n^{(s)}(u)$ and $P_n^{(s)}(u)$ are delayed Lanczos polynomials of the first and second kind, respectively. They can be defined via their recursions:

$$\left. \begin{aligned} \beta_{n+1}^{(s)} P_{n+1}^{(s)}(u) &= [u - \alpha_n^{(s)}] P_n^{(s)}(u) - \beta_n^{(s)} P_{n-1}^{(s)}(u) \\ P_0^{(s)}(u) &= 0; \quad P_1^{(s)}(u) = 1 \end{aligned} \right\}, \quad (106)$$

$$\left. \begin{aligned} \beta_{n+1}^{(s)} Q_{n+1}^{(s)}(u) &= [u - \alpha_n^{(s)}] Q_n^{(s)}(u) - \beta_n^{(s)} Q_{n-1}^{(s)}(u) \\ Q_{-1}^{(s)}(u) &= 0; \quad Q_0^{(s)}(u) = 1 \end{aligned} \right\}. \quad (107)$$

Equivalently, the polynomials $P_n^{(s)}(u)$ and $Q_n^{(s)}(u)$ can be introduced by their power series:

$$P_n^{(s)}(u) = \sum_{r=0}^{n-1} p_{n,n-r}^{(s)} u^r, \quad Q_n^{(s)}(u) = \sum_{r=0}^n q_{n,n-r}^{(s)} u^r. \quad (108)$$

The expansion coefficients $p_{n,n-r}^{(s)}$ and $q_{n,n-r}^{(s)}$ are generated recursively via:

$$\left. \begin{aligned} \beta_{n+1}^{(s)} p_{n+1,n+1-r}^{(s)} &= p_{n,n+1-r}^{(s)} - \alpha_n^{(s)} p_{n,n-r}^{(s)} - \beta_n^{(s)} p_{n-1,n-1-r}^{(s)} \\ p_{0,0}^{(s)} &= 0; \quad p_{1,1}^{(s)} = 1 \end{aligned} \right\}, \quad (109)$$

$$\left. \begin{aligned} \beta_{n+1}^{(s)} q_{n+1,n+1-r}^{(s)} &= q_{n,n+1-r}^{(s)} - \alpha_n^{(s)} q_{n,n-r}^{(s)} - \beta_n^{(s)} q_{n-1,n-1-r}^{(s)} \\ q_{0,0}^{(s)} &= 1; \quad q_{1,1}^{(s)} = -\frac{\alpha_0^{(s)}}{\beta_1^{(s)}} \end{aligned} \right\}, \quad (110)$$

$$p_{n,-1}^{(s)} = 0, \quad q_{n,-1}^{(s)} = 0, \quad p_{n,m}^{(s)} = 0, \quad q_{n,m}^{(s)} = 0 \quad (m > n). \quad (111)$$

The degrees of the polynomials $P_n^{(s)}(u)$ and $Q_n^{(s)}(u)$ are $n-1$ and n , respectively. The recursion (106) and (107) for these two latter polynomials are exactly the same, except for the different initializations.

Next, we want to establish the connections of $G_{e,n}^{\text{LCF}(s)}(u)$ and $G_{o,n}^{\text{LCF}(s)}(u)$ with the delayed PLA (104). For this purpose, we need the first few explicit delayed Lanczos polynomials from Eqs. (106) and (107):

$$\left. \begin{aligned} P_0^{(s)}(u) &= 0; \quad P_1^{(s)}(u) = 1; \quad \beta_2^{(s)} P_2^{(s)}(u) = u - \alpha_1^{(s)} \\ \beta_2^{(s)} \beta_3^{(s)} P_3^{(s)}(u) &= u^2 - [\alpha_1^{(s)} + \alpha_2^{(s)}]u + \{\alpha_1^{(s)} \alpha_2^{(s)} - [\beta_2^{(s)}]^2\} \end{aligned} \right\}, \quad (112)$$

$$\left. \begin{aligned} Q_0^{(s)}(u) &= 1; \quad \beta_1^{(s)} Q_1^{(s)}(u) = u - \alpha_0^{(s)} \\ \beta_1^{(s)} \beta_2^{(s)} Q_2^{(s)}(u) &= u^2 - [\alpha_0^{(s)} + \alpha_1^{(s)}]u + \{\alpha_0^{(s)} \alpha_1^{(s)} - [\beta_1^{(s)}]^2\} \end{aligned} \right\}. \quad (113)$$

Therefore, using Eqs. (112) and (113), it follows from Eq. (104) for $n=1$, for example, that:

$$G_1^{\text{PLA}(s)}(u) = \frac{c_s}{u - \alpha_0^{(s)}}. \quad (114)$$

The results (59) and (114) are seen to coincide with each other:

$$G_1^{\text{PLA}(s)}(u) = G_{e,1}^{\text{LCF}(s)}(u). \quad (115)$$

Similarly, for $n=2$, using Eqs. (104), (112), and (113), we have:

$$G_2^{\text{PLA}(s)}(u) = c_s \frac{u - \alpha_1^{(s)}}{u^2 - [\alpha_0^{(s)} + \alpha_1^{(s)}]u + \{\alpha_0^{(s)}\alpha_1^{(s)} - [\beta_1^{(s)}]^2\}}. \quad (116)$$

On the other hand, using Eq. (57), we have:

$$G_{e,2}^{\text{LCF}(s)}(u) = \frac{c_s}{u - \alpha_0^{(s)} - \frac{[\beta_1^{(s)}]^2}{u - \alpha_1^{(s)}}} = c_s \frac{u - \alpha_1^{(s)}}{[u - \alpha_0^{(s)}][u - \alpha_1^{(s)}] - [\beta_1^{(s)}]^2}, \quad (117)$$

$$\therefore G_{e,2}^{\text{LCF}(s)}(u) = c_s \frac{u - \alpha_1^{(s)}}{u^2 - [\alpha_0^{(s)} + \alpha_1^{(s)}]u + \{\alpha_0^{(s)}\alpha_1^{(s)} - [\beta_1^{(s)}]^2\}}.$$

Hence, it follows from Eqs. (116) and (117) that:

$$G_2^{\text{PLA}(s)}(u) = G_{e,2}^{\text{LCF}(s)}(u). \quad (118)$$

We continued further with similar calculations for $n \geq 3$ and recorded that all the particular cases (115), (118), and so on are in accord with the general rule:

$$G_n^{\text{PLA}(s)}(u) = G_{e,n}^{\text{LCF}(s)}(u) \quad (n=1, 2, 3, \dots). \quad (119)$$

Hence, the delayed PLA $G_n^{\text{PLA}(s)}(u)$ and the even part of the delayed LCF $G_{e,n}^{\text{LCF}(s)}(u)$ give exactly the same results for any order n .

Obviously, it will be important to see whether the odd part of the delayed LCF, namely, $G_{o,n}^{\text{LCF}(s)}(u)$, could also be found among the elements of the Padé–Lanczos general table for $G_{n,m}^{\text{PLA}(s)}(u)$. For instance, let us consider the diagonal case ($L=K+1$) in Eq. (104) and write:

$$G_{n+1,n}^{\text{PLA}(s)}(u) \equiv \tilde{G}_n^{\text{PLA}(s)}(u) = \frac{c_s}{\beta_1^{(s)}} \frac{P_{n+1}^{(s)}(u)}{Q_n^{(s)}(u)}. \quad (120)$$

In this case, using Eqs. (112) and (113), we have for $n=1$:

$$\tilde{G}_1^{\text{PLA}(s)}(u) = \frac{c_s}{\beta_1^{(s)}} \frac{u - \alpha_1^{(s)}}{u - \alpha_0^{(s)}}. \quad (121)$$

Thus, it follows from Eqs. (77) and (121) that:

$$\tilde{G}_1^{\text{PLA}(s)}(u) \neq G_{o,1}^{\text{LCF}(s)}(u). \quad (122)$$

We have calculated explicitly $\tilde{G}_n^{\text{PLA}(s)}(u)$ for the next few higher orders n and always confirmed the inequality:

$$\tilde{G}_n^{\text{PLA}(s)}(u) \neq G_{o,n}^{\text{LCF}(s)}(u) \quad (n = 1, 2, \dots). \quad (123)$$

More generally, there are no integers n and m for which $G_{n,m}^{\text{PLA}(s)}(u)$ will match $G_{o,n}^{\text{LCF}(s)}(u)$. This is because the denominator in $G_{o,n}^{\text{LCF}(s)}(u)$ is a polynomial with no free term ($\propto u^0$), namely, $\gamma_0 u + \gamma_1 u^2 + \dots + \gamma_n u^{n+1}$. This extra u in the denominator of $G_{o,n}^{\text{LCF}(s)}(u)$ relative to $G_{e,n}^{\text{LCF}(s)}(u)$ suggests that $G_{o,n}^{\text{LCF}(s)}(u)$ could stem from the PA in the variable u^{-1} rather than u . In the next Section, we shall see that this is indeed the case.

11. FAST PADÉ TRANSFORM $\text{FPT}^{(-)}$ OUTSIDE THE UNIT CIRCLE

Here, our starting point of the analysis is the exact delayed Green function (12). The series (12) is the Maclaurin expansion in powers of $u^{-1} \equiv z = \exp(i\omega\tau)$ and, therefore, convergent for $|u| > 1$, that is, outside the unit circle. Let us first introduce an auxiliary function $\mathcal{G}^{(s)}(u^{-1})$:

$$G^{(s)}(u) = \sum_{n=0}^{\infty} c_{n+s} u^{-n-1} = u^{-1} \mathcal{G}^{(s)}(u^{-1}), \quad (124)$$

$$\mathcal{G}^{(s)}(u^{-1}) = \sum_{n=0}^{\infty} c_{n+s} u^{-n} = \lim_{N \rightarrow \infty} \mathcal{G}_N^{(s)}(u^{-1}), \quad (125)$$

$$\mathcal{G}_N^{(s)}(u^{-1}) = \sum_{n=0}^{N-1} c_{n+s} u^{-n}, \quad (126)$$

$$G_N^{(s)}(u) \equiv \sum_{n=0}^{N-1} c_{n+s} u^{-n-1} = u^{-1} \mathcal{G}_N^{(s)}(u^{-1}). \quad (127)$$

Then, we define the diagonal delayed PA $\mathcal{G}_K^{\text{PA}(s)-}(u^{-1})$ to $\mathcal{G}_N^{(s)}(u^{-1})$ by:

$$\mathcal{G}_K^{\text{PA}(s)-}(u^{-1}) = \frac{A_K^{(s)-}(u^{-1})}{B_K^{(s)-}(u^{-1})}. \quad (128)$$

The corresponding diagonal delayed PA to $G_N^{(s)}(u)$ is:

$$G_K^{\text{PA}(s)-}(u^{-1}) \equiv u^{-1} \mathcal{G}_K^{\text{PA}(s)-}(u^{-1}) = u^{-1} \frac{A_K^{(s)-}(u^{-1})}{B_K^{(s)-}(u^{-1})}. \quad (129)$$

Here, the numerator and denominator polynomials $A_K^{(s)-}(u^{-1})$ and $B_K^{(s)-}(u^{-1})$ are in the same variable u^{-1} as the function $\mathcal{G}_K^{(s)}(u^{-1})$ itself. Both polynomials $A_K^{(s)-}(u^{-1})$ and $B_K^{(s)-}(u^{-1})$ are of the same degree K :

$$A_K^{(s)-}(u^{-1}) = \sum_{r=0}^K a_r^{(s)-} u^{-r}, \quad B_K^{(s)-}(u^{-1}) = \sum_{r=0}^K b_r^{(s)-} u^{-r}. \quad (130)$$

We shall determine the unknown expansion coefficients $a_r^{(s)-}$ and $b_r^{(s)-}$ from Eq. (130) by imposing the equality $\mathcal{G}_N^{(s)}(u^{-1}) = \mathcal{G}_K^{\text{PA}(s)-}(u^{-1})$, that is:

$$\mathcal{G}_N^{(s)}(u) \equiv \sum_{n=0}^{N-1} c_{n+s} u^{-n} = \frac{A_K^{(s)-}(u^{-1})}{B_K^{(s)-}(u^{-1})}. \quad (131)$$

Then, we multiply Eq. (131) by $B_K^{(s)-}(u^{-1})$ to write:

$$\left. \begin{aligned} B_K^{(s)-}(u^{-1}) \sum_{n=0}^{N-1} c_{n+s} u^{-n} &= A_K^{(s)-}(u^{-1}) \\ \left[\sum_{r=0}^K b_r^{(s)-} u^{-r} \right] \left[\sum_{n=0}^{N-1} c_{n+s} u^{-n} \right] &= \sum_{r=0}^K a_r^{(s)-} u^{-r} \end{aligned} \right\}. \quad (132)$$

When the two sums on the lhs of Eq. (132) are multiplied out as indicated and the ensuing coefficients of the same powers of u^{-1} are equated with their counterparts from the rhs of Eq. (132), the following results emerge:

$$a_\nu^{(s)-} = \sum_{r=0}^{\nu} b_r^{(s)-} c_{\nu-r+s} \quad (0 \leq \nu \leq K), \quad (133)$$

$$b_0^{(s)-} c_\nu = - \sum_{r=1}^K b_r^{(s)-} c_{\nu-r}. \quad (134)$$

Let us set:

$$M = N - 1 - K - s, \quad (135)$$

so that we can rewrite Eq. (134) as:

$$b_0^{(s)-} c_{K+s+m} + \sum_{r=1}^K b_r^{(s)-} c_{K+s+m-r} = 0, \quad 0 \leq m \leq M. \quad (136)$$

This is an implicit system of linear equations for the unknown coefficients $b_r^{(s)-}$. The system can be made explicit by varying the integer m from 1 to M , as follows:

$$\left. \begin{aligned} c_{K+s+1}b_0^{(s)-} + c_{K+s}b_1^{(s)-} + \cdots + c_{s+1}b_K^{(s)-} &= 0 \\ c_{K+s+2}b_0^{(s)-} + c_{K+s+1}b_1^{(s)-} + \cdots + c_{s+2}b_K^{(s)-} &= 0 \\ &\vdots \\ c_{M+K+s}b_0^{(s)-} + c_{M+K+s-1}b_1^{(s)-} + \cdots + c_{M+s}b_K^{(s)-} &= 0 \end{aligned} \right\}. \quad (137)$$

It is also clear that Eq. (133) represents a system of linear equations when the suffix ν is varied from 0 to K and thus:

$$\left. \begin{aligned} a_0^{(s)-} &= c_s b_0^{(s)-} \\ a_1^{(s)-} &= c_{s+1} b_0^{(s)-} + c_s b_1^{(s)-} \\ &\vdots \\ a_K^{(s)-} &= c_{K+s} b_0^{(s)-} + c_{K+s-1} b_1^{(s)-} + \cdots + c_s b_K^{(s)-} \end{aligned} \right\}. \quad (138)$$

Both systems (137) and (138) can equivalently be cast into their respective matrix forms, namely:

$$\begin{pmatrix} c_{K+s} & c_{K-1+s} & \cdots & c_{s+1} \\ c_{K+s+1} & c_{K+s} & \cdots & c_{s+2} \\ \vdots & \vdots & \ddots & \vdots \\ c_{K+s+M-1} & c_{K+s+M-2} & \cdots & c_{s+M} \end{pmatrix} \begin{pmatrix} b_1^{(s)-} \\ b_2^{(s)-} \\ \vdots \\ b_K^{(s)-} \end{pmatrix} \equiv -b_0^{(s)-} \begin{pmatrix} c_{K+s+1} \\ c_{K+s+2} \\ \vdots \\ c_{K+s+M} \end{pmatrix}, \quad (139)$$

$$\begin{pmatrix} a_0^{(s)-} \\ a_1^{(s)-} \\ \vdots \\ a_K^{(s)-} \end{pmatrix} = \begin{pmatrix} c_s & 0 & \cdots & 0 \\ c_{s+1} & c_s & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ c_{K+s} & c_{K+s-1} & \cdots & c_s \end{pmatrix} \begin{pmatrix} b_0^{(s)-} \\ b_1^{(s)-} \\ \vdots \\ b_K^{(s)-} \end{pmatrix}. \quad (140)$$

It will prove convenient to write:

$$\tilde{a}_{r,K}^{(s)-} \equiv \frac{a_r^{(s)-}}{c_s b_0^{(s)-}}; \quad \tilde{b}_{r,K}^{(s)-} \equiv \frac{b_r^{(s)-}}{b_0^{(s)-}}, \quad (141)$$

where it is understood that the coefficients $a_r^{(s)-}$ and $b_r^{(s)-}$ are implicitly dependent upon K . For an illustration, we set $K=1$ and obtain:

$$\tilde{b}_{1,1}^{(s)-} = -\frac{c_{s+2}}{c_{s+1}}, \quad (142)$$

$$\tilde{a}_{0,1}^{(s)-} = 1; \quad \tilde{a}_{1,1}^{(s)-} = \frac{c_{s+1}^2 - c_s c_{s+2}}{c_s c_{s+1}}. \quad (143)$$

Substituting Eqs. (141)–(143) in Eq. (130) yields:

$$A_1^{(s)-}(u^{-1}) = c_s b_0^{(s)-} [1 + \tilde{a}_{1,1}^{(s)-} u^{-1}], \quad (144)$$

$$B_1^{(s)-}(u^{-1}) = b_0^{(s)-} [1 + \tilde{b}_{1,1}^{(s)-} u^{-1}]. \quad (145)$$

Substituting Eqs. (144) and (145) in Eq. (129) gives:

$$G_1^{\text{PA}(s)-}(u^{-1}) = \frac{c_s}{u} \frac{1 + \tilde{a}_{1,1}^{(s)-} u^{-1}}{1 + \tilde{b}_{1,1}^{(s)-} u^{-1}}. \quad (146)$$

It follows from Eqs. (86), (142), and (143) that:

$$\alpha_0^{(s+1)} = -\tilde{b}_{1,1}^{(s)-}, \quad \alpha_0^{(s+1)} - \alpha_0^{(s)} = -\tilde{a}_{1,1}^{(s)-}. \quad (147)$$

This permits recasting (85) in the form:

$$G_{0,1}^{\text{LCF}(s)}(u) = \frac{c_s}{u} \frac{1 + \tilde{a}_{1,1}^{(s)-} u^{-1}}{1 + \tilde{b}_{1,1}^{(s)-} u^{-1}}, \quad (148)$$

which coincides with Eq. (146):

$$\therefore G_1^{\text{PA}(s)-}(u^{-1}) = G_{0,1}^{\text{LCF}(s)}(u). \quad (149)$$

In the same way, we consider the case with $K=2$ for which Eqs. (137) and (138) yield:

$$\tilde{b}_{1,2}^{(s)-} = \frac{c_{s+1}c_{s+4} - c_{s+3}c_{s+2}}{c_{s+2}^2 - c_{s+1}c_{s+3}}; \quad \tilde{b}_{2,2}^{(s)-} = \frac{c_{s+3}^2 - c_{s+2}c_{s+4}}{c_{s+2}^2 - c_{s+1}c_{s+3}}, \quad (150)$$

$$\tilde{a}_{0,2}^{(s)-} = 1, \quad (151)$$

$$\tilde{a}_{1,2}^{(s)-} = \frac{c_{s+1}(c_{s+2}^2 - c_{s+1}c_{s+3}) + c_s(c_{s+1}c_{s+4} - c_{s+2}c_{s+3})}{c_s(c_{s+2}^2 - c_{s+1}c_{s+3})}, \quad (152)$$

$$\tilde{a}_{2,2}^{(s)-} = \frac{c_{s+2}^3 - 2c_{s+1}c_{s+2}c_{s+3} + c_{s+1}^2c_{s+4} + c_sc_{s+2}^2 - c_sc_{s+2}c_{s+4}}{c_s(c_{s+2}^2 - c_{s+1}c_{s+3})}. \quad (153)$$

Placing Eqs. (150)–(153) into Eq. (130) gives:

$$A_2^{(s)-}(u^{-1}) = b_0^{(s)-} c_s [1 + \tilde{a}_{1,2}^{(s)-} u^{-1} + \tilde{a}_{2,2}^{(s)-} u^{-2}], \quad (154)$$

$$B_2^{(s)-}(u^{-1}) = b_0^{(s)-} [1 + \tilde{b}_{1,2}^{(s)-} u^{-1} + \tilde{b}_{2,2}^{(s)-} u^{-2}]. \quad (155)$$

Substituting Eqs. (154) and (155) in Eq. (129) yields:

$$G_2^{\text{PA}(s)-}(u^{-1}) = \frac{c_s}{u} \frac{1 + \tilde{a}_{1,2}^{(s)-} u^{-1} + \tilde{a}_{2,2}^{(s)-} u^{-2}}{1 + \tilde{b}_{1,2}^{(s)-} u^{-1} + \tilde{b}_{2,2}^{(s)-} u^{-2}}. \quad (156)$$

Comparing Eqs. (96)–(99) with Eqs. (150)–(153) leads to:

$$\alpha_0^{(s+1)} + \alpha_1^{(s+1)} = -\tilde{b}_{1,2}^{(s)-} = a_2^{(s)} + a_3^{(s)} + a_4^{(s)} + a_5^{(s)}, \quad (157)$$

$$\alpha_0^{(s+1)} \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2 = \tilde{b}_{2,2}^{(s)-} = a_2^{(s)} [a_4^{(s)} + a_5^{(s)}] + a_3^{(s)} a_5^{(s)}, \quad (158)$$

$$\alpha_0^{(s+1)} - \alpha_0^{(s)} + \alpha_1^{(s+1)} = -\tilde{a}_{1,2}^{(s)-} = a_3^{(s)} + a_4^{(s)} + a_5^{(s)}, \quad (159)$$

$$[\alpha_0^{(s+1)} - \alpha_0^{(s)}] \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2 = \tilde{a}_{2,2}^{(s)-} = a_3^{(s)} a_5^{(s)}. \quad (160)$$

Here, we have:

$$\left. \begin{aligned} & [\alpha_0^{(s+1)} - \alpha_0^{(s)}] \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2 = \{ \alpha_0^{(s+1)} \alpha_1^{(s+1)} - [\beta_1^{(s+1)}]^2 \} \\ & - \alpha_0^{(s)} \alpha_1^{(s+1)} = a_2^{(s)} [a_4^{(s)} + a_5^{(s)}] + a_3^{(s)} a_5^{(s)} = a_3^{(s)} a_5^{(s)} \iff a_2^{(s)} = 0 \end{aligned} \right\}, \quad (161)$$

$$(162)$$

$$\therefore a_r^{(s)-} = \{b_r^{(s)-}\}_{a_2^{(s)}=0} \quad (0 \leq r \leq 2), \quad (163)$$

$$A_2^{(s)-}(u^{-1}) = \{B_2^{(s)-}(u^{-1})\}_{a_2^{(s)}=0}. \quad (164)$$

Moreover, it follows, in general, that:

$$a_r^{(s)-} = \{b_r^{(s)-}\}_{a_2^{(s)}=0} \quad (0 \leq r \leq K), \quad (165)$$

$$A_n^{(s)-}(u^{-1}) = \{B_n^{(s)-}(u^{-1})\}_{a_2^{(s)}=0}. \quad (166)$$

Using Eqs. (157)–(160), we can rewrite Eq. (101) as:

$$G_{0,2}^{\text{LCF}(s)}(u) = \frac{c_s}{u} \frac{1 + \tilde{a}_{1,2}^{(s)-} u^{-1} + \tilde{a}_{2,2}^{(s)-} u^{-2}}{1 + \tilde{b}_{1,2}^{(s)-} u^{-1} + \tilde{b}_{2,2}^{(s)-} u^{-2}}, \quad (167)$$

which agrees exactly with Eq. (156) and, therefore:

$$G_2^{\text{PA}(s)-}(u^{-1}) = G_{0,2}^{\text{LCF}(s)}(u). \quad (168)$$

This type of derivation has been pursued further for $K \geq 3$ and all these particular results for Eqs. (149), (168), and so on, are found to invariably obey the following general relation:

$$G_n^{\text{PA}(s)-}(u^{-1}) = G_{0,n}^{\text{LCF}(s)}(u) \quad (n = 1, 2, 3, \dots). \quad (169)$$

Hence, we can conclude that the delayed PA with the convergence region outside the unit circle ($|u| > 1$) is identical to the odd part of the delayed LCF to any order n , as per Eq. (169). Moreover, both $G_n^{\text{PA}(s)-}(u^{-1})$ and the original truncated Green function (126) are convergent for $|u| > 1$ as $N \rightarrow \infty$. Therefore, outside the unit circle, the delayed PA $G_n^{\text{PA}(s)-}(u^{-1})$ plays the role of an accelerator of an already convergent series which is the Green function (124).

12. FAST PADÉ TRANSFORM $\text{FPT}^{(+)}$ INSIDE THE UNIT CIRCLE

There is another variant of the delayed diagonal PA for the same function $\mathcal{G}_N^{(s)}(u^{-1})$ from Eq. (126). This variant can be deduced from Eq. (15), which we rewrite as:

$$\mathcal{G}^{(s)}(u) = \sum_{n=0}^{\infty} c_{n+s} u^{-n} = \sum_{k=1}^K \frac{d_k^{(s)} u}{u - u_k}. \quad (170)$$

Here, the sum over k is an implicit quotient of two polynomials in the variable u , and hence, it is the PA. A special feature of Eq. (170) is that the numerator polynomial has no free term independent of u . Thus, it is natural that the needed version of the delayed diagonal PA, hereafter denoted by $G_K^{\text{PA}(s)+}(u)$, should be a polynomial quotient in u . Thus, the PA to $\mathcal{G}_N^{(s)}(u^{-1})$ will be introduced by:

$$G_K^{\text{PA}(s)+}(u) = \frac{A_K^{(s)+}(u)}{B_K^{(s)+}(u)}. \quad (171)$$

The corresponding delayed PA to the truncated Green function $\mathcal{G}_N^{(s)}(u^{-1})$ from Eq. (126) is:

$$G_K^{\text{PA}(s)+}(u) = u^{-1} \mathcal{G}_K^{\text{PA}(s)+}(u) = u^{-1} \frac{A_K^{(s)+}(u)}{B_K^{(s)+}(u)}. \quad (172)$$

Both polynomials $A_K^{(s)+}(u)$ and $B_K^{(s)+}(u)$ are of the same degree K . Following Eq. (170), the variable of the numerator and denominator polynomials in Eq. (172) is set to be u as opposed to u^{-1} in the original sum (127):

$$A_K^{(s)+}(u) = \sum_{r=1}^K a_r^{(s)+} u^r, \quad B_K^{(s)+}(u) = \sum_{r=0}^K b_r^{(s)+} u^r. \quad (173)$$

Here, as per Eq. (170), the numerator polynomial $A_K^{(s)+}(u)$ does not have the free term, that is, $a_0^{(s)+} = 0$, so that the sum starts from $r = 1$ with the first term $a_1^{(s)+} u$. The convergence range of $G_K^{\text{PA}(s)+}(u)$ is inside the unit circle ($|u| < 1$) where the original sum $\mathcal{G}^{(s)}(u^{-1})$ from Eq. (125) is divergent. The polynomials $A_K^{(s)+}(u)$ and $B_K^{(s)+}(u)$ are readily identified from the condition:

$$\mathcal{G}_N^{(s)}(u) \equiv \sum_{n=0}^{N-1} c_{n+s} u^{-n} = \frac{A_K^{(s)+}(u)}{B_K^{(s)+}(u)}. \quad (174)$$

We multiply Eq. (174) by $B_K^{(s)+}(u)$ so that:

$$\left. \begin{aligned} B_K^{(s)+}(u) \sum_{n=0}^{N-1} c_{n+s} u^{-n} &= A_K^{(s)+}(u) \\ \left[\sum_{r=0}^K b_r^{(s)+} u^r \right] \left[\sum_{n=0}^{N-1} c_{n+s} u^{-n} \right] &= \sum_{r=1}^K a_r^{(s)+} u^r \end{aligned} \right\}. \quad (175)$$

The same procedure as in Eq. (132) followed by equating the coefficients of like powers of the expansion variable gives:

$$b_0^{(s)+} c_{n+s} + \sum_{r=1}^K b_r^{(s)+} c_{n+s+r} = 0 \quad (n = 1, 2, \dots, M). \quad (176)$$

Using Eq. (135), we can write Eq. (176) explicitly as:

$$\left. \begin{aligned} c_s b_0^{(s)+} + c_{s+1} b_1^{(s)+} + c_{s+2} b_2^{(s)+} + \dots + c_{s+K} b_K^{(s)+} &= 0 \\ c_{s+1} b_0^{(s)+} + c_{s+2} b_1^{(s)+} + c_{s+3} b_2^{(s)+} + \dots + c_{s+K+1} b_K^{(s)+} &= 0 \\ &\vdots \\ c_{M+s} b_0^{(s)+} + c_{M+s+1} b_1^{(s)+} + c_{M+s+2} b_2^{(s)+} + \dots + c_{M+s+K} b_K^{(s)+} &= 0 \end{aligned} \right\}, \quad (177)$$

or in the equivalent matrix form,

$$\begin{pmatrix} c_{s+1} & c_{s+2} & c_{s+3} & \cdots & c_{s+K} \\ c_{s+2} & c_{s+3} & c_{s+4} & \cdots & c_{s+K+1} \\ c_{s+3} & c_{s+4} & c_{s+5} & \cdots & c_{s+K+2} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ c_{s+M+1} & c_{s+M+2} & c_{s+M+3} & \cdots & c_{s+K+M} \end{pmatrix} \begin{pmatrix} b_1^{(s)+} \\ b_2^{(s)+} \\ b_3^{(s)+} \\ \vdots \\ b_K^{(s)+} \end{pmatrix} = - \begin{pmatrix} c_s b_0^{(s)+} \\ c_{s+1} b_0^{(s)+} \\ c_{s+2} b_0^{(s)+} \\ \vdots \\ c_{s+M} b_0^{(s)+} \end{pmatrix}. \quad (178)$$

The coefficients $\{a_r^{(s)+}\}$ of the numerator polynomial $A_K^{(s)+}(u)$ follow from the inhomogeneous part of the positive powers of the expansion variable from Eq. (175):

$$\left. \begin{aligned} c_s b_1^{(s)+} + c_{s+1} b_2^{(s)+} + c_{s+3} b_3^{(s)+} + \cdots + c_{s+K-1} b_K^{(s)+} &= a_1^{(s)+} \\ c_s b_2^{(s)+} + c_{s+1} b_3^{(s)+} + \cdots + c_{s+K-2} b_K^{(s)+} &= a_2^{(s)+} \\ &\vdots \\ c_s b_K^{(s)+} &= a_K^{(s)+} \end{aligned} \right\}, \quad (179)$$

or via the matrix representation,

$$\begin{pmatrix} a_1^{(s)+} \\ a_2^{(s)+} \\ a_3^{(s)+} \\ \vdots \\ a_K^{(s)+} \end{pmatrix} = \begin{pmatrix} c_s & c_{s+1} & c_{s+2} & \cdots & c_{s+K-1} \\ 0 & c_s & c_{s+1} & \cdots & c_{s+K-2} \\ 0 & 0 & c_s & \cdots & c_{s+K-3} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & c_s \end{pmatrix} \begin{pmatrix} b_1^{(s)+} \\ b_2^{(s)+} \\ b_3^{(s)+} \\ \vdots \\ b_K^{(s)+} \end{pmatrix}. \quad (180)$$

For convenience, let us write:

$$\tilde{a}_{r,K}^{(s)-} \equiv \frac{a_r^{(s)+}}{b_0^{(s)+}}; \quad \tilde{b}_{r,K}^{(s)+} = \frac{b_r^{(s)+}}{b_0^{(s)+}}, \quad (181)$$

where the K -dependence of $a_r^{(s)+}$ and $b_r^{(s)+}$ is implicit. To illustrate this variant of the delayed PA, we shall again consider a few examples. For $K=1$, it follows from Eqs. (177) and (179) that:

$$\tilde{b}_{1,1}^{(s)+} = - \frac{c_s}{c_{s+1}}, \quad (182)$$

$$\tilde{a}_{1,1}^{(s)+} = - \frac{c_s^2}{c_{s+1}} = c_s \tilde{b}_{1,1}^{(s)+}. \quad (183)$$

With this, the polynomials from Eq. (173) become:

$$B_1^{(s)+}(u) = b_0^{(s)+} [1 + \tilde{b}_{1,1}^{(s)+} u], \quad (184)$$

$$A_1^{(s)+}(u) = b_0^{(s)+} \tilde{a}_{1,1}^{(s)+}. \quad (185)$$

Substituting Eqs. (184) and (185) in Eq. (172) gives:

$$G_1^{\text{PA}(s)+}(u) = \frac{\tilde{a}_{1,1}^{(s)+}}{1 + \tilde{b}_{1,1}^{(s)+} u}. \quad (186)$$

Using Eqs. (22), (182), and (183), it follows that:

$$\alpha_0^{(s)} = -\frac{1}{\tilde{b}_{1,1}^{(s)+}} = -\frac{c_s}{\tilde{a}_{1,1}^{(s)+}}. \quad (187)$$

This maps Eq. (59) into the form:

$$G_{e,1}^{\text{LCF}(s)+}(u) = \frac{\tilde{a}_{1,1}^{(s)+}}{1 + \tilde{b}_{1,1}^{(s)+} u}, \quad (188)$$

which agrees with Eq. (186), so that

$$G_1^{\text{PA}(s)+}(u) = G_{e,1}^{\text{LCF}(s)+}(u). \quad (189)$$

Likewise, for $K=2$, it follows from Eqs. (177) and (179) that:

$$\tilde{b}_{1,2}^{(s)+} = \frac{c_{s+1}c_{s+2} - c_s c_{s+3}}{c_{s+1}c_{s+3} - c_{s+2}^2}, \quad (190)$$

$$\tilde{b}_{2,2}^{(s)+} = \frac{c_s c_{s+2} - c_{s+1}^2}{c_{s+1}c_{s+3} - c_{s+2}^2}, \quad (191)$$

$$\tilde{a}_{1,2}^{(s)+} = \frac{2c_s c_{s+1}c_{s+2} - c_s^2 c_{s+3} - c_{s+1}^3}{c_{s+1}c_{s+3} - c_{s+2}^2}, \quad (192)$$

$$\tilde{a}_{2,2}^{(s)+} = c_s \frac{c_s c_{s+2} - c_{s+1}^2}{c_{s+1}c_{s+3} - c_{s+2}^2} = c_s \tilde{b}_{2,2}^{(s)+}. \quad (193)$$

By substituting Eqs. (190)–(193) in Eq. (173), we obtain:

$$B_2^{(s)+}(u) = b_0^{(s)+} [1 + \tilde{b}_{1,2}^{(s)+} u + \tilde{b}_{2,2}^{(s)+} u^2], \quad (194)$$

$$A_2^{(s)+}(u) = b_0^{(s)+} u [\tilde{a}_{1,2}^{(s)+} + \tilde{a}_{2,2}^{(s)+} u]. \quad (195)$$

Substituting Eqs. (194) and (195) in Eq. (172) leads to:

$$G_2^{\text{PA}(s)+}(u) = \frac{\tilde{a}_{1,2}^{(s)+} + \tilde{a}_{2,2}^{(s)+} u}{1 + \tilde{b}_{1,2}^{(s)+} u + \tilde{b}_{2,2}^{(s)+} u^2}. \quad (196)$$

Comparing Eqs. (64)–(66) with Eqs. (190)–(193) yields:

$$\left. \begin{aligned} \alpha_1^{(s)} &= -\frac{\tilde{a}_{1,2}^{(s)+}}{c_s \tilde{b}_{2,2}^{(s)+}} \\ \alpha_0^{(s)} + \alpha_1^{(s)} &= -\frac{\tilde{b}_{1,2}^{(s)+}}{\tilde{b}_{2,2}^{(s)+}} \\ \alpha_0^{(s)} \alpha_1^{(s)} - [\beta_1^{(s)}]^2 &= \frac{1}{\tilde{b}_{2,2}^{(s)+}} \end{aligned} \right\}. \quad (197)$$

This converts Eq. (62) into the following form:

$$G_{e,2}^{\text{LCF}(s)}(u) = \frac{\tilde{a}_{1,2}^{(s)+} + \tilde{a}_{2,2}^{(s)+} u}{1 + \tilde{b}_{1,2}^{(s)+} u + \tilde{b}_{2,2}^{(s)+} u^2}, \quad (198)$$

which is identical to Eq. (196):

$$\therefore G_2^{\text{PA}(s)+}(u) = G_{e,2}^{\text{LCF}(s)}(u). \quad (199)$$

Our further explicit calculation for $K \geq 3$ revealed that all the particular cases (189), (199), and so on, satisfy the general relationship:

$$G_n^{\text{PA}(s)+}(u) = G_{e,n}^{\text{LCF}(s)}(u) \quad (n = 1, 2, 3, \dots). \quad (200)$$

Thus, it follows that the delayed PA with the convergence region inside the unit circle ($|u| < 1$) is identical to the even part of the delayed LCF to any order n , as given by Eq. (200). Here, $G_n^{\text{PA}(s)+}(u)$ is convergent for $|u| < 1$, whereas the original truncated Green function Eq. (126) is divergent in the same region, that is, inside the unit circle. Hence, inside the unit circle, the delayed PA $G_n^{\text{PA}(s)+}(u)$ uses the Cauchy concept of analytical continuation to induce/force convergence into the initially divergent series, that is, the Green function (124).

Overall, we see that the introduction of $G_n^{\text{PA}(s)\pm}(u^{\pm 1})$ helped to prove that the same LCF, that is, $G_n^{\text{LCF}(s)}(u)$ contains both $G_n^{\text{PA}(s)-}(u^{-1})$ (as an accelerator of monotonically converging series/sequences) and $G_n^{\text{PA}(s)+}(u)$ (as an analytical continuator of divergent series/sequences), where

$G_n^{\text{PA}(s)-}(u^{-1})$ and $G_n^{\text{PA}(s)+}(u)$ are equal to the odd and even part of $G_n^{\text{CF}(s)}(u)$, that is, $G_{o,n}^{\text{LCF}(s)}(u) = G_{2n+1}^{\text{CF}(s)}(u)$ and $G_{e,n}^{\text{LCF}(s)}(u) = G_{2n}^{\text{CF}(s)}(u)$, respectively. Once these equivalences/correspondences have been established, clearly it is optimal to use only the quantities $G_{e,n}^{\text{LCF}(s)}(u)$ and $G_{o,n}^{\text{LCF}(s)}(u)$, for a fixed s , to extract the LCF in the forms $G_{2n}^{\text{LCF}(s)}(u)$ and $G_{2n+1}^{\text{LCF}(s)}(u)$ for obtaining the two sets of observables that converge inside $|u| < 1$ and outside $|u| > 1$ the unit circle. These results represent, respectively, the lower and upper bounds of the computed observables (spectra, eigenfrequencies, density of states, etc). For example, $|G_{e,n}^{\text{LCF}(s)}(u)|$ and $|G_{o,n}^{\text{LCF}(s)}(u)|$ are, respectively, the lower and the upper limits of the envelope of the magnitude shape spectrum for a given signal $\{c_{n+s}\}$ ($0 \leq n \leq N-1$). Similarly, the eigenfrequencies and residues $\{\omega_k^{(s)+}, d_k^{(s)+}\}$ and $\{\omega_k^{(s)-}, d_k^{(s)-}\}$ that emanate from $G_K^{\text{PA}(s)+}(u) = G_{e,K}^{\text{LCF}(s)+}(u)$ and $G_K^{\text{PA}(s)-}(u^{-1}) = G_{o,K}^{\text{LCF}(s)}(u)$ represent, respectively, the lower and upper limits of the true (exact) values $\{\omega_k, d_k\}$.

13. SIGNAL–NOISE SEPARATION VIA FROISSART DOUBLET (POLE–ZERO CANCELLATIONS)

Convergence in the FPT is achieved through stabilization or constancy of the reconstructed frequencies and amplitudes. Moreover, the accomplished stabilization is a veritable signature of the exact number of resonances. With any further increase in the partial signal length N_P toward the full signal length N , that is, passing the stage at which full convergence has been reached, it has been found that all the fundamental frequencies and amplitudes “stay put,” that is, they still remain constant, as shown in Refs. [87–89]. Moreover, in the present study, we intend to check whether machine accuracy could be achieved for solving the quantification problem. Specifically, our challenging task is to verify whether the FPT, for the cases nearing convergence, could reach the exact result with the exponential convergence rate (also called the spectral convergence) [48]. In other words, we set up to test the FPT for the feasibility of yielding an exponentially accurate approximation for functions customarily encountered in spectral analysis in, for example, MRS [77]. The prospect for the mechanism by which this could be achieved (i.e., the mechanism securing the maintenance of stability of all the spectral parameters, as well as the constancy of the estimate for the true number of resonances) lies within the so-called pole–zero cancellations, or equivalently, the Froissart doublets [25]. This signifies that all the additional poles and zeros of the Padé spectrum $P_{K+m}^{\pm}/Q_{K+m}^{\pm}$ for $m > 1$, that is, beyond the stabilized number K of resonances, will cancel each other, leading to a remarkable feature of the FPT [87–89]:

$$\frac{P_{K+m}^{\pm}(z^{\pm 1})}{Q_{K+m}^{\pm}(z^{\pm 1})} = \frac{P_K^{\pm}(z^{\pm 1})}{Q_K^{\pm}(z^{\pm 1})} \quad (m = 1, 2, \dots). \quad (201)$$

In other words, the FPT is safe-guarded against contamination of the final results by extraneous resonances, since each pole due to spurious resonances stemming from the denominator polynomial will automatically coincide with the corresponding zero of the numerator polynomial, thus leading to pole-zero cancellation in the polynomial quotient of the FPT, as per Eq. (201). Such pole-zero cancellations can be advantageously exploited to differentiate between spurious and genuine content of the signal. Since these unphysical poles and zeros always appear as pairs in the FPT, they are viewed as doublets. More precisely, they are called the Froissart doublets after Froissart [25] who was the first to discover empirically this extremely useful phenomenon, which is unique to the versatile Padé methodology. By definition, noise is spurious information by which the genuine part of the signal is corrupted. Therefore, pole-zero cancellations could be used to disentangle noise (as an unphysical burden) from the physical content in the considered signal, and this is the most important application of the Froissart doublets in MRS [87–89], as well as in many other applications of the FPT [77].

14. CRITICAL IMPORTANCE OF POLES AND ZEROS IN GENERIC SPECTRA

As mentioned in Section 13, a spectral doublet called the Froissart doublet [25] represents a couple consisting of a pole and a zero that coincide with each other. Therefore, a study of Froissart doublets necessitates both the zeros and poles of the complex spectra $P_K^\pm(z^{\pm 1})/Q_K^\pm(z^{\pm 1})$ in the FPT^(±). These spectral zeros and poles are obtained by solving the characteristic equations for the numerator and denominator polynomials:

$$P_K^\pm(z^{\pm 1}) = 0, \quad Q_K^\pm(z^{\pm 1}) = 0, \quad (202)$$

respectively. The solution of the denominator characteristic equation is usually denoted by $z_K^\pm$ [87]. The same notation will also be used in the present work whenever the analysis or discussion concerns only the polynomials $Q_K^\pm(z^{\pm 1})$. However, as soon as we need to analyze the zeros of polynomials $P_K^\pm(z^{\pm 1})$ and $Q_K^\pm(z^{\pm 1})$ in concert, as required for the Froissart doublets, there is a need for a supplementary suffix in $z_K^\pm$ to distinguish between the zeros of the numerator $P_K^\pm(z^{\pm 1})$ and denominator $Q_K^\pm(z^{\pm 1})$ polynomials. For this reason, the harmonic variables $z_K^\pm$ are set to acquire the second subscript like $z_{K,P}^\pm$ and $z_{K,Q}^\pm$ to remind us that they satisfy the characteristic equations $P_K^\pm(z_{K,P}^\pm) = 0$ and $Q_K^\pm(z_{K,Q}^\pm) = 0$, respectively, as per Eq. (202).

15. SPECTRAL REPRESENTATIONS VIA PADÉ POLES AND ZEROS: pFPT^(±) AND zFPT^(±)

The Froissart concept naturally introduces the following two new complementary representations of the FPT^(±): the “zeros of the FPT^(±)” denoted as zFPT^(±) and the “poles of the FPT^(±)” labeled by pFPT^(±). Each of these two representations, the zFPT^(±) and the pFPT^(±), can provide the spectra in their own right by using exclusively either the zeros $\{z_{k,P}^\pm\}$ or the poles $\{z_{k,Q}^\pm\}$ at a time via:

$$\text{Spectra in zFPT}^{(\pm)} \propto g_{K,P}^\pm \prod_{r=1}^K (z^{\pm 1} - z_{r,P}^\pm), \quad (203)$$

$$\text{Spectra in pFPT}^{(\pm)} \propto g_{K,Q}^\pm \prod_{s=1}^K (z^{\pm 1} - z_{s,Q}^\pm), \quad (204)$$

where $g_{K,P}^\pm$ and $g_{K,Q}^\pm$ are the gain factors. Of course, when both the zeros $\{z_{k,P}^\pm\}$ and poles $\{z_{k,Q}^\pm\}$ are used simultaneously to create the spectrum and/or to perform quantification, the old composite representations FPT^(±) are recovered as the union of the two new constituent representations, the zFPT^(±) and the pFPT^(±).

The zFPT^(±) and the pFPT^(±) can be analyzed through the canonical forms of the polynomials $P_K^\pm(z^{\pm 1})$ and $Q_K^\pm(z^{\pm 1})$, respectively:

$$P_K^\pm(z^{\pm 1}) = p_K^\pm \prod_{r=1}^K (z^{\pm 1} - z_{r,P}^\pm), \quad Q_K^\pm(z^{\pm 1}) = q_K^\pm \prod_{s=1}^K (z^{\pm 1} - z_{s,Q}^\pm). \quad (205)$$

These expressions also permit writing down directly the formulae for the general derivatives of the polynomials $P_K^\pm(z^{\pm 1})$ and $Q_K^\pm(z^{\pm 1})$. For example, the first derivatives of $Q_K^\pm(z^{\pm 1})$, which will be needed in this Section at $z^{\pm 1} = z_{k,Q}^\pm$, are given by the following simple expressions:

$$Q_K^{\pm'}(z_{k,Q}^\pm) = q_K^\pm \prod_{s=1, s \neq k}^K (z_{k,Q}^\pm - z_{s,Q}^\pm), \quad Q_K^{\pm'}(z^{\pm 1}) \equiv \frac{d}{dz^{\pm 1}} Q_K^\pm(z^{\pm 1}). \quad (206)$$

It is clear from here that for simple poles, defined as the noncoincident zeros $z_{k',Q}^\pm \neq z_{k,Q}^\pm$ ($k' \neq k$) of the denominator polynomial $Q_K^\pm(z^{\pm 1})$, the first derivative $Q_K^{\pm'}(z_{k,Q}^\pm)$ is never equal to zero:

$$Q_K^{\pm'}(z_{k,Q}^\pm) \neq 0. \quad (207)$$

16. PADÉ CANONICAL SPECTRA

Substituting Eqs. (205) and (206) in Eq. (208) yields the canonical forms of the rational polynomials in the FPT, $P_K^\pm(z^{\pm 1})/Q_K^\pm(z^{\pm 1})$:

$$\frac{P_K^\pm(z^{\pm 1})}{Q_K^\pm(z^{\pm 1})} = \frac{p_K^\pm \prod_{r=1}^K (z^{\pm 1} - z_{r,P}^\pm)}{q_K^\pm \prod_{s=1}^K (z^{\pm 1} - z_{s,Q}^\pm)}. \quad (208)$$

Representations from Eq. (208) can also be written more succinctly by using a single product symbol:

$$\frac{P_K^\pm(z^{\pm 1})}{Q_K^\pm(z^{\pm 1})} = \frac{p_K^\pm \prod_{k=1}^K (z^{\pm 1} - z_{k,P}^\pm)}{q_K^\pm \prod_{k=1}^K (z^{\pm 1} - z_{k,Q}^\pm)}. \quad (209)$$

The physical meaning of the degree K of the denominator polynomials in the FPT^(±) is in representing the total number K_T of poles, $K_T \equiv K$. The number K_T is given by the sum of the numbers of the genuine (K_G) and spurious (K_S) poles, $K_T = K_G + K_S$. Genuine poles, or equivalently, the signal poles, are those that represent the truly physical content of the studied FID. Spurious (extraneous) poles represent the nonphysical constituents of the input FID and, therefore, must be discarded from the final results of the spectral analysis. Of course, a noiseless input FID does not have any spurious part in its content. Nevertheless, spuriousness can appear also during the spectral analysis of a noiseless FID in any signal processor. One of the main sources of such theoretical noise (without counting the obvious round-off errors) is underestimation or overestimation of the otherwise unknown, true number K_G . In general, spurious poles are predominantly composed of the Froissart doublets that are the couples of the coincident Froissart zeros and poles:

$$z_{k,P}^\pm = z_{k,Q}^\pm, \quad k \in \mathcal{K}_F. \quad (210)$$

Here, $\mathcal{K}_F$ is the set of the counting indices k for the Froissart poles whose number is denoted by K_F . There could also be some extraneous isolated poles (called ghost poles) that do not have the matching zeros. Further, there might, as well, be some extraneous isolated zeros (called ghost zeros) that are unmatched by the like poles. An example of such a ghost zero in the FPT⁽⁺⁾ is the point $z = 0$, which is one of the K zeros of $P_K^+(z)$. A numerical computation within the FPT⁽⁺⁾ will certainly find the trivial zero $z = 0$ for any order K . This zero should be ignored in signal processing, since the domain of the definition of the original Maclaurin expansion (126), from which the FPT⁽⁺⁾ is derived, excludes the point $z = 0$. This latter point corresponds precisely to

$z^{-1} = \infty$ in the $\text{FPT}^{(-)}$, because the harmonic expansion variable in this variant of the FPT is z^{-1} . In other words, the ghost zero $z^{-1} = \infty$ is one of the K zeros of $P_K^-(z^{-1})$ in the $\text{FPT}^{(-)}$ and, as such, should be discarded for the same reason stated for $z = 0$ in the $\text{FPT}^{(+)}$. Of course, numerically, the point $z^{-1} = \infty$ cannot be detected exactly, but one of the zeros from the whole set $\{z_{k,p}^-\}$ must have a very large real and imaginary part, and this should be more pronounced as the degree K of $P_K^-(z^{-1})$ in the $\text{FPT}^{(-)}$ is increased. These two ghost zeros, $z = 0$ and $z^{-1} = \infty$ in the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$, respectively, have been found in the present computations, precisely as per description. The same computations in the present review with noise-free as well as noise-corrupted FIDs find no ghost poles at all and, therefore, it follows that

$$K_T = K_G + K_F. \quad (211)$$

17. SIGNAL–NOISE SEPARATION: EXCLUSIVE RELIANCE UPON RESONANT FREQUENCIES

The sets of all the poles $\{z_{k,Q}^\pm\}$ are composed of the two disjoint subsets of the genuine and Froissart poles:

$$\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_T} = \{z_{k,Q}^\pm\}_{k \in \mathcal{K}_G} \oplus \{z_{k,Q}^\pm\}_{k \in \mathcal{K}_F}, \quad (212)$$

where $\mathcal{K}_G$ is the set of the counting indices k for the genuine poles, whereas the set of all the values of k is denoted by $\mathcal{K}_T$. No common element exists in the two subsets $\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_G}$ and $\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_F}$ and, therefore, their sums in (212) are the so-called direct sums as denoted by the standard symbol $\oplus$ for disjoint sets. Hence, it is sufficient to count the number K_F of the Froissart doublets to determine the exact number K_G of the genuine poles via $K_G = K_T - K_F$ as per Eq. (211). In other words, once the $\text{FPT}^{(\pm)}$ have converged fully, a simple grouping of all the reconstructed poles $\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_T}$ into two sets $\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_F}$ and $\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_G}$ according to whether or not $z_{k,Q}^\pm = z_{k,P}^\pm$, that is, whether or not Eq. (210) is satisfied, is performed, thus permitting the unequivocal reconstruction of the true number K_G of the genuine poles and the exact numerical values of the corresponding harmonic variables:

$$\{z_{k,Q}^\pm\}_{k \in \mathcal{K}_T} = \begin{cases} \{z_{k,Q}^\pm\}_{k \in \mathcal{K}_G}, & z_{k,Q}^\pm \neq z_{k,P}^\pm: & \text{genuine poles,} \\ \{z_{k,Q}^\pm\}_{k \in \mathcal{K}_F}, & z_{k,Q}^\pm = z_{k,P}^\pm: & \text{Froissart poles.} \end{cases} \quad (213)$$

This allows the identification of the genuine fundamental frequencies $\{f_{k,Q}^\pm\}_{k \in \mathcal{K}_G}$ from the whole set $\{f_{k,Q}^\pm\}_{k \in \mathcal{K}_T}$ as

$$\{f_{k,Q}^\pm\}_{k \in \mathcal{K}_T} = \begin{cases} \{f_{k,Q}^\pm\}_{k \in \mathcal{K}_G}, & f_{k,Q}^\pm \neq f_{k,P}^\pm: & \text{genuine poles,} \\ \{f_{k,Q}^\pm\}_{k \in \mathcal{K}_F}, & f_{k,Q}^\pm = f_{k,P}^\pm: & \text{Froissart poles.} \end{cases} \quad (214)$$

Here, we used the following definitions of $f_{k,P}^\pm$ and $f_{k,Q}^\pm$ in terms of $z_{k,P}^\pm$ and $z_{k,Q}^\pm$, respectively:

$$f_{k,P}^\pm = \mp \frac{i}{2\pi\tau} \ln(z_{k,P}^\pm), \quad f_{k,Q}^\pm = \mp \frac{i}{2\pi\tau} \ln(z_{k,Q}^\pm). \quad (215)$$

18. MODEL REDUCTION PROBLEM VIA PADÉ CANONICAL SPECTRA

Using Eq. (211), it is convenient to recast the canonical representations from Eq. (208) into the following forms:

$$\begin{aligned} \frac{P_{K_T}^\pm(z^{\pm 1})}{Q_{K_T}^\pm(z^{\pm 1})} &= \frac{p_K^\pm \prod_{r=1}^{K_T} (z^{\pm 1} - z_{r,P}^\pm)}{q_K^\pm \prod_{s=1}^{K_T} (z^{\pm 1} - z_{s,Q}^\pm)} \\ &= \frac{p_K^\pm \prod_{r=1}^{K_G} (z^{\pm 1} - z_{r,P}^\pm)}{q_K^\pm \prod_{s=1}^{K_G} (z^{\pm 1} - z_{s,Q}^\pm)} \left\{ \frac{\prod_{r=K_G+1}^{K_G+K_F} (z^{\pm 1} - z_{r,P}^\pm)}{\prod_{s=K_G+1}^{K_G+K_F} (z^{\pm 1} - z_{s,Q}^\pm)} \right\}_{r,s \in K_F}. \end{aligned} \quad (216)$$

Here, after the reduction of the canonical quotient in the curly brackets to unity by the exact cancellation of the numerator and denominator polynomials, due to the equality of the poles and zeros via Eq. (210) in the Froissart doublets, we obtain:

$$\frac{P_{K_T}^\pm(z^{\pm 1})}{Q_{K_T}^\pm(z^{\pm 1})} = \frac{p_K^\pm \prod_{r=1}^{K_G+K_F} (z^{\pm 1} - z_{r,P}^\pm)}{q_K^\pm \prod_{s=1}^{K_G+K_F} (z^{\pm 1} - z_{s,Q}^\pm)} = \frac{p_K^\pm \prod_{r=1}^{K_G} (z^{\pm 1} - z_{r,P}^\pm)}{q_K^\pm \prod_{s=1}^{K_G} (z^{\pm 1} - z_{s,Q}^\pm)}. \quad (217)$$

When convergence is reached in the $FPT^{(\pm)}$, we have:

$$p_{K_G+K_F}^\pm = p_{K_G}^\pm, \quad q_{K_G+K_F}^\pm = q_{K_G}^\pm, \quad (218)$$

and this reduces Eq. (217) to:

$$\frac{P_{K_G+K_F}^\pm(z^{\pm 1})}{Q_{K_G+K_F}^\pm(z^{\pm 1})} = \frac{P_{K_G}^\pm(z^{\pm 1})}{Q_{K_G}^\pm(z^{\pm 1})} \quad (K_F = 1, 2, 3, \dots), \quad (219)$$

which is the proof for the already stated result from Eq. (201). Alternatively, from the onset, one can avoid dealing with the equalities in Eq. (218) by defining $P_K^\pm$ and $Q_K^\pm$ as the so-called monic polynomials. A polynomial is said to be monic if its coefficient, which multiplies the highest power of the expansion variable, is equal to unity. Thus, $P_K^\pm$ and $Q_K^\pm$ can be monic polynomials if all their expansion coefficients are divided by $p_K^\pm$ and $q_K^\pm$, respectively. Relationship (219) gives a transparent visualization of Froissart doublets through pole–zero cancellations. Moreover, such cancellations effectively diminish the order of the FPT from $K = K_T$ to $K_T - K_F = K_G$. Hence, the Froissart pole–zero cancellation represents an efficient way to reduce the order of the model for the Padé-based quantification in MRS. In other words, pole–zero cancellations reduce the dimensionality of the interim problem, which otherwise without the elimination of the K_F Froissart doublets would be of the order $K_T = K_F + K_G$. In other words, when the K_F Froissart doublets are discarded altogether, we are left with the order K_G which is then necessarily the exact order of the original problem. Physically, this means that the reconstructed order K_G represents the exact number of the genuine poles. This is how the true number of the genuine resonances is unequivocally retrieved from the input FID by using the $\text{FPT}^{(\pm)}$.

19. DENOISING FROISSART FILTER

The key to finding the true number K_G is the capability of the $\text{FPT}^{(\pm)}$ to unambiguously discriminate between the genuine (Padé) and spurious (Froissart) poles. Such an accomplishment proceeds by using pole–zero cancellations to filter out all the spurious, that is, Froissart poles from the solution of the quantification problem, thus leaving us with the genuine poles alone, as it should be. It is, therefore, appropriate to term this procedure as the denoising Froissart filter (DFF). Here, one of the obvious meanings of the term “denoising” is a “noise reduction,” where Froissart doublets are viewed as noise due to their spuriousness. This term is equally valid for noise-corrupted as well as noise-free input FIDs. This is true because in either case, the exact number K_G is unknown prior to the analysis, so that any estimate $K' \neq K_G$ inevitably yields a nonzero difference $\text{FID}(\text{input}) - \text{FID}(\text{reconstructed by using } K')$, which is spurious and, as such, acts implicitly as noise for both noiseless and noisy input FIDs.

20. SIGNAL–NOISE SEPARATION: EXCLUSIVE RELIANCE UPON RESONANT AMPLITUDES

The expounded proof of finding the exact number of genuine resonances relies exclusively upon the reconstructed signal poles $z_k^\pm$, that is, the

quantities that include the complex frequencies alone, without any recourse to the corresponding complex amplitudes $d_k^\pm$. Nevertheless, it is also important to know whether the genuine and spurious resonances could also be disentangled by their amplitudes. To address this issue, we derive the closed, analytical expressions for the amplitudes $d_k^\pm$ associated with the signal poles $z_k^\pm$. By definition, the amplitudes $d_k^\pm$ are the Cauchy residues of the rational polynomial $P_K^\pm(z^{\pm 1})/Q_K^\pm(z^{\pm 1})$. These residues for the simple poles of $Q_K^\pm(z^{\pm 1})$ are introduced by the formulae:

$$d_k^\pm = \lim_{z^{\pm 1} \rightarrow z_{k,Q}^\pm} \left\{ (z^{\pm 1} - z_{k,Q}^\pm) \frac{P_K^\pm(z^{\pm 1})}{Q_K^\pm(z^{\pm 1})} \right\}. \quad (220)$$

The limiting process in Eq. (220) can be carried out directly by using the canonical form (210) so that:

$$d_k^\pm = \frac{p_K^\pm}{q_K^\pm} \times \lim_{z^{\pm 1} \rightarrow z_{k,Q}^\pm} \left\{ \frac{[z^{\pm 1} - z_{k,Q}^\pm] \prod_{r=1}^K (z^{\pm 1} - z_{r,P}^\pm)}{(z^{\pm 1} - z_{1,Q}^\pm) \cdots (z^{\pm 1} - z_{k-1,Q}^\pm) [z^{\pm 1} - z_{k,Q}^\pm] (z^{\pm 1} - z_{k+1,Q}^\pm) \cdots (z^{\pm 1} - z_{K,Q}^\pm)} \right\}.$$

Here, cancellation of the common term in the square brackets, $[z^{\pm 1} - z_{k,Q}^\pm]$, from the numerator and denominator leaves a remainder where the replacement of $z^{\pm 1}$ by $z_{k,Q}^\pm$ can be made directly, thus yielding:

$$d_k^\pm = \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^K (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^K (z_{k,Q}^\pm - z_{s,Q}^\pm)}; \quad k \in \mathcal{K}_T, \quad (221)$$

or in the more concise forms along the lines of the expressions from Eq. (209):

$$d_k^\pm = \frac{p_K^\pm}{q_K^\pm} \prod_{k'=1}^K \frac{(z_{k,Q}^\pm - z_{k',P}^\pm)}{(z_{k,Q}^\pm - z_{k',Q}^\pm)_{k' \neq k}}. \quad (222)$$

It is obvious that the denominator in Eq. (221) or (222) is always nonzero for simple poles, as in Eqs. (206) and (207). Further, the numerator in Eq. (221) is seen to be the canonical form of $P_K^\pm(z_{k,Q}^\pm)$ by virtue of Eq. (205). Likewise, the denominator in Eq. (221) is recognized as the canonical form of the first derivative with respect to $z^{\pm 1}$ of $Q_K^\pm(z)$ evaluated at $z^{\pm 1} = z_{k,Q}^\pm$ as per

Eq. (206). Such an observation leads at once to the following equivalent expressions for $d_k^\pm$:

$$d_k^\pm = \frac{P_K^\pm(z_{k,Q}^\pm)}{Q_K^{\pm'}(z_{k,Q}^\pm)}, \quad (223)$$

where we always have $Q_K^{\pm'}(z_{k,Q}^\pm) \neq 0$, as in Eq. (207). Expressions in Eq. (223) can also be derived from the definition (220) without recourse to any particular representation of the invoked polynomials. To this end, we use the characteristic equation $Q_K^\pm(z_{k,Q}^\pm) = 0$ from Eq. (202) together with the definition of the first derivative, $Q_K^{\pm'}(z_{k,Q}^\pm) = \lim_{z^{\pm 1} \rightarrow z_{k,Q}^\pm} [Q_K^\pm(z^{\pm 1}) - Q_K^\pm(z_{k,Q}^\pm)](z^{\pm 1} - z_{k,Q}^\pm)$, to reproduce precisely Eq. (223):

$$\begin{aligned} d_k^\pm &= \lim_{z^{\pm 1} \rightarrow z_{k,Q}^\pm} \left\{ (z^{\pm 1} - z_{k,Q}^\pm) \frac{P_K^\pm(z^{\pm 1})}{Q_K^\pm(z^{\pm 1})} \right\} \\ &= P_K^\pm(z_{k,Q}^\pm) \left\{ \lim_{z^{\pm 1} \rightarrow z_{k,Q}^\pm} \frac{Q_K^\pm(z^{\pm 1}) - Q_K^\pm(z_{k,Q}^\pm)}{z^{\pm 1} - z_{k,Q}^\pm} \right\}^{-1} \\ &= \frac{P_K^\pm(z_{k,Q}^\pm)}{Q_K^{\pm'}(z_{k,Q}^\pm)} \quad (\text{QED}). \end{aligned}$$

In order to see whether the amplitudes $d_k^\pm$ can be used to discriminate between the genuine and spurious resonances, we rewrite Eq. (221) according to the same prescription as in Eq. (216):

$$\begin{aligned} d_k^\pm &= \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_T} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_T} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \\ &= \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_G} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_G} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \left\{ \frac{\prod_{r=K_G+1}^{K_G+K_F} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=K_G+1, s \neq k}^{K_G+K_F} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \right\}_{r,s \in \mathcal{K}_F}, \quad k \in \mathcal{K}_T. \end{aligned} \quad (224)$$

Disjointness of the two sets $\mathcal{K}_G$ and $\mathcal{K}_F$ implies that if $k \in \mathcal{K}_G$ (respectively, $k \in \mathcal{K}_F$), then the amplitudes $d_k^\pm$ on the lhs of (224) are the genuine (respectively, spurious) ones. Therefore, for example, for $k \in \mathcal{K}_G$ (which

automatically means that $k \notin \mathcal{K}_F$ or, stated equivalently, $k \neq k'$ for $k' \in \mathcal{K}_F$), the genuine amplitudes are extracted from Eq. (224) as:

$$\begin{aligned}
 d_k^\pm &= \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_T} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_T} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \\
 &= \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_G} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_G} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \left\{ \frac{\prod_{r=K_G+1, r \neq k}^{K_G+K_F} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=K_G+1, s \neq k}^{K_G+K_F} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \right\}_{r,s \in \mathcal{K}_F}, \quad k \in \mathcal{K}_G.
 \end{aligned} \tag{225}$$

Here, the rational polynomial in the curly brackets is equal to unity, due to the coincidence of the corresponding constituent polynomials in the numerators, $\prod_{r=K_G+1, r \neq k}^{K_G+K_F} (z_{k,Q}^\pm - z_{r,P}^\pm)$ and denominators, $\prod_{s=K_G+1, s \neq k}^{K_G+K_F} (z_{k,Q}^\pm - z_{s,Q}^\pm)$ because $z_{j,P}^\pm = z_{j,Q}^\pm$ for $j \in \mathcal{K}_F$ ($j = r, s$). This reduces Eq. (225) to:

$$d_k^\pm = \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_G} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_G} (z_{k,Q}^\pm - z_{s,Q}^\pm)}, \quad k \in \mathcal{K}_G. \tag{226}$$

Likewise, for $k \in \mathcal{K}_F$, the Froissart amplitudes are identified from Eq. (224) via:

$$\begin{aligned}
 d_k^\pm &= \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_T} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_T} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \\
 &= \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_G} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_G} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \left\{ \frac{\prod_{r=K_G+1}^{K_G+K_F} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=K_G+1, s \neq k}^{K_G+K_F} (z_{k,Q}^\pm - z_{s,Q}^\pm)} \right\}_{r,s \in \mathcal{K}_F}.
 \end{aligned} \tag{227}$$

The rational polynomials in the curly brackets from Eq. (227) are equal to zero, since the corresponding numerator polynomials $\prod_{r=K_G+1}^{K_G+K_F} (z_{k,Q}^\pm - z_{r,P}^\pm)$ are equal to zero, because when $r=k$ the following null factors are always present in the product: $[(z_{k,Q}^\pm - z_{r,P}^\pm)]_{r=k} = (z_{k,Q}^\pm - z_{k,P}^\pm) = 0$ for $z_{k,Q}^\pm = z_{k,P}^\pm$ where

$k \in \mathcal{K}_F$, as per definition (210) of Froissart doublets via pole–zero cancellations. Thus, *all* the Froissart amplitudes are zero-valued:

$$d_k^\pm = 0, \quad k \in \mathcal{K}_F. \quad (228)$$

Similarly to Eq. (212), we can decompose the whole sets $\{d_k^\pm\}$ of the amplitudes into two disjoint sets of the genuine and spurious amplitudes:

$$\{d_k^\pm\}_{k \in \mathcal{K}_T} = \{d_k^\pm\}_{k \in \mathcal{K}_G} \oplus \{d_k^\pm\}_{k \in \mathcal{K}_F}. \quad (229)$$

The explicit members of the two subsets in Eq. (229) are given by Eqs. (226) and (228) that are recapitulated as:

$$d_k^\pm = \begin{cases} \frac{p_K^\pm}{q_K^\pm} \frac{\prod_{r=1}^{K_G} (z_{k,Q}^\pm - z_{r,P}^\pm)}{\prod_{s=1, s \neq k}^{K_G} (z_{k,Q}^\pm - z_{s,Q}^\pm)}; & k \in \mathcal{K}_G: \quad \text{genuine amplitudes,} \\ 0; & k \in \mathcal{K}_F: \quad \text{Froissart amplitudes.} \end{cases} \quad (230)$$

21. PADÉ PARTIAL FRACTION SPECTRA

Once the spectral parameters $\{z_{k,Q}^\pm, d_k^\pm\}$ become available, as per the outlined procedure in the $\text{FPT}^{(\pm)}$, we can set up yet another form for the Padé complex mode spectra $P_K^\pm(z^{\pm 1})/Q_K^\pm(z^{\pm 1})$. These are the Heaviside or Padé partial fractions that have the following forms for the diagonal versions of $\text{FPT}^{(\pm)}$ in which the numerator and denominator polynomials are of the same degree K :

$$\frac{P_K^\pm(z^{\pm 1})}{Q_K^\pm(z^{\pm 1})} = b_0^\pm + \sum_{k=1}^K \frac{d_k^\pm z^{\pm 1}}{z^{\pm 1} - z_{k,Q}^\pm}. \quad (231)$$

Here, the factored terms $b_0^\pm$ are the so-called baseline constants that describe the corresponding flat backgrounds:

$$b_0^\pm \equiv \frac{p_0^\pm}{q_0^\pm}. \quad (232)$$

The frequency spectra in Eq. (231) can be inverted by a procedure called the inverse fast Padé transforms (IFPT). The results of such inversions are the corresponding time signals obtained as:

$$c_n^\pm = b_0^\pm \delta(n) + \sum_{k=1}^K d_k^\pm z_{k,Q}^{\pm n} = b_0^\pm \delta(n) + \sum_{k=1}^K d_k^\pm e^{\pm 2i\pi n \tau_{k,Q}^\pm}, \quad (233)$$

where the n th power of $z_{k,Q}^{\pm}$ is denoted by $z_{k,Q}^{\pm n} \equiv (z_{k,Q}^{\pm})^n$. The quantity $\delta(n)$ is the standard discrete unit impulse (or discrete unit sample, or discrete unit-step time signal). This is defined by the usual Kronecker δ -symbol $\delta_{n,0}$, that is, $\delta(n) = 1$ for $n = 0$ and $\delta(n) = 0$ for $n \neq 0$. For this reason, $\delta(n)$ is also called the Kronecker discrete time sequence. Care must be exercised not to interpret $\delta(n)$ as a sampled version of the corresponding continuous Dirac delta function $\delta(t)$. The latter function $\delta(t)$ *cannot* be sampled, since it is infinite at the time $t = 0$ [77].

In the $\text{FPT}^{(+)}$, the expressions (231) and (233) for the spectrum and the reconstructed time signal, respectively, can further be simplified using the relation:

$$b_0^+ = 0, \quad (234)$$

which stems from $p_0^+ \equiv 0$ as per derivation in Section 10. Therefore, it follows from Eqs. (231) and (233) that:

$$\left. \begin{aligned} \frac{P_K^+(z)}{Q_K^+(z)} &= \sum_{k=1}^K \frac{d_k^+ z}{z - z_{k,Q}^+} \\ c_n^+ &= \sum_{k=1}^K d_k^+ z_{k,Q}^{+n} = \sum_{k=1}^K d_k^+ e^{2i\pi n \tau f_{k,Q}^+} \end{aligned} \right\}, \quad (235)$$

$$\left. \begin{aligned} \frac{P_K^-(z)}{Q_K^-(z)} &= \frac{p_0^-}{q_0^-} + \sum_{k=1}^K \frac{d_k^- z^{-1}}{z^{-1} - z_{k,Q}^-} \\ c_n^- &= \frac{p_0^-}{q_0^-} + \sum_{k=1}^K d_k^- z_{k,Q}^{-n} = \sum_{k=1}^K d_k^- e^{-2i\pi n \tau f_{k,Q}^-} \end{aligned} \right\}. \quad (236)$$

22. MODEL REDUCTION PROBLEM VIA PADÉ PARTIAL FRACTION SPECTRA

The model order reduction can also be carried out within the expressions (231) and (233) for the Padé partial fractions and the time signals, respectively:

$$\begin{aligned} \frac{P_{K_T}^{\pm}(z^{\pm 1})}{Q_{K_T}^{\pm}(z^{\pm 1})} &= b_0^{\pm} + \sum_{k=1}^{K_G+K_F} \frac{d_k^{\pm} z^{\pm 1}}{z^{\pm 1} - z_{k,Q}^{\pm}} \\ &= b_0^{\pm} + \sum_{k=1}^{K_G} \frac{d_k^{\pm} z^{\pm 1}}{z^{\pm 1} - z_{k,Q}^{\pm}} + \left\{ \sum_{k=K_G+1}^{K_G+K_F} \frac{d_k^{\pm} z^{\pm 1}}{z^{\pm 1} - z_{k,Q}^{\pm}} \right\}_{k \in \mathcal{K}_F}, \end{aligned} \quad (237)$$

$$\begin{aligned}
c_n^\pm &= b_0^\pm \delta(n) + \sum_{k=1}^{K_T} d_k^\pm z_{k,Q}^{\pm n} = b_0^\pm \delta(n) + \sum_{k=1}^{K_G+K_F} d_k^\pm z_{k,Q}^{\pm n} \\
&= b_0^\pm \delta(n) + \sum_{k=1}^{K_G} d_k^\pm z_{k,Q}^{\pm n} + \left\{ \sum_{k=K_G+1}^{K_G+K_F} d_k^\pm z_{k,Q}^{\pm n} \right\}_{k \in \mathcal{K}_F}.
\end{aligned} \tag{238}$$

The sums within the curly brackets in Eqs (237) and (238) are equal to zero, due to the invoked vanishing Froissart amplitudes $\{d_k^\pm\}_{k \in \mathcal{K}_F}$, as per Eq. (230), so that:

$$\begin{aligned}
\frac{P_{K_G+K_F}^\pm(z^{\pm 1})}{Q_{K_G+K_F}^\pm(z^{\pm 1})} &= b_0^\pm + \sum_{k=1}^{K_G+K_F} \frac{d_k^\pm z^{\pm 1}}{z^{\pm 1} - z_{k,Q}^\pm} = b_0^\pm + \sum_{k=1}^{K_G} \frac{d_k^\pm z^{\pm 1}}{z^{\pm 1} - z_{k,Q}^\pm} = \frac{P_{K_G}^\pm(z^{\pm 1})}{Q_{K_G}^\pm(z^{\pm 1})}, \\
\therefore \frac{P_{K_G+K_F}^\pm(z^{\pm 1})}{Q_{K_G+K_F}^\pm(z^{\pm 1})} &= \frac{P_{K_G}^\pm(z^{\pm 1})}{Q_{K_G}^\pm(z^{\pm 1})},
\end{aligned} \tag{239}$$

$$\begin{aligned}
c_n^\pm &= b_0^\pm \delta(n) + \sum_{k=1}^{K_G+K_F} d_k^\pm z_{k,Q}^{\pm n} = b_0^\pm \delta(n) + \sum_{k=1}^{K_G} d_k^\pm z_{k,Q}^{\pm n} \\
&= b_0^\pm \delta(n) + \sum_{k=1}^{K_G} d_k^\pm e^{\pm 2i\pi n \tau f_{k,Q}^\pm}. \\
\therefore c_n^\pm &= b_0^\pm \delta(n) + \sum_{k=1}^{K_G+K_F} d_k^\pm z_{k,Q}^{\pm n} = b_0^\pm \delta(n) + \sum_{k=1}^{K_G} d_k^\pm z_{k,Q}^{\pm n}.
\end{aligned} \tag{240}$$

The model order reduction in the $\text{FPT}^{(+)}$ can also be performed either using directly Eq. (235) or substituting Eq. (234) into Eqs. (239) and (240) with the final results:

$$\frac{P_{K_G+K_F}^+(z)}{Q_{K_G+K_F}^+(z)} = \sum_{k=1}^{K_G+K_F} \frac{d_k^+ z}{z - z_{k,Q}^+} = \sum_{k=1}^{K_G} \frac{d_k^+ z}{z - z_{k,Q}^+} = \frac{P_{K_G}^+(z)}{Q_{K_G}^+(z)}, \tag{241}$$

$$c_n^+ = \sum_{k=1}^{K_G+K_F} d_k^+ z_{k,Q}^{+n} = \sum_{k=1}^{K_G} d_k^+ z_{k,Q}^{+n} = \sum_{k=1}^{K_G} d_k^+ e^{2i\pi n \tau f_{k,Q}^+}. \tag{242}$$

23. DISENTANGLING GENUINE FROM SPURIOUS RESONANCES

When both the $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ reach convergence, they give the same spectral parameters for the genuine resonances, so that:

$$\left. \begin{aligned} z_{k,P}^+ &= z_{k,P}^-, & z_{k,Q}^+ &= z_{k,Q}^-, \\ f_{k,P}^+ &= f_{k,P}^-, & f_{k,Q}^+ &= f_{k,Q}^-, \\ d_k^+ &= d_k^- \end{aligned} \right\}, \quad k \in \mathcal{K}_G: \quad \text{genuine resonances.} \tag{243}$$

Simultaneously, despite the convergence of genuine resonances, the remaining spectral parameters for all the Froissart resonances never converge due to their spuriousness, such that even the slightest increase in the signal length can alter appreciably the distributions of the latter parameters in the complex planes. Moreover, the Froissart harmonic variables and the Froissart frequencies are different in the $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$:

$$\left. \begin{aligned} z_{k,P}^+ &\neq z_{k,P}^-, & z_{k,Q}^+ &\neq z_{k,Q}^- \\ f_{k,P}^+ &\neq f_{k,P}^-, & f_{k,Q}^+ &\neq f_{k,Q}^- \\ d_k^+ &= 0 = d_k^- \end{aligned} \right\}, \quad k \in \mathcal{K}_F: \quad \text{Froissart resonances.} \quad (244)$$

As seen in Eq. (244), both sets of the Froissart amplitudes $\{d_k^\pm\} (k \in \mathcal{K}_F)$ in the $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ are equal to zero, as proven earlier in Eq. (230).

24. RESULTS

Accuracy, resolving power, convergence rate, and robustness of any signal processor depend on such obvious input parameters as the signal-to-noise ratio (SNR) and the total acquisition time of the investigated FID, or equivalently, the signal length for a given bandwidth. However, a number of more subtle features of spectral analysis play a decisive role in the enhancement of the overall performance capability of a given estimator. These include the configurations of the poles and zeros in the complex plane, their density in the selected part of the Nyquist range, the smallest distance among poles on one hand and zeros on the other, interseparations among poles and zeros, their distance from the real frequency axis, and the smallest imaginary frequencies (the largest lifetimes of resonant states) in the spectrum. As initiated in Ref. [87], among the most suitable mathematical tools for investigating the effects of the enumerated features are the Argand plots, which show the imaginary part as a function of the corresponding real part of given complex-valued quantities, such as the harmonic variables $z_k^\pm$, the fundamental frequencies $f_k^\pm$, and the corresponding amplitudes $d_k^\pm$, as it will be seen in the illustrations. Equally instructive is to display the dependence of the absolute values of the amplitudes, $|d_k^\pm|$, or the peak heights $|d_k^\pm|/\text{Im}(f_k^\pm)$, which are proportional to the concentrations of the associated resonances/metabolites for $\text{Im}(f_k^\pm) > 0$ [87]. These extremely informative types of graphs will also be plotted in this Section, with special ramifications stemming from the powerful and versatile concept of the Froissart doublets via their mechanism of pole-zero cancellations.

The input data for the investigated quantification problem are given in Table 3.1. Such data are the complex fundamental frequencies and the corresponding amplitudes from a synthesized noiseless time signal whose corresponding true spectrum contains 25 tightly packed, overlapped and

Table 3.1 Input data for spectral parameters of a synthesized time signal or FID

N_k	$\text{Re}(f_k)(\text{ppm})$	$\text{Im}(f_k) (\text{ppm})$	$\lambda_k (\text{s})$	$ d_k (\text{au})$
1	0.98500435837	0.17994026683	0.08701928761	0.12202495867
2	1.11203465946	0.25651431281	0.06104249568	0.16104189750
3	1.54802587629	0.17199827375	0.09103738945	0.13500597856
4	1.68901549872	0.11770620050	0.13302845360	0.03401879347
5	1.95904239874	0.06238209710	0.25100589047	0.05602645983
6	2.06500583927	0.03125300573	0.50101657312	0.17103549765
7	2.14503254628	0.05002248274	0.31302472356	0.11600564789
8	2.26102461207	0.06237415874	0.25103783601	0.09201635984
9	2.41100529746	0.06237323971	0.25104153487	0.08504389576
10	2.51901475439	0.03599364925	0.43502879426	0.03703275984
11	2.67602379684	0.03282604370	0.47700764592	0.00802396485
12	2.67602379685	0.06237874512	0.25101937852	0.06300598750
13	2.85503174712	0.01612522180	0.97104238475	0.00501539487
14	3.00900463265	0.06390480723	0.24502497560	0.06502465938
15	3.06702174372	0.03599347264	0.43503092876	0.10104286591
16	3.23904145893	0.05002587757	0.31300348127	0.09603784265
17	3.30103548792	0.06390039525	0.24504189324	0.06500492987
18	3.48102435176	0.03106709099	0.50401480576	0.01104173860
19	3.58400324349	0.02821151210	0.55503135648	0.03601895643
20	3.69401184814	0.03632795345	0.43102548712	0.04102548756
21	3.80304301929	0.02390412693	0.65504479103	0.03100438719
22	3.94402479731	0.04153288222	0.37700908276	0.06803457962
23	3.96501243276	0.06237782909	0.25102306475	0.01301387365
24	4.27100347747	0.05493777424	0.28501835120	0.01602437598
25	4.68000000000	0.13611453358	0.11503748659	0.11304283387

Twelve-digit accurate numerical values for all the input spectral parameters are shown: the real $\text{Re}(f_k)$ and the imaginary $\text{Im}(f_k)$ part of frequencies f_k , and the absolute values $|d_k|$ of amplitudes d_k of 25 damped complex exponentials from the synthesized time signal similar to a short echo time (~ 20 ms) encoded FID via MRS at the magnetic field strength $B_0 = 1.5$ T from a healthy human brain as in Ref. [96]. Every phase $\{\phi_k\}$ of the amplitudes is equal to zero, such that each d_k is purely real, $d_k = |d_k| \exp(i\phi_k) = |d_k|$. Damping constants λ_k in seconds are the inverses of $\text{Im}(f_k)$ in hertz.

nearly degenerate resonances. Figure 3.1 also shows these input spectral parameters of the theoretically generated time signal. The concrete values of the spectral parameters are chosen to closely match the typical frequencies and amplitudes encountered in quantification of the corresponding FIDs encoded via proton MRS from the brain of a healthy volunteer at 1.5 T [96] (for the corresponding FID data measured at 4T and 7T, see Ref. [97]).

The present results of the fast Padé transform for the exact reconstruction of the input spectral parameters are shown in Table 3.2 and 3.3 as well

as in Figures 3.2–3.15. Table 3.2 displays the achieved high accuracy of the retrieved spectral parameters from the $\text{FPT}^{(-)}$ near full convergence at the two partial signal lengths $N_P=180, 220$. In panel (i) at $N_P=180$, prior to full convergence, the number of the exact reconstructed digits varies from 2 to 7. However, in panel (ii) at $N_P=220$, a spectacular increase in accuracy through all the 12 input digits is obtained for each reconstructed spectral parameter. This demonstrates that the $\text{FPT}^{(-)}$ has the spectral convergence, that is, the exponential convergence rate to the exact numerical values of all the reconstructed fundamental frequencies and amplitudes [48]. Table 3.3 shows the accuracy when the partial signal length N_P is chosen in the form of the composite number 2^m ($m > 1$) as used in the FFT. This is illustrated in the $\text{FPT}^{(-)}$ at a quarter $N/4=256$ and the full signal length

Table 3.2 Proof-of-principle accuracy of $\text{FPT}^{(-)}$ for quantification (signal length: $N_P=180, 220$)

(i) Partial signal length: $N_P=180$ (Accuracy of $\text{FPT}^{(-)}$ for every parameter of each resonance: 2–7 exact digits (ED_k^-))

N_k	$\text{Re}(f_k^-)$ (ppm)	ED_k^-	$\text{Im}(f_k^-)$ (ppm)	ED_k^-	$ d_k^- $ (au)	ED_k^-
1	0.9850144	5	0.1799453	6	0.1220558	5
2	1.1120550	5	0.2564834	5	0.1609861	4
3	1.5480125	5	0.1719806	5	0.1349332	4
4	1.6890750	4	0.1177081	6	0.0340222	6
5	1.9589685	4	0.0623722	5	0.0559110	4
6	2.0649796	4	0.0312332	5	0.1707292	4
7	2.1452850	4	0.0498913	3	0.1152942	3
8	2.2613892	4	0.0629386	3	0.0939533	3
9	2.4107292	4	0.0636088	3	0.0885762	2
10	2.5177708	3	0.0357784	4	0.0366056	4
12	2.6756860	4	0.0542827	2	0.0659756	3
13	2.8555671	3	0.0145610	2	0.0044815	3
14	3.0111090	3	0.0585455	3	0.0592638	3
15	3.0660722	3	0.0367388	3	0.1077992	2
16	3.2404677	3	0.0510603	3	0.1040487	2
17	3.2992547	2	0.0604351	3	0.0609011	3
18	3.4798565	3	0.0301829	3	0.0105069	3
19	3.5841084	4	0.0278826	4	0.0353704	3
20	3.6942770	4	0.0362695	5	0.0408475	4
21	3.8030958	4	0.0239509	4	0.0310756	4
22	3.9440801	4	0.0413630	3	0.0670586	3
23	3.9638210	3	0.0613931	3	0.0141493	3
24	4.2710029	7	0.0549388	6	0.0160250	6
25	4.6800001	7	0.1361142	7	0.1130423	6

Table 3.2 (Continued)(ii) Partial signal length: $N_P = 220$ (Accuracy of $\text{FPT}^{(-)}$ for every parameter of each resonance: 12 exact digits (ED_k^-))

N_k	$\text{Re}(f_k^-)$ (ppm)	ED_k^-	$\text{Im}(f_k^-)$ (ppm)	ED_k^-	$ d_k^- $ (au)	ED_k^-
1	0.98500435837	12	0.17994026683	12	0.12202495867	12
2	1.11203465946	12	0.25651431281	12	0.16104189750	12
3	1.54802587629	12	0.17199827375	12	0.13500597856	12
4	1.68901549872	12	0.11770620050	12	0.03401879347	12
5	1.95904239874	12	0.06238209710	12	0.05602645983	12
6	2.06500583927	12	0.03125300573	12	0.17103549765	12
7	2.14503254628	12	0.05002248274	12	0.11600564789	12
8	2.26102461207	12	0.06237415874	12	0.09201635984	12
9	2.41100529746	12	0.06237323971	12	0.08504389576	12
10	2.51901475439	12	0.03599364925	12	0.03703275984	12
11	2.67602379684	12	0.03282604370	12	0.00802396485	12
12	2.67602379685	12	0.06237874512	12	0.06300598750	12
13	2.85503174712	12	0.01612522180	12	0.00501539487	12
14	3.00900463265	12	0.06390480723	12	0.06502465938	12
15	3.06702174372	12	0.03599347264	12	0.10104286591	12
16	3.23904145893	12	0.05002587757	12	0.09603784265	12
17	3.30103548792	12	0.06390039525	12	0.06500492987	12
18	3.48102435176	12	0.03106709099	12	0.01104173860	12
19	3.58400324349	12	0.02821151210	12	0.03601895643	12
20	3.69401184814	12	0.03632795345	12	0.04102548756	12
21	3.80304301929	12	0.02390412693	12	0.03100438719	12
22	3.94402479731	12	0.04153288222	12	0.06803457962	12
23	3.96501243276	12	0.06237782909	12	0.01301387365	12
24	4.27100347747	12	0.05493777424	12	0.01602437598	12
25	4.68000000000	12	0.13611453358	12	0.11304283387	12

Extended accuracy all the way up to 12 exact digits for the numerical values of the complex frequencies and amplitudes reconstructed by the $\text{FPT}^{(-)}$ at two partial signal lengths $N_P = 180$ (panel (i)) and 220 (panel (ii)) is shown. Notice, especially, that using only 220 signal points out of 1024 entries available from the full FID, the $\text{FPT}^{(-)}$ resolves unequivocally the two near degenerate frequencies separated from each other by 10^{-11} ppm.

$N = 1024$ in panels (i) and (ii), respectively. These two panels give the identical 12-digit accurate results, and the same is checked to be also true for one-half of the full signal length, $N/2 = 512$ (not shown). The joint findings from [Tables 3.2 and 3.3](#) prove that the FPT remains stable beyond the stage at which full convergence is reached, so that adding further signal points does not change the stabilized results. Such a feature is very important for the robustness of the FPT in quantification within MRS.

Overall, it is seen from [Tables 3.1 and 3.2](#) as well as [Figures 3.2–3.7](#) that the FPT does not need even a quarter of the full signal length to reconstruct all the exact spectral parameters. From such accurately retrieved spectral parameters displayed in [Figures 3.4 and 3.5](#), the absorption total shape spectra (envelope spectra) are seen to converge fully in the FPT by exhausting merely 220 signal points out of 1024 entry data points $\{c_n\}$ from the input FID, with no undesirable spectral deformations, such as artifacts, Gibbs ringing, aliasing, or other typical defects prior to attaining stability. This is highly advantageous relative to the FFT and all the other estimators from MRS.

The FFT requires the full signal length ($N = 1024$) to converge, as is clear from [Figure 3.3](#). No convergence occurs in the FFT at $N/2 = 512$ (not

Table 3.3 Machine accuracy of $\text{FPT}^{(-)}$ for quantification (signal length: $N/4 = 256$, $N = 1024$)

(i) Signal length: $N/4 = 256$ (Accuracy of $\text{FPT}^{(-)}$ for every parameter of each resonance: 12 exact digits (ED_k^-))

N_k	$\text{Re}(f_k^-)$ (ppm)	ED_k^-	$\text{Im}(f_k^-)$ (ppm)	ED_k^-	$ d_k^- $ (au)	ED_k^-
1	0.98500435837	12	0.17994026683	12	0.12202495867	12
2	1.11203465946	12	0.25651431281	12	0.16104189750	12
3	1.54802587629	12	0.17199827375	12	0.13500597856	12
4	1.68901549872	12	0.11770620050	12	0.03401879347	12
5	1.95904239874	12	0.06238209710	12	0.05602645983	12
6	2.06500583927	12	0.03125300573	12	0.17103549765	12
7	2.14503254628	12	0.05002248274	12	0.11600564789	12
8	2.26102461207	12	0.06237415874	12	0.09201635984	12
9	2.41100529746	12	0.06237323971	12	0.08504389576	12
10	2.51901475439	12	0.03599364925	12	0.03703275984	12
11	2.67602379684	12	0.03282604370	12	0.00802396485	12
12	2.67602379685	12	0.06237874512	12	0.06300598750	12
13	2.85503174712	12	0.01612522180	12	0.00501539487	12
14	3.00900463265	12	0.06390480723	12	0.06502465938	12
15	3.06702174372	12	0.03599347264	12	0.10104286591	12
16	3.23904145893	12	0.05002587757	12	0.09603784265	12
17	3.30103548792	12	0.06390039525	12	0.06500492987	12
18	3.48102435176	12	0.03106709099	12	0.01104173860	12
19	3.58400324349	12	0.02821151210	12	0.03601895643	12
20	3.69401184814	12	0.03632795345	12	0.04102548756	12
21	3.80304301929	12	0.02390412693	12	0.03100438719	12
22	3.94402479731	12	0.04153288222	12	0.06803457962	12
23	3.96501243276	12	0.06237782909	12	0.01301387365	12
24	4.27100347747	12	0.05493777424	12	0.01602437598	12
25	4.68000000000	12	0.13611453358	12	0.11304283387	12

Table 3.3 (Continued)(ii) Signal length: $N = 1024$ (Accuracy of $\text{FPT}^{(-)}$ for every parameter of each resonance:
12 exact digits (ED_k^-))

N_k	$\text{Re}(f_k^-)$ (ppm)	ED_k^-	$\text{Im}(f_k^-)$ (ppm)	ED_k^-	$ d_k^- $ (au)	ED_k^-
1	0.98500435837	12	0.17994026683	12	0.12202495867	12
2	1.11203465946	12	0.25651431281	12	0.16104189750	12
3	1.54802587629	12	0.17199827375	12	0.13500597856	12
4	1.68901549872	12	0.11770620050	12	0.03401879347	12
5	1.95904239874	12	0.06238209710	12	0.05602645983	12
6	2.06500583927	12	0.03125300573	12	0.17103549765	12
7	2.14503254628	12	0.05002248274	12	0.11600564789	12
8	2.26102461207	12	0.06237415874	12	0.09201635984	12
9	2.41100529746	12	0.06237323971	12	0.08504389576	12
10	2.51901475439	12	0.03599364925	12	0.03703275984	12
11	2.67602379684	12	0.03282604370	12	0.00802396485	12
12	2.67602379685	12	0.06237874512	12	0.06300598750	12
13	2.85503174712	12	0.01612522180	12	0.00501539487	12
14	3.00900463265	12	0.06390480723	12	0.06502465938	12
15	3.06702174372	12	0.03599347264	12	0.10104286591	12
16	3.23904145893	12	0.05002587757	12	0.09603784265	12
17	3.30103548792	12	0.06390039525	12	0.06500492987	12
18	3.48102435176	12	0.03106709099	12	0.01104173860	12
19	3.58400324349	12	0.02821151210	12	0.03601895643	12
20	3.69401184814	12	0.03632795345	12	0.04102548756	12
21	3.80304301929	12	0.02390412693	12	0.03100438719	12
22	3.94402479731	12	0.04153288222	12	0.06803457962	12
23	3.96501243276	12	0.06237782909	12	0.01301387365	12
24	4.27100347747	12	0.05493777424	12	0.01602437598	12
25	4.68000000000	12	0.13611453358	12	0.11304283387	12

Persistent, 12-digit accuracy for the numerical values for all the 25 complex frequencies and amplitudes reconstructed by the $\text{FPT}^{(-)}$ at $N/4 = 256$ and $N_P = 1024 = N$ is shown. Constancy of all the spectral parameters is steadily maintained beyond the partial signal length $N_P = 220$ where the first machine accurate convergence occurs.

shown). Moreover, the FFT yields no quantification on its own. Attempts to handle this most severe drawback of using the FFT for MRS are usually based on fitting in postprocessing via some free-parameter adjustments that are, however, inherently nonunique. This nonuniqueness of fitting in MRS [69–71] implies that many subjectively chosen numbers of resonances can equally well fit a given peak in the total shape spectrum. Hence, any estimate of the true number of resonances by fitting the envelope spectra in MRS is unreliable and, as such, of limited use in diagnostics.

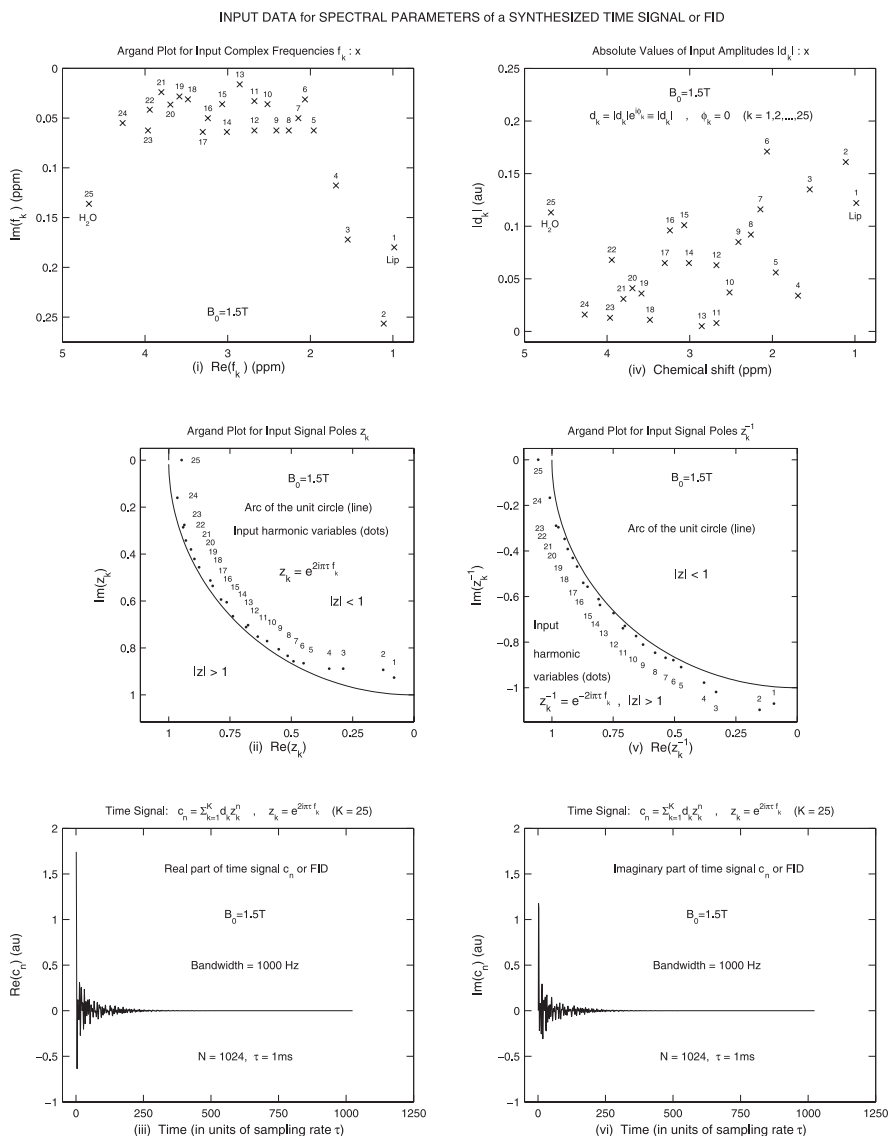


Figure 3.1 Argand plot for input complex frequencies f_k and a graphical display of absolute values of amplitudes $d_k = |d_k|$: panels (i) and (iv). Argand plots for input signal poles or harmonic variables z_k and their inverses z_k^{-1} : panels (ii) and (v). Input time signal or FID as a sum of 25 damped complex exponentials with constant amplitudes: panels (iii) and (vi).

CONVERGED RECONSTRUCTED DATA for SPECTRAL PARAMETERS in $FPT^{(+)}$ and $FPT^{(-)}$; SIGNAL LENGTH: $N_p = 256$

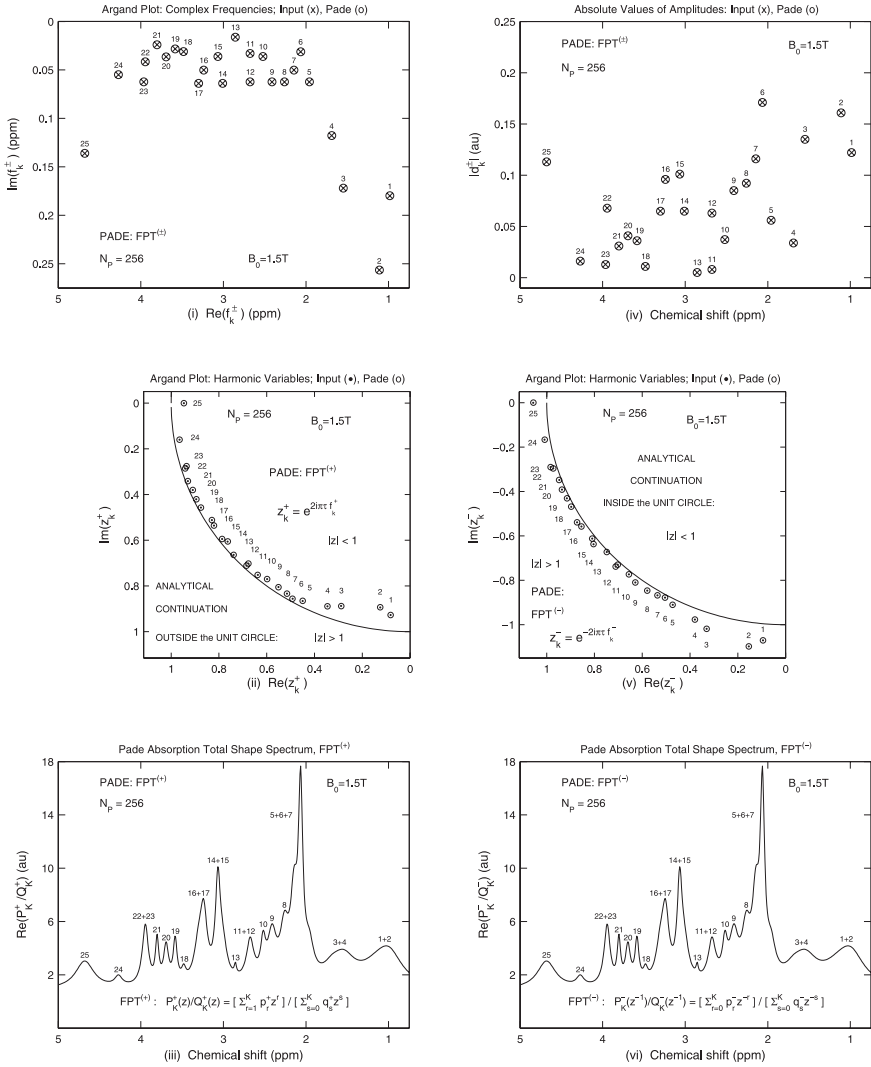


Figure 3.2 Exact reconstructions in the $FPT^{(\pm)}$ using only a quarter of the full signal length $N_p = N/4 = 256$. Complex fundamental frequencies $f_k^{\pm}$ and amplitudes $d_k^{\pm} = |d_k^{\pm}|$: panels (i) and (iv). Signal poles or harmonic variables $z_k^{\pm}$: panels (ii) and (v). Padé spectra in the $FPT^{(+)}$ and $FPT^{(-)}$ as the unique polynomial quotients with the initial convergence regions inside and outside the unit circle, respectively: panels (iii) and (vi).

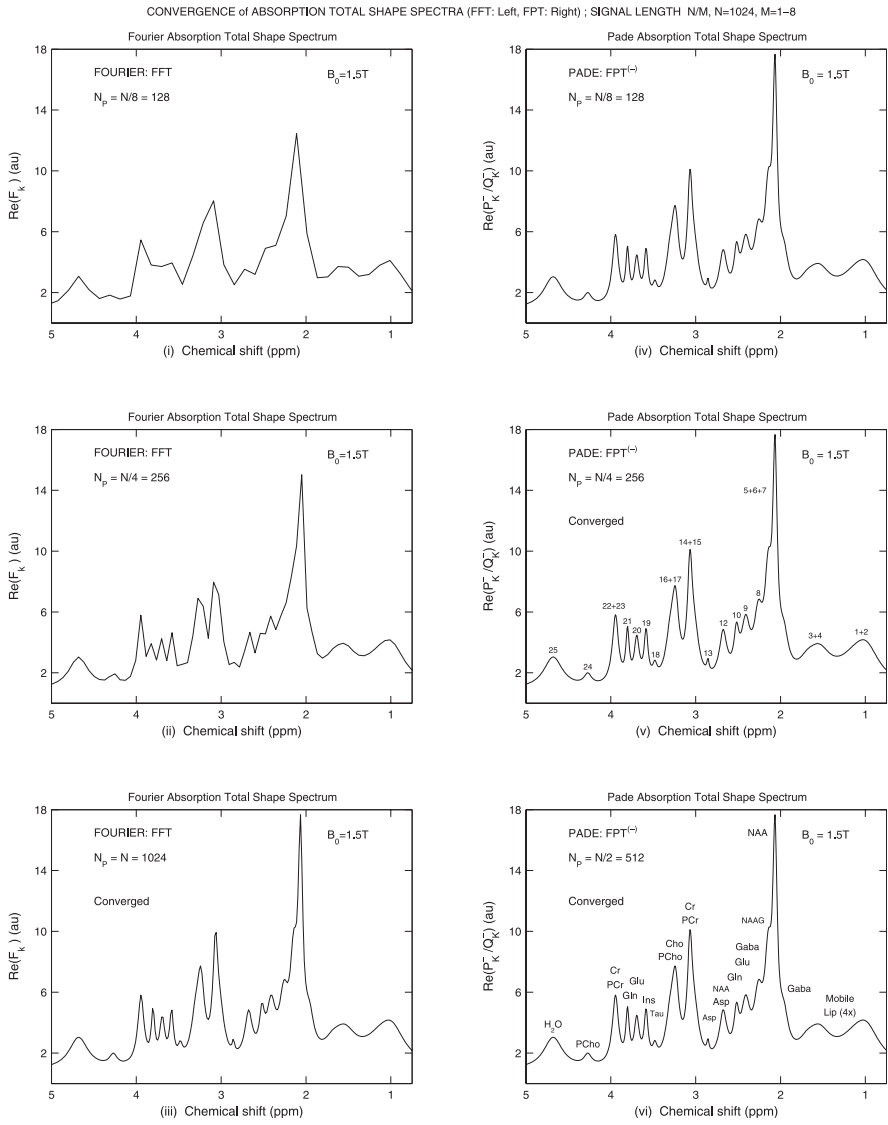


Figure 3.3 Comparison of convergence rates of absorption total shape spectra in the FFT (left) and the $\text{FPT}^{(-)}$ (right) as a function of the signal length. Acronyms associated with resonances are the standard abbreviations for metabolite molecules in the healthy brain tissue.

Underestimating or overestimating the true number of resonances by underfitting (undermodeling) or overfitting (overmodeling) leads, respectively, to missing some genuine or introducing arbitrarily some nonexistent, that is, extraneous metabolites. Both these possible outcomes of fitting techniques in MRS are anathema to diagnostics. In sharp contrast to these unavoidable inconsistencies of fitting, the FPT gives the unique reconstruction of the true number of resonances with no adjustable or initializing parameters at all. This is clearly seen in [Figures 3.4 and 3.5](#) where both variants, the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$, converge to the same result independently of each other as a function of the partial signal length, N_P . As opposed to the standard FFT, the signal length used by the FPT is not limited only to composite numbers of the form 2^m , where m is a non-negative integer. Rather, the full and/or partial signal length can be an arbitrary positive integer, for example, $N_P = 180, 220, 260$, as used in the present computations within the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$.

[Figure 3.6](#) illustrates the comparative convergence of the component and total shape spectra. The component shape spectra are generated from the reconstructed fundamental frequencies and the corresponding amplitudes $\{\omega_k^\pm, d_k^\pm\}$ in the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$. The total shape spectrum is simply the sum of all the component shape spectra for every retrieved physical resonance. It is seen here that the component shape spectra have converged at $N_P = 220$ in panel (v) of [Figure 3.6](#), as expected on the basis of the achieved stability of the spectral parameters at this number of the signal points ([Figures 3.4 and 3.5](#)). Of course, the same convergence also occurs for the total shape spectrum at $N_P = 220$ in panel (ii) of [Figure 3.6](#).

The most intriguing fact is the situation that occurs prior to convergence of the component shape spectra. In this case, it is seen in panel (iv) of [Figure 3.6](#) for $N_P = 180$ that peak 11 is unresolved, and that peak 12 is overestimated. Yet, the corresponding total shape spectrum at the same partial signal length, $N_P = 180$, has fully converged in panel (i) of [Figure 3.6](#). Here, an apparent indication of convergence of the envelope spectrum at $N_P = 180$ is the fact that practically no difference exists between any two spectra on the right column of [Figure 3.6](#) at $N_P = 180, 220, 260$. This is so in particular for $N_P = 180$ because the area of the peak 12 is overestimated precisely by the amount of the corresponding area of the unresolved peak 11 in panels (i) and (iv) of [Figure 3.6](#).

[Figure 3.7](#) displays the absorption component as well as total shape spectra in the $\text{FPT}^{(-)}$ (left) and the corresponding residual absorption total shape spectra (right). These latter residual spectra are computed via $\text{Re}(P_{\bar{k}}/Q_{\bar{k}})[N] - \text{Re}(P_{\bar{k}}/Q_{\bar{k}})[N_P]$, where $N_P = 180, 220, 260$. It can be seen that all the shown residual or error spectra in the $\text{FPT}^{(-)}$ are practically equal to zero throughout the considered frequency range. This proves full convergence of all the total shape spectra even at $N_P = 180$ where the peak $k = 11$ is unresolved, as seen earlier in panel (i) of [Table 3.2](#) and in panel (iv) of [Figure 3.6](#).

Let us now briefly summarize [Figures 3.6 and 3.7](#). It is seen that the two nearly identical total shape spectra at $N_P = 180$ and $N_P = 220$ in panels (ii) and

Convergence of Spectral Parameters in $FPT^{(+)}$ (Left: Frequencies, Right: Amplitudes); Signal Lengths: $N_p = 180, 220, 260$

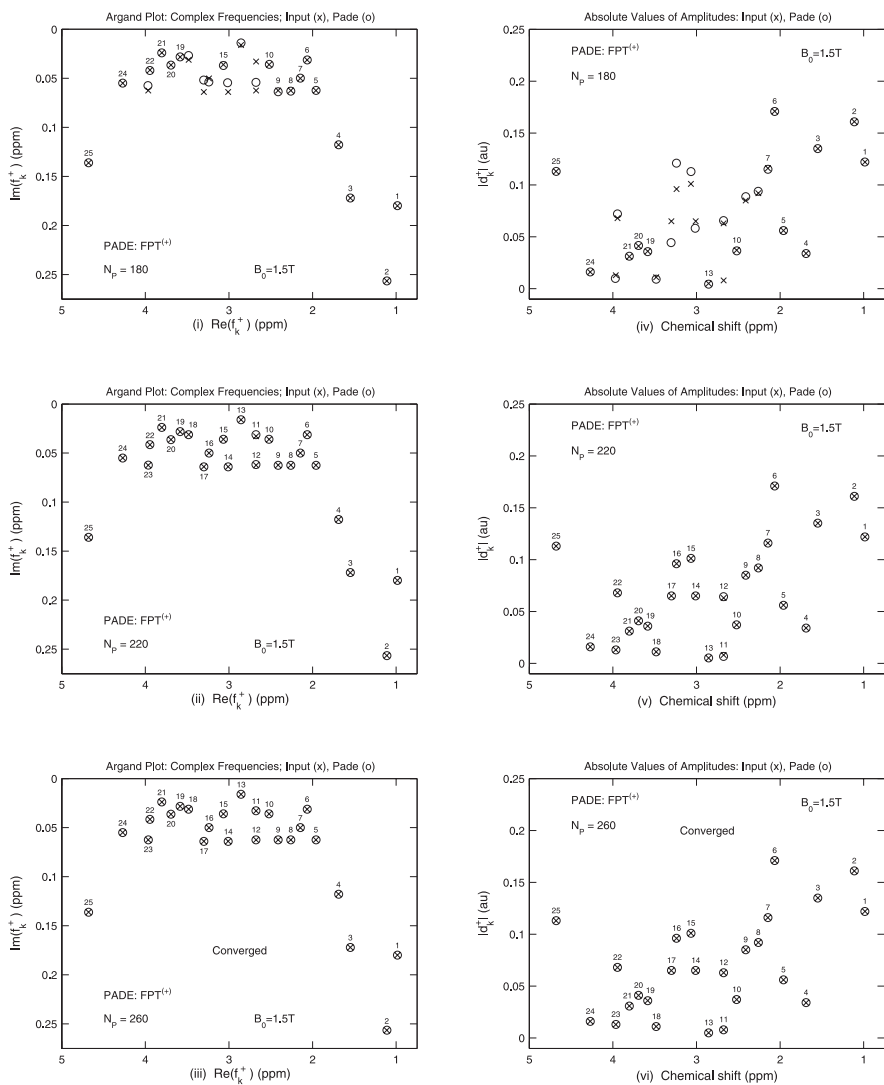


Figure 3.4 Convergence of the reconstructed fundamental frequencies f_k^+ (left) and absolute values of amplitudes $|d_k^+|$ (right) in the $FPT^{(+)}$ at three partial signal lengths $N_p = 180, 220$, and 260 .

Convergence of Spectral Parameters in $\text{FPT}^{(-)}$ (Left: Frequencies, Right: |Amplitudes|); Signal Lengths: $N_p = 180, 220, 260$

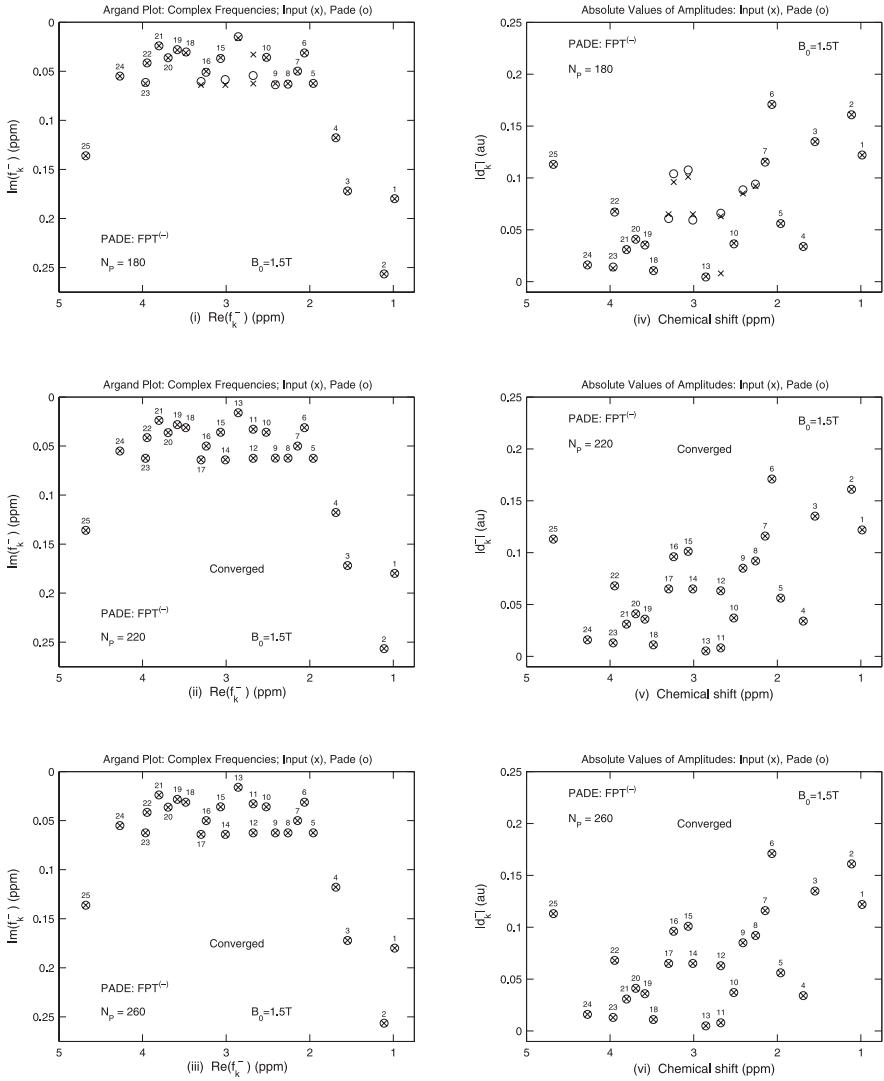


Figure 3.5 Convergence of the reconstructed fundamental frequencies f_k^- (left) and absolute values of amplitudes $|d_k^-|$ (right) in the $\text{FPT}^{(-)}$ at three partial signal lengths $N_p = 180, 220, 260$.

ABSORPTION SHAPE SPECTRA (TOTAL: Left & COMPONENT: Right) in $\text{FPT}^{(-)}$; SIGNAL LENGTHS: $N_p = 180, 220, 260$

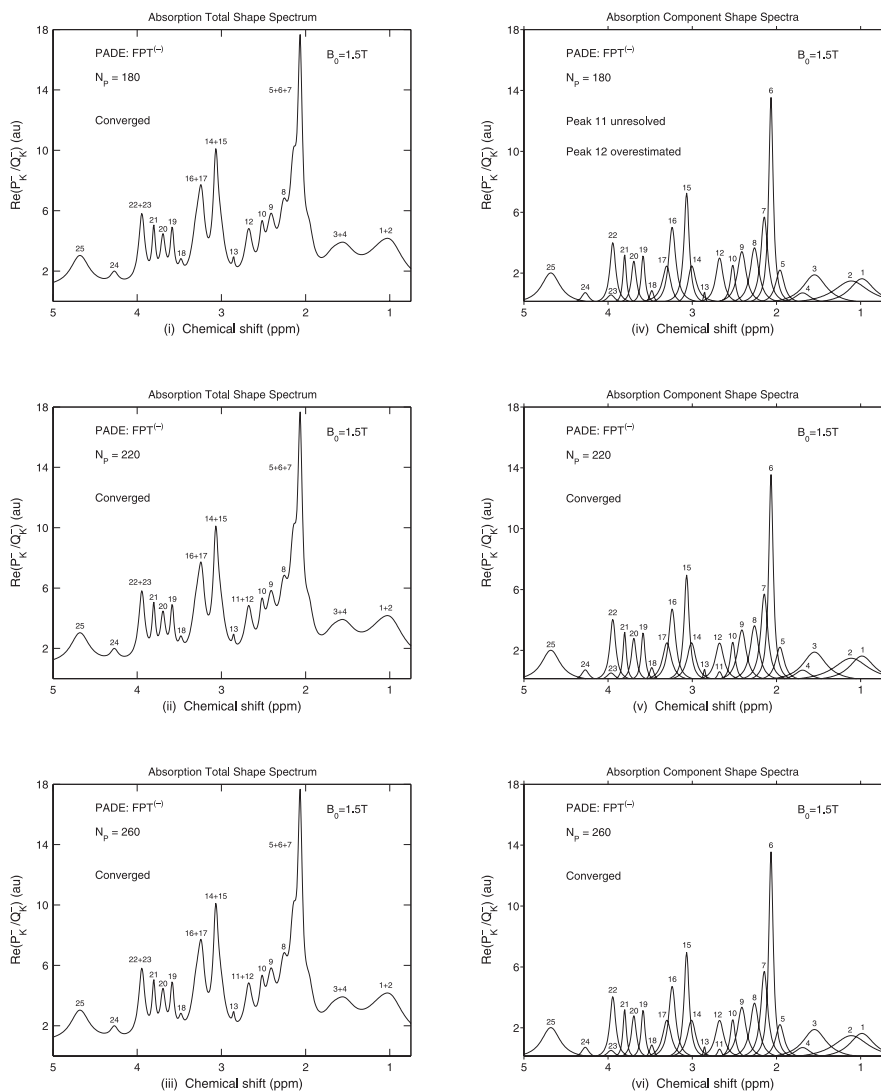


Figure 3.6 Component shape spectra in the $\text{FPT}^{(-)}$ for each resonance (right) and their sums as the total shape spectra (left) at three partial signal lengths $N_p = 180, 220$, and 260 . Notice that the total shape spectrum at $N_p = 180$ in panel (iv) converged despite the unresolved peak 11 and the related overestimate of peak 12.

Error Analysis in $FPT^{(-)}$ via Shape Spectra (Component and Total: Left, Residual: Right) ; Signal Lengths: $N_p = 180, 220, 260$

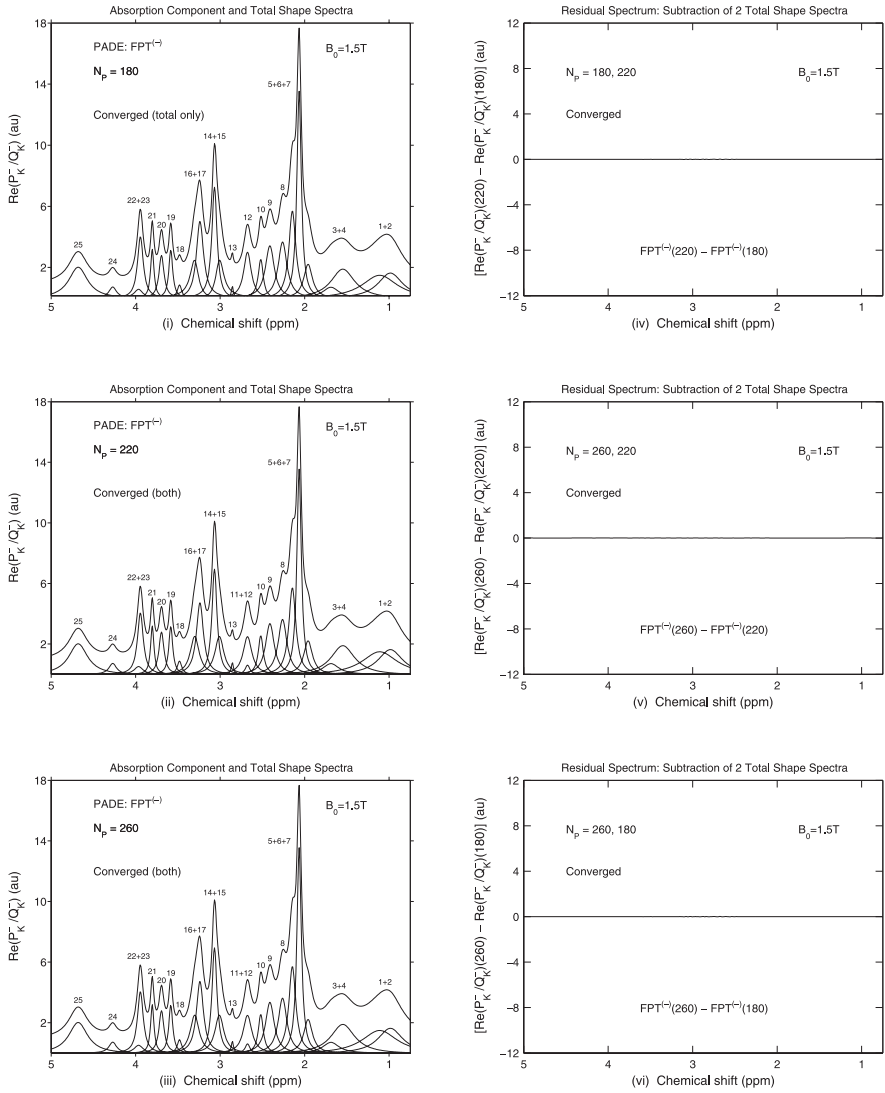


Figure 3.7 Absorption component and total shape spectra in the $FPT^{(-)}$ at three partial signal lengths $N_p = 180, 220$ and 260 (left) and the corresponding residual or error spectra (right) for absorption total shape spectra at the same partial signal lengths.

(iii) in Figure 3.6 contain 24 and 25 resonances, respectively. This discrepancy in the number of the reconstructed resonances is not detected at all by the residual or error spectra shown on the right column in Figure 3.7. Therefore, it is not reliable to use the converged total shape spectrum as the only criterion for the validity of the estimated number of the reconstructed resonances. Precisely, this latter criterion is most frequently used in MRS through fitting techniques [69–71] that rely heavily upon the residual spectrum defined as difference between the spectrum from the FFT and a modeled spectrum.

In contradistinction to fittings from MRS, the FPT does not assess at all the adequacy of the performed quantification upon the appearance of the total shape spectra. Quite the contrary, such spectra are drawn merely for convenience and visual comparison with the FFT, but this is totally irrelevant for solving the quantification problem as the main task in MRS. Of primary importance for quantification is to monitor the convergence pattern of the reconstructed fundamental frequencies and amplitudes as a function of the partial signal length N_P , as done in Figures 3.4 and 3.5. Only when the values of all the spectral parameters stabilize fully can the quantification be considered as successfully completed. This is the case with $N_P \geq 220$, but not with $N_P = 180$, as seen in Figures 3.4 and 3.5.

All told, even within the FPT itself, the residual or error spectra can, at best, represent only a necessary, but not a sufficient, condition for validity of the reconstructed frequencies and amplitudes from which these spectra are generated. The only way to gain confidence in the obtained results is to search for the full stabilization of all the spectral parameters as a function of the partial length of the investigated time signal. Moreover, such a stabilization is done in the FPT independently in both variants, the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$, as illustrated in the present study. This is an invaluable cross-validation of the performed quantification, such that only those fundamental frequencies and amplitudes that are reconstructed by both $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ via convergence and stabilization are retained in the final list of the obtained exact solutions of the quantification problems in MRS.

Figures 3.8–3.15 illustrate the overall benefit from the concept of the Froissart doublets within the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$ applied to the synthesized noise-free and noise-corrupted time signals whose input data for all the spectral parameters $\{f_k, d_k\}$ are set to be exact to within three decimal places. We take such a noiseless FID from Ref. [87]³ and create the corresponding noisy FID by adding random Gauss-distributed zero-mean noise (orthogonal in its real and imaginary parts) with the standard deviation $\sigma = 0.00289$ rms, where rms denotes the root mean square of the noiseless

³ Alternatively, the same noise-free FID, as in Ref. [87], can also be generated using the spectral parameters from Table 3.1 rounded to three decimals, and subsequently supplemented with the redefinition, $\text{Re}(f_{11}) \equiv 2.675$ ppm to avoid dealing with the ensuing exact degeneracy of the 11th and 12th peak.

EXACT RECONSTRUCTION of the TRUE NUMBER of GENUINE HARMONICS by FPT⁽⁺⁾ : NOISELESS FID

$$\text{POLE – ZERO CANONICAL FORM of FPT}^{(+)} : P_K^+(z)/Q_K^+(z) = (p_K^+/q_K^+) \prod_{k=1}^K (z - z_{k,P}^+)/(z - z_{k,Q}^+)$$

zFPT⁽⁺⁾ and pFPT⁽⁺⁾ ; TWO COMPLEMENTARY SPECTRAL REPRESENTATIONS of FPT⁽⁺⁾ :

zFPT⁽⁺⁾ (•) : ZEROS of FPT⁽⁺⁾ ; ARGAND PLOT for ALL ZEROS $z_{k,P}^+$ in FPT⁽⁺⁾ from $P_K^+(z) = 0$

pFPT⁽⁺⁾ (o) : POLES of FPT⁽⁺⁾ ; ARGAND PLOT for ALL POLES $z_{k,Q}^+$ in FPT⁽⁺⁾ from $Q_K^+(z) = 0$

FROISSART DOUBLETS (POLE – ZERO CANCELLATIONS) : $z_{k,P}^+ = z_{k,Q}^+$ (coincidence of '•' and 'o')

GENUINE HARMONICS in the FIRST QUADRANT, INSIDE the UNIT CIRCLE C ($|z| < 1$), RANGING from # 1 (Lipid) to # 25 (Water)

FROISSART DOUBLETS OUTSIDE C : GENUINE and SPURIOUS HARMONICS SEPARATED in TWO DISJOINT REGIONS $|z| < 1$ and $|z| > 1$

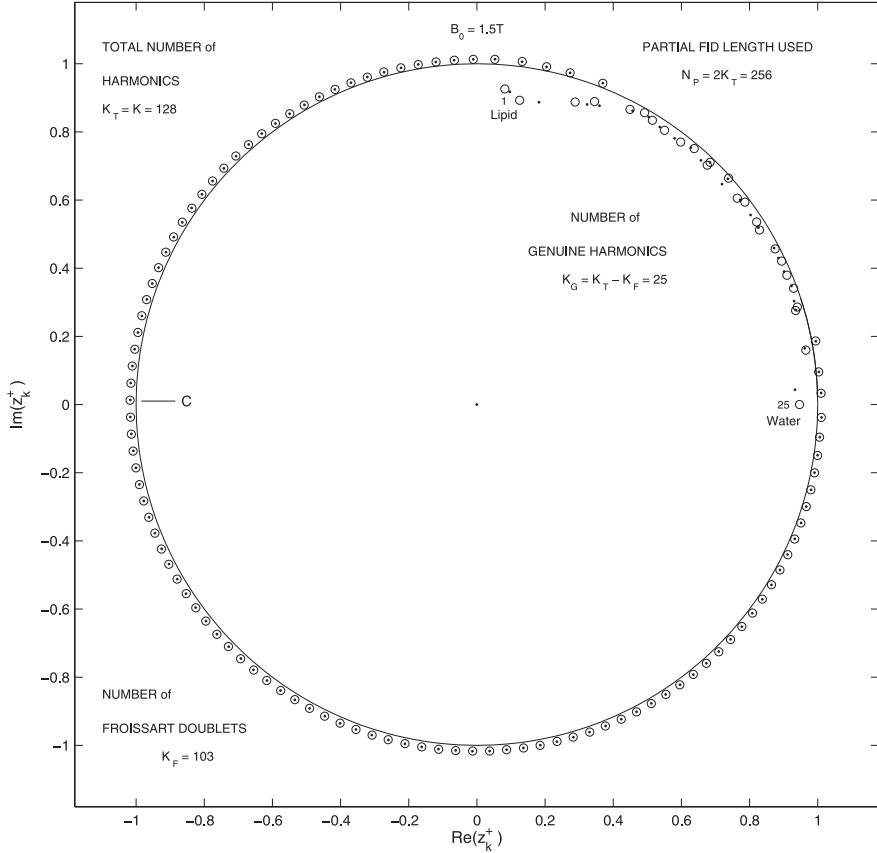


Figure 3.8 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine harmonics from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the FPT⁽⁺⁾ for the noise-free time signal. The FPT⁽⁺⁾ separates the genuine from the spurious harmonics in the two nonoverlapping regions, inside and outside the unit circle C, respectively.

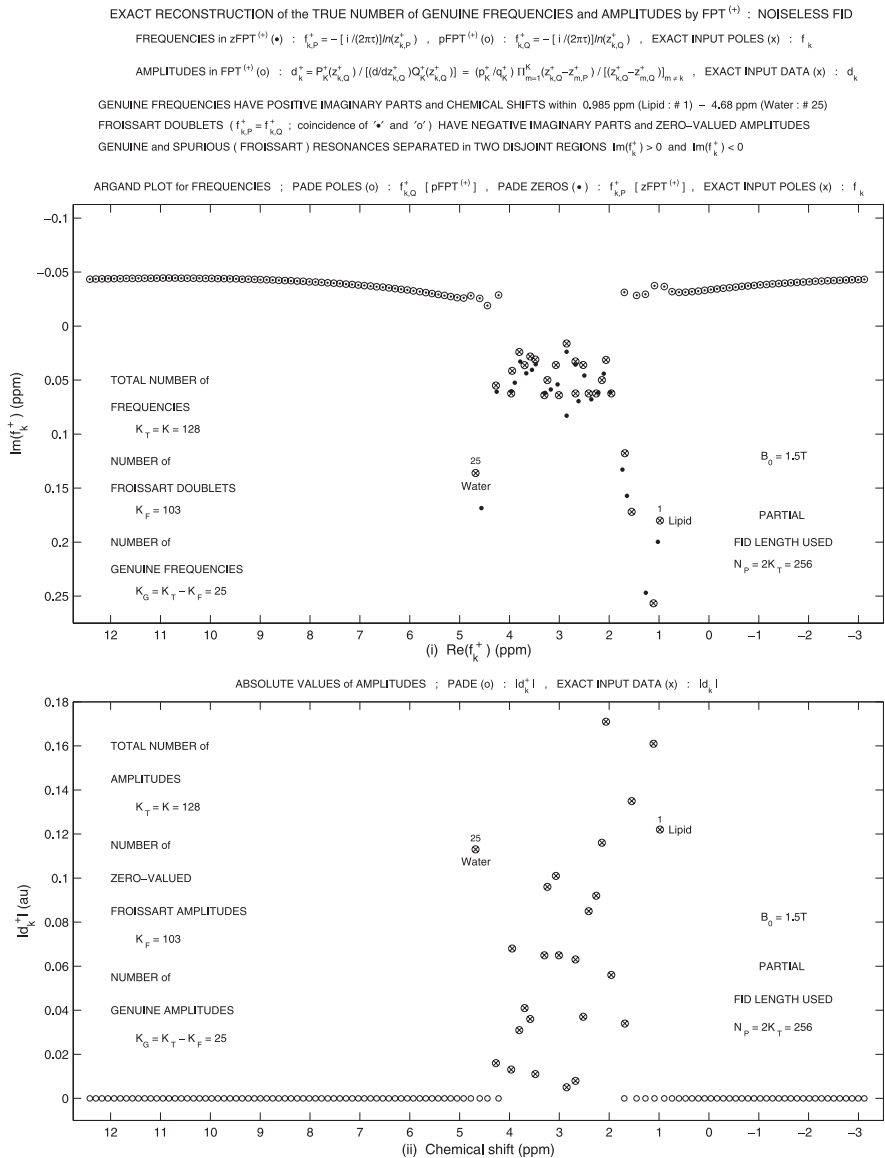


Figure 3.9 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine frequencies and amplitudes from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the FPT⁽⁺⁾ for the noise-free time signal. The FPT⁽⁺⁾ separates the genuine from the spurious frequencies in the two nonoverlapping regions, $\text{Im}(f_k^+) > 0$ and $\text{Im}(f_k^+) < 0$, respectively. All the spurious (Froissart) amplitudes are uniquely identified by their zero values.

EXACT RECONSTRUCTION of the TRUE NUMBER of GENUINE HARMONICS by FPT⁽⁺⁾ : NOISY FID

$$\text{POLE – ZERO CANONICAL FORM of FPT}^{(+)} : P_K^+(z)/Q_K^+(z) = (p_K^+/q_K^+) \prod_{k=1}^K (z - z_{k,P}^+)/(z - z_{k,Q}^+)$$

zFPT⁽⁺⁾ and pFPT⁽⁺⁾ : TWO COMPLEMENTARY SPECTRAL REPRESENTATIONS of FPT⁽⁺⁾ :

zFPT⁽⁺⁾ (•) : ZEROS of FPT⁽⁺⁾ ; ARGAND PLOT for ALL ZEROS $z_{k,P}^+$ in FPT⁽⁺⁾ from $P_K^+(z) = 0$

pFPT⁽⁺⁾ (o) : POLES of FPT⁽⁺⁾ ; ARGAND PLOT for ALL POLES $z_{k,Q}^+$ in FPT⁽⁺⁾ from $Q_K^+(z) = 0$

FROISSART DOUBLETS (POLE – ZERO CANCELLATIONS) : $z_{k,P}^+ = z_{k,Q}^+$ (coincidence of '•' and 'o')

GENUINE HARMONICS in the FIRST QUADRANT, INSIDE the UNIT CIRCLE C ($|z| < 1$), RANGING from # 1 (Lipid) to # 25 (Water)

FROISSART DOUBLETS OUTSIDE C : GENUINE and SPURIOUS HARMONICS SEPARATED in TWO DISJOINT REGIONS $|z| < 1$ & $|z| > 1$

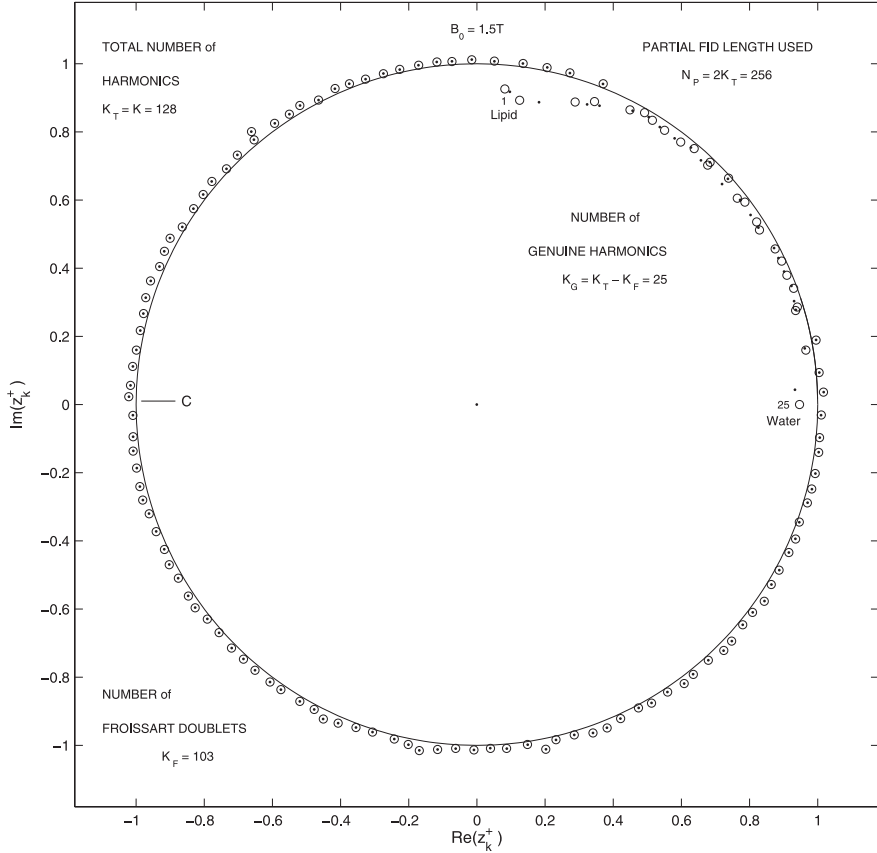


Figure 3.10 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine harmonics from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the FPT⁽⁺⁾ for the noise-corrupted time signal. The FPT⁽⁺⁾ separates the genuine from the spurious harmonics in the two nonoverlapping regions, inside and outside the unit circle C, respectively.

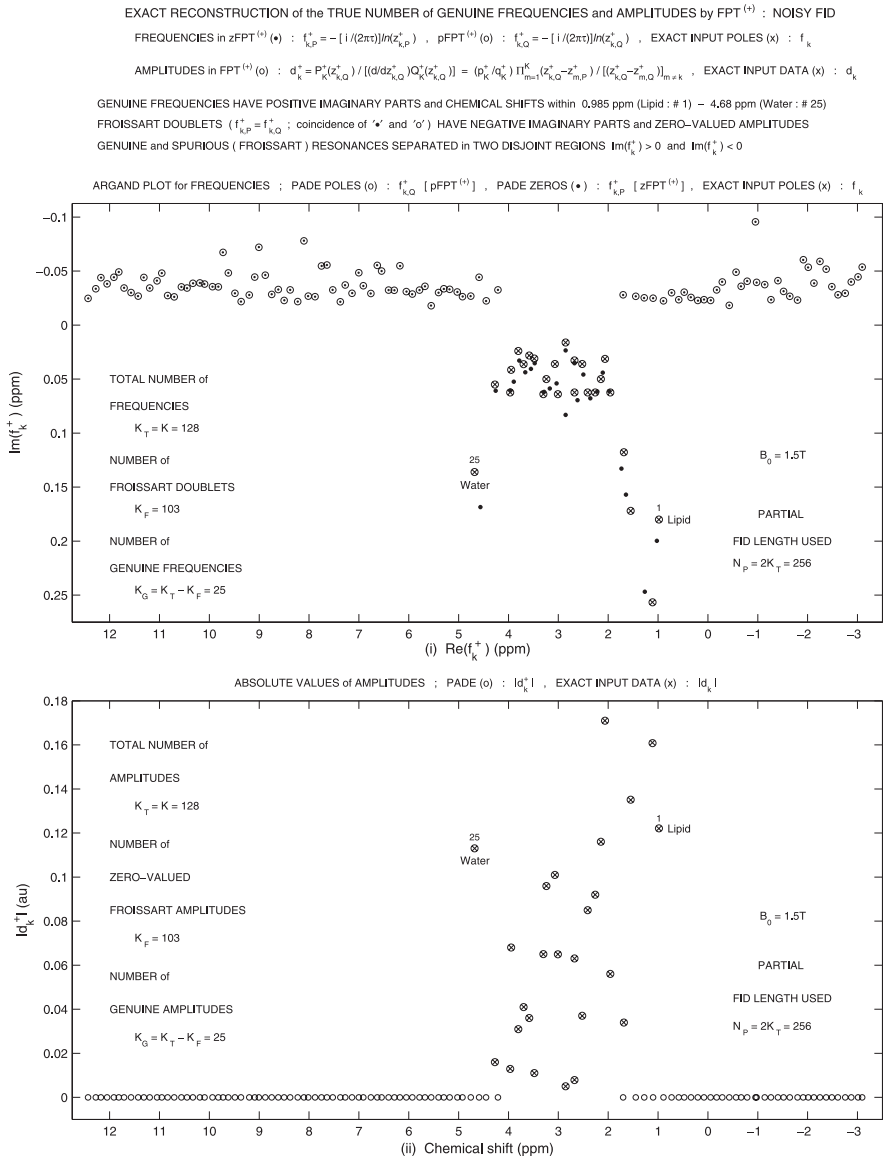


Figure 3.11 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine frequencies and amplitudes from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the FPT⁽⁺⁾ for the noise-corrupted time signal. The FPT⁽⁺⁾ separates the genuine from the spurious frequencies in the two nonoverlapping regions, $\text{Im}(f_k^+) > 0$ and $\text{Im}(f_k^+) < 0$, respectively. All the spurious (Froissart) amplitudes are uniquely identified by their zero values.

EXACT RECONSTRUCTION of the TRUE NUMBER of GENUINE HARMONICS by $FPT^{(-)}$: NOISELESS FID

$$\text{POLE – ZERO CANONICAL FORM of } FPT^{(-)} : P_K^-(z^{-1})/Q_K^-(z^{-1}) = (p_K^-(q_K^-) \prod_{k=1}^K (z^{-1} - z_{k,P}^-)/(z^{-1} - z_{k,Q}^-))$$

$zFPT^{(-)}$ and $pFPT^{(-)}$; TWO COMPLEMENTARY SPECTRAL REPRESENTATIONS of $FPT^{(-)}$:

$zFPT^{(-)}$ (•) : ZEROS of $FPT^{(-)}$; ARGAND PLOT for ALL ZEROS $z_{k,P}^-$ in $FPT^{(-)}$ from $P_K^-(z^{-1}) = 0$

$pFPT^{(-)}$ (o) : POLES of $FPT^{(-)}$; ARGAND PLOT for ALL POLES $z_{k,Q}^-$ in $FPT^{(-)}$ from $Q_K^-(z^{-1}) = 0$

FROISSART DOUBLETS (POLE – ZERO CANCELLATIONS) : $z_{k,P}^- = z_{k,Q}^-$ (coincidence of '•' and 'o')

GENUINE HARMONICS in the FOURTH QUADRANT, OUTSIDE the UNIT CIRCLE C ($|z| > 1$), RANGING from # 1 (Lipid) to # 25 (Water)

FROISSART DOUBLETS OUTSIDE the UNIT CIRCLE C : GENUINE and SPURIOUS HARMONICS MIXED in the SAME REGION $|z| > 1$

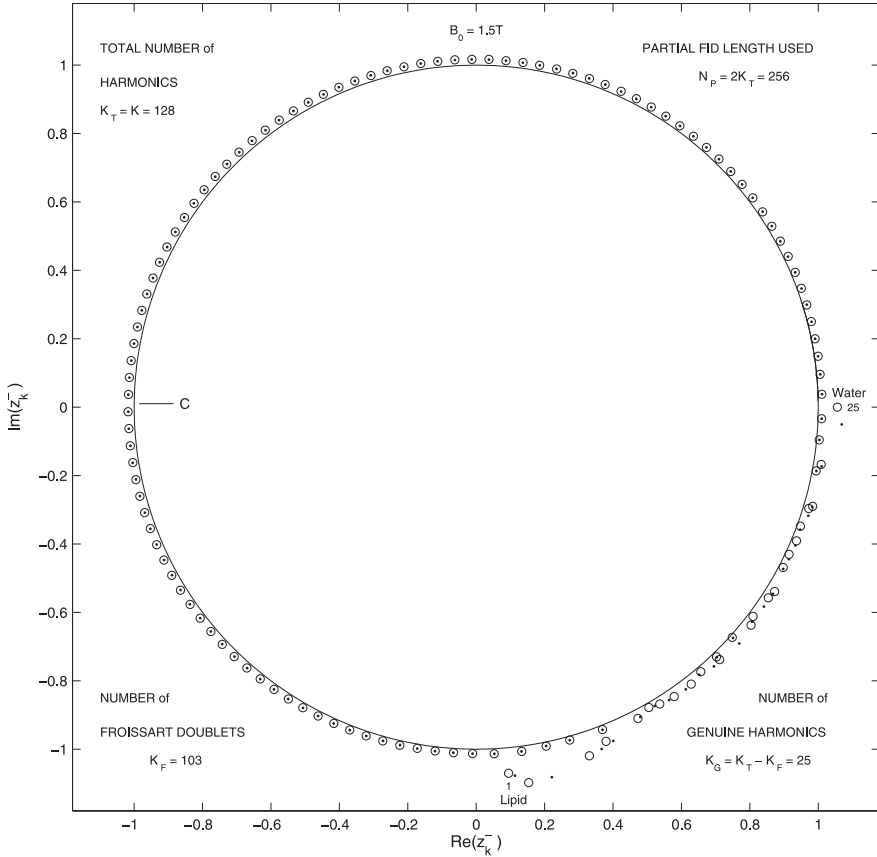


Figure 3.12 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine harmonics from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the $FPT^{(-)}$ for the noise-free time signal. The $FPT^{(-)}$ mixes the genuine and the spurious harmonics in the same region, outside the unit circle C .

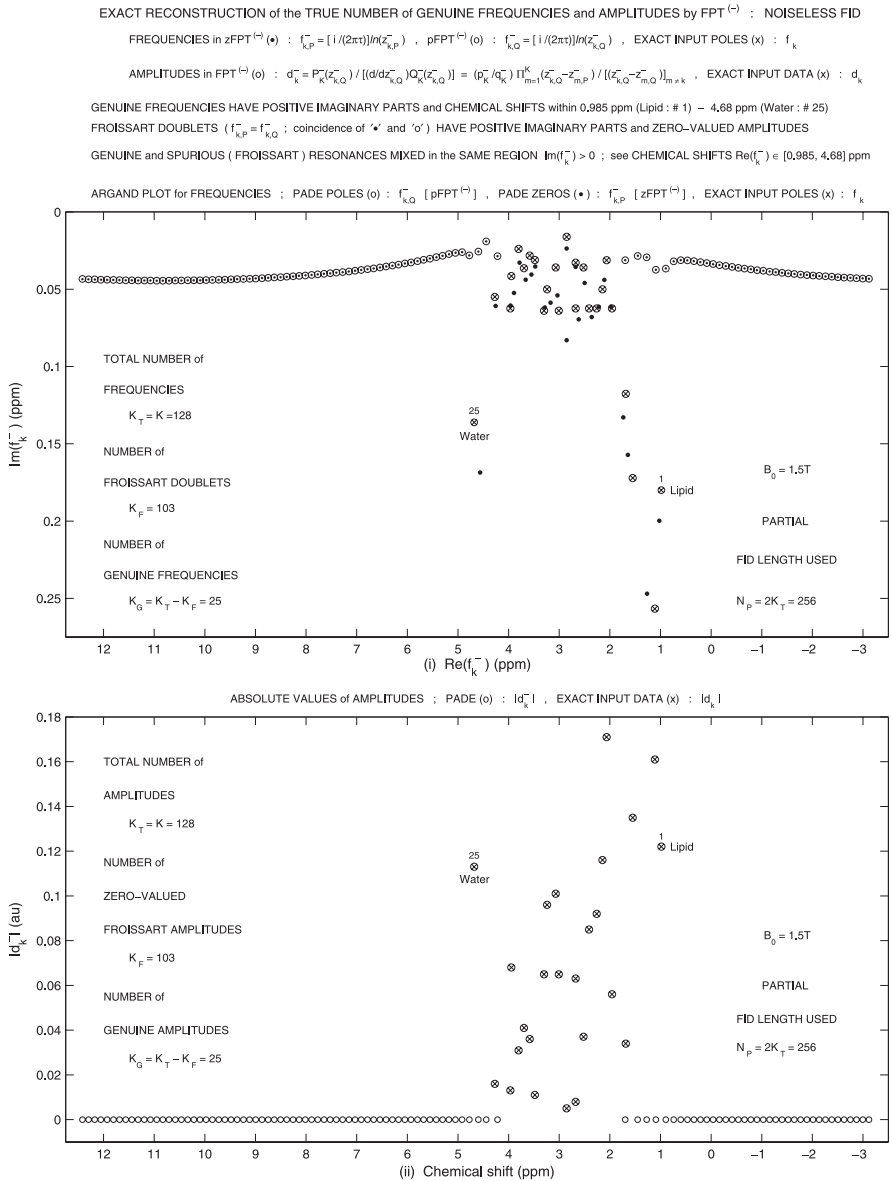


Figure 3.13 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine frequencies and amplitudes from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the FPT⁽⁻⁾ for the noise-free time signal. The FPT⁽⁻⁾ mixes the genuine and the spurious frequencies in the same region, $\text{Im}(f_k^-) > 0$. All the spurious (Froissart) amplitudes are uniquely identified by their zero values.

EXACT RECONSTRUCTION of the TRUE NUMBER of GENUINE HARMONICS by $FPT^{(-)}$: NOISY FID

$$\text{POLE – ZERO CANONICAL FORM of } FPT^{(-)} : P_K^-(z^{-1})/Q_K^-(z^{-1}) = (p_K^-(q_K^-) \prod_{k=1}^K (z^{-1} - z_{k,P}^-)/(z^{-1} - z_{k,Q}^-))$$

$zFPT^{(-)}$ and $pFPT^{(-)}$; TWO COMPLEMENTARY SPECTRAL REPRESENTATIONS of $FPT^{(-)}$:

$zFPT^{(-)}$ (•) : ZEROS of $FPT^{(-)}$; ARGAND PLOT for ALL ZEROS $z_{k,P}^-$ in $FPT^{(-)}$ from $P_K^-(z^{-1}) = 0$

$pFPT^{(-)}$ (o) : POLES of $FPT^{(-)}$; ARGAND PLOT for ALL POLES $z_{k,Q}^-$ in $FPT^{(-)}$ from $Q_K^-(z^{-1}) = 0$

FROISSART DOUBLETS (POLE – ZERO CANCELLATIONS) : $z_{k,P}^- = z_{k,Q}^-$ (coincidence of '•' and 'o')

GENUINE HARMONICS in the FOURTH QUADRANT, OUTSIDE the UNIT CIRCLE C ($|z| > 1$), RANGING from # 1 (Lipid) to # 25 (Water)

FROISSART DOUBLETS OUTSIDE the UNIT CIRCLE C : GENUINE and SPURIOUS HARMONICS MIXED in the SAME REGION $|z| > 1$

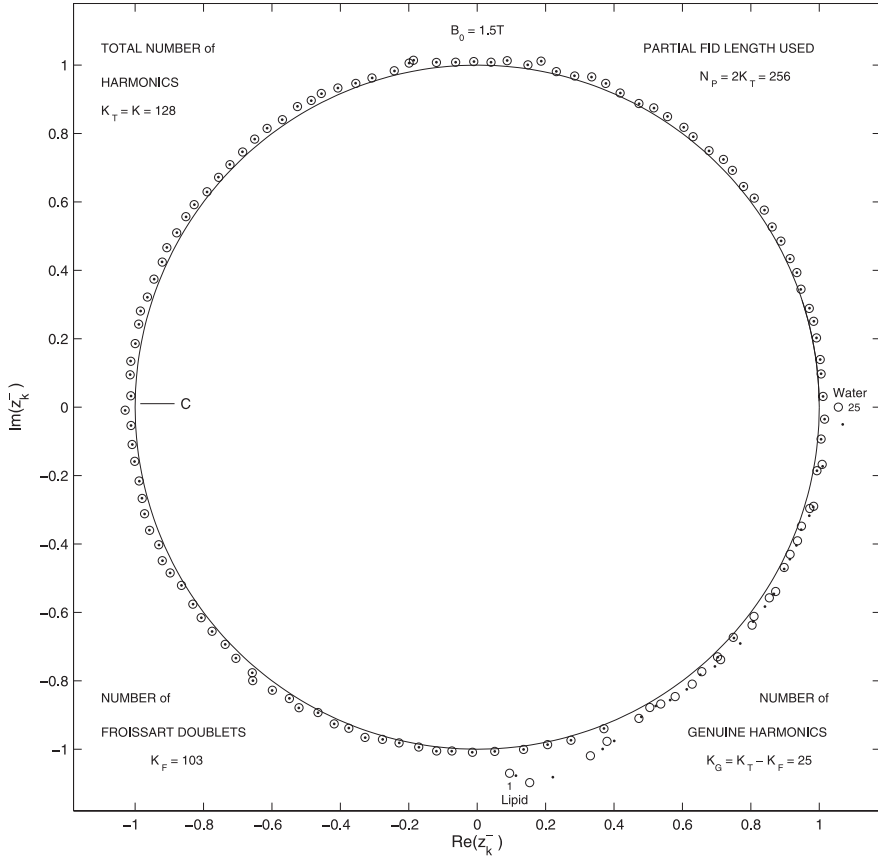


Figure 3.14 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine harmonics from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the $FPT^{(-)}$ for the noise-corrupted time signal. The $FPT^{(-)}$ mixes the genuine and the spurious harmonics in the same region, outside the unit circle C.

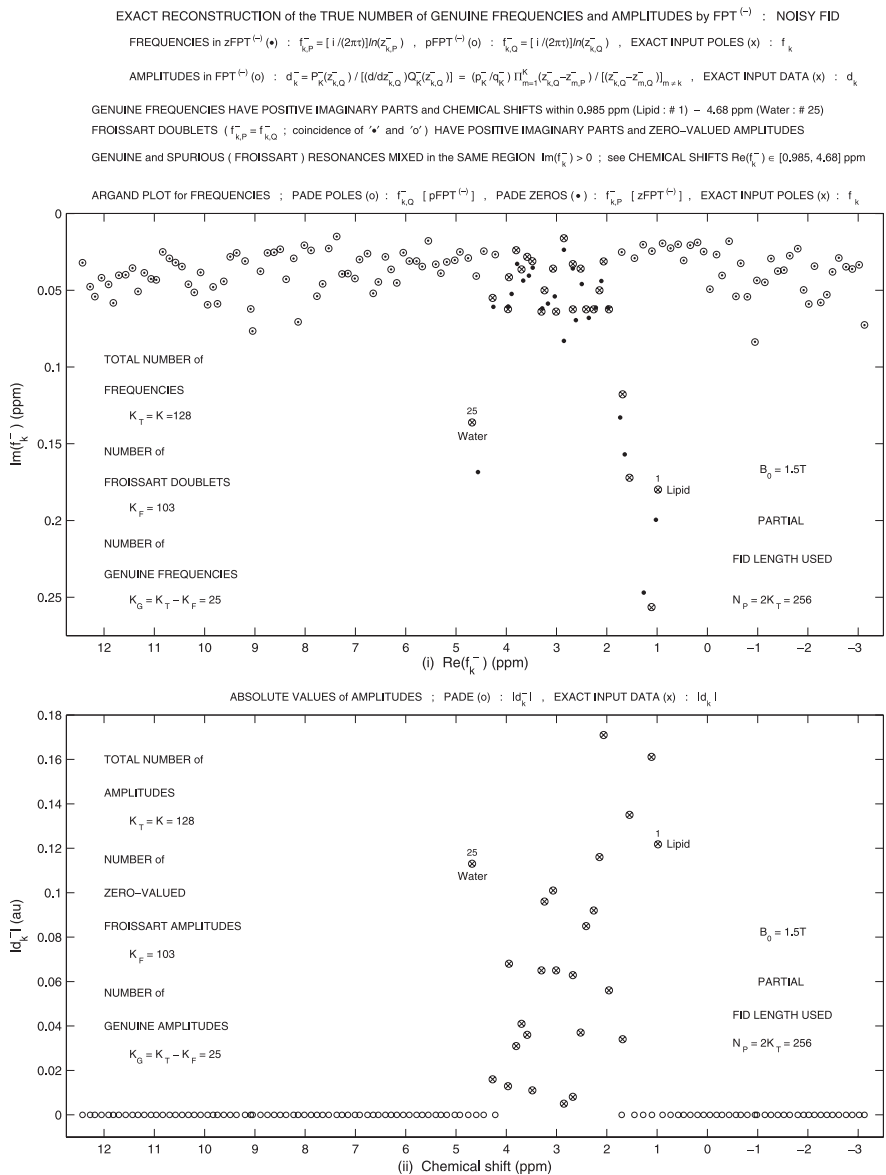


Figure 3.15 Use of the Froissart doublets to extract unequivocally the exact number K_G of the genuine harmonics from the total number $K_T \equiv K$ of the spectral parameters reconstructed by the FPT⁽⁻⁾ for the noise-corrupted time signal. The FPT⁽⁻⁾ mixes the genuine and the spurious frequencies in the same region, $\text{Im}(f_k^-) > 0$. All the spurious (Froissart) amplitudes are uniquely identified by their zero values.

FID. The chosen number 0.00289 represents about 1.5% of the height of the weakest resonance in the spectrum ($N_k = 13$). At present, this noise level is deemed sufficient to provide a clear illustration of the principles of the Froissart doublets. Higher noise levels up to 100% of the height of the 13th peak have also been employed in the present study, and these results will be reported separately.

Figures 3.8–3.11 and 3.12–3.15 display the results from the $\text{FPT}^{(+)}$ and the $\text{FPT}^{(-)}$, respectively, for noiseless (Figures 3.8, 3.9, 3.12, and 3.13) and noisy (Figures 3.10, 3.11, 3.14, and 3.15) FIDs. In particular, Figures 3.8, 3.10, 3.12, and 3.14 give the Argand plots of the harmonic variables in the $\text{FPT}^{(\pm)}$ as the distributions of the reconstructed poles $z_{k,Q}^{\pm}$ and zeros $z_{k,P}^{\pm}$ with respect to the unit circle in the Euler polar coordinates. Likewise, Figures 3.9, 3.11, 3.13, and 3.15 in panel (i) show the Argand plots of linear frequencies of the reconstructed poles $f_{k,Q}^{\pm}$ and zeros $f_{k,P}^{\pm}$ in the Descartes rectangular coordinates. Also shown in Figures 3.9, 3.11, 3.13, and 3.15 in panel (ii) are the absolute values of the reconstructed amplitudes, $|d_k^{\pm}|$. The input data f_k and $|d_k|$ are also displayed on Figures 3.9, 3.11, 3.13, and 3.15. Overall, it is seen in Figures 3.8–3.15 that the Froissart doublets are distributed along circles and lines in the polar and rectangular coordinates, respectively. These distributions are configured in a very regular and even fashion for the noise-free FID (Figures 3.8, 3.9, 3.12, and 3.13). For the noise-corrupted FID, the distributions of the Froissart doublets are disturbed, as expected, since these are unstable spectral structures. However, for both noiseless and noisy FIDs, pole–zero cancellations occur systematically in the same manner, thus permitting a clear distinction between the spurious and genuine resonances. Such an unequivocal distinction between the noise-free and noise-corrupted FIDs allows the exact reconstruction of all the true values for the genuine spectral parameters, including the fundamental frequencies, the corresponding amplitudes, and the original number of the physical resonances. The unique pole–zero cancellations for Froissart doublets seen via the harmonic variables (Figures 3.8, 3.10, 3.12, and 3.14) and frequencies (panel i in Figures 3.9, 3.11, 3.13, and 3.15) are simultaneously accompanied by the corresponding remarkable zero-valued amplitudes (panel (ii) in Figures 3.9, 3.11, 3.13, and 3.15) as yet another illustration of the FPT to distinguish genuine from spurious resonances. The $\text{FPT}^{(-)}$ is seen in Figures 3.12–3.15 to mix the genuine and spurious resonances in the same region $|z| > 1$ and $\text{Im}(f_k^+) > 0$. Nevertheless, the clear pattern of the Froissart doublets for harmonic variables, linear frequencies, and amplitudes still permits the exact solution of the quantification problem by the $\text{FPT}^{(-)}$. On the other hand, the $\text{FPT}^{(+)}$ is observed in Figures 3.8–3.11 to separate sharply the genuine from the spurious resonances in the two disjoint regions inside $|z| < 1$ and outside $|z| > 1$ the unit circle for the harmonic variable, as well as $\text{Im}(f_k^+) > 0$ and $\text{Im}(f_k^+) < 0$ for the

frequencies. Such an unprecedented separation of the physical from the unphysical (noise-like and noisy) informational content of the investigated data by using the $\text{FPT}^{(+)}$ is expected to play a key role in optimally reliable spectral analysis not only for quantifications in MRS, but also in other areas of signal processing across interdisciplinary fields [77].

25. CONCLUSION

This review deals with the theory of quantum-mechanical spectral analysis based upon the Padé approximant (PA), the Lanczos algorithm, as well as on their combination called the Padé-Lanczos approximant (PLA) and the Lanczos continued fractions (LCFs). Their equivalences are established. LCFs belong to the category of contracted continued fractions (CCFs) that contain twice as many expansion terms as the ordinary continued fractions for the same order or rank. Specifically for signal processing, the PA is alternatively called the fast Padé transform (FPT), which has two equivalent forms denoted by $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ with their initial definitions inside and outside the unit circle for complex harmonic variables. By the Cauchy analytical continuation, both versions are defined everywhere in the complex plane. This is reminiscent of the usual outgoing and incoming boundary conditions ingrained in the standard Green function. It is shown that the $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ versions are equivalent to the LCFs of the even and odd order, respectively. Using both variants of the FPT, the results of explicit computations are reported in the finite arithmetics with the goal of reconstructing exactly all the machine accurate input spectral parameters of every resonance from noiseless and noisy generic time signals, or equivalently, autocorrelation functions. When convergence has been reached, the results of the $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ are the same. This is one of the invaluable intrinsic validity checks of the FPT. In the illustrations, it is proven that the FPT is a highly reliable method for quantifying noise-corrupted time signals reminiscent of those measured experimentally by means of MRS in neurodiagnostics, for example.

The stumbling block of spectral analysis is the problem of unambiguous separation of physical from nonphysical information in time signals. We demonstrate that this critical and most difficult problem can be solved by means of the powerful concept of the exact signal-noise separation by using Froissart doublets, or equivalently, pole-zero cancellations. It is shown that this separation is unique to the FPT, because of the polynomial quotient form P_K/Q_K of the frequency-dependent response function, which is the total Green function of the investigated system. The true number K_G of the genuine resonances, as the exact order or rank K_{ex} of the FPT with $K_G = K_{\text{ex}}$, is reconstructed by reaching the constancy of P_K/Q_K when the polynomial degree K is

systematically augmented. By increasing the “running order” K beyond the plateau attained at $K = K_{\text{ex}}$, the same values of P_K/Q_K are obtained via $P_{K_{\text{ex}}+m}/Q_{K_{\text{ex}}+m} = P_{K_{\text{ex}}}/Q_{K_{\text{ex}}}$ ($m = 1, 2, \dots$). It is demonstrated that this could only be possible when, for $K > K_{\text{ex}}$, all the poles and zeros coincide with each other, so that they are canceled from the canonical representation of P_K/Q_K . Further, it is shown that precisely the same saturation $P_{K_{\text{ex}}+m}/Q_{K_{\text{ex}}+m} = P_{K_{\text{ex}}}/Q_{K_{\text{ex}}}$ ($m = 1, 2, \dots$) also occurs in the equivalent Heaviside partial fraction representation of the Padé polynomial quotient by proving that all the associated amplitudes are strictly equal to zero for any $K > K_{\text{ex}}$. Moreover, pole–zero confluences can also occur at any $K \leq K_{\text{ex}}$, but the corresponding amplitudes are invariably found to be equal to zero. As such, this review establishes that all zero-valued amplitudes and the associated pole–zero coincidences represent the unambiguous signatures of the spurious information (noise and noise-like) encountered during spectral analysis. This is the essence of the exact signal–noise separation by pole–zero cancellations in the FPT. The equivalent name, Froissart doublets, is associated with the fact that spurious poles and zeros always appear as a pair (a doublet), as first found empirically by Froissart. This new kind of signal denoising via the Froissart filter is expected to have critical and widespread applications in the field of signal processing, which was awaiting such a method for more than half a century.

We give a number of informative graphical illustrations on machine accurate reconstructions of all the fundamental frequencies and amplitudes, including the unambiguous retrieval of the true number of resonances. Convergence under the imposed most stringent conditions (exact 12-digit output for exact 12-digit input data) is achieved, demonstrating unprecedented robustness of the FPT even against round-off errors. Such an accomplishment is based solely upon the two regular computational routines from MATLAB for solving a system of linear equations and rooting the characteristic equation. Therefore, the robustness of the FPT is primarily due to the rational model for the response function, rather than to some specially designed algorithms. It is the Padé model of polynomial quotients that is intrinsically robust, first and foremost from the physics viewpoint (as dictated by quantum mechanics through Green functions that invariably reduce to the ratio of two polynomials), and then from subsequent computations that merely translate the firm theoretical basis into the exact numbers.

Resonance is a special phenomenon of a true phase transition. This is clearly seen in phase spectra through sharp jumps by π at every resonant frequency, as prescribed by the Levinson theorem. When many resonances appear in a given spectrum, like those studied in the present review, reconstruction of four machine accurate spectral parameters for each resonance (frequencies and amplitudes both complex-valued) represents a great numerical challenge. For example, some 25 resonances would require the

numerically exact solutions for 100 spectral parameters. This optimization problem is equivalent to a search of the global minimum of an objective function in a hyperspace of 100 dimensions. Convergence is always first achieved for the outermost frequencies in the studied range as is also known from the Lanczos algorithm. The innermost and densely packed frequencies are the last to converge. The density of states is one of the most critical features for both resolution and convergence rate. The average number of fundamental frequencies in the window of interest determines the resolution in the FPT (and in all other parametric estimators) rather the distance between the two adjacent frequencies, as encountered in the fast Fourier transform (FFT). The approach to the said global minimum can indirectly be monitored by checking for the constancy of spectral parameters as a function of the truncated signal length at a fixed bandwidth. When all the spectral parameters stabilize such that adding more signal points leaves the results unaltered, the exact results for all the 100 parameters are obtained to within machine accuracy. This does not occur in a smooth fashion by obtaining the exact outer frequencies first and then waiting for the remaining frequencies to attain their exact values one by one. Quite the contrary happens. The physical outermost frequencies do emerge first, although not initially with machine accuracy. Machine accurate values for outermost frequencies are attained simultaneously with achieving machine accurate results for all the remaining genuine frequencies. This is achieved as an extremely sharp transition. Very near the global minimum of objective function, all the spectral parameters fluctuate around their optimal (true) values. At resonance, all the parameters match their exact values, and for this to happen, the running order K of the FPT suffices to change only by one unit, which needs two additional signal points. After this stage, any new added signal point does not introduce any change in the results within the required 12-digit accuracy. We call this a phase transition, since indeed all the quantities are complex-valued and their phases are critical to the emergence of simultaneous resonance for all the fundamental harmonics. This is most dramatically seen by fixing the phases of the input amplitudes of each fundamental harmonic to zero as done in the present analysis. The reconstructed phases fluctuate around zero, but no exact value of the remaining spectral parameters for any resonance is attained until all machine accurate zero-valued phases are obtained.

The distributions of poles and zeros in complex frequency planes are vital to spectral analysis. Argand plots are extremely useful in this study to visualize pole-zero cancellations for complex-valued frequencies in both polar and rectangular coordinates. As a function of chemical shift, zero-valued spurious amplitudes for nonphysical resonances are also graphically illustrated alongside the corresponding values of the amplitudes for physical, that is, genuine resonances. Both the $\text{FPT}^{(+)}$ and $\text{FPT}^{(-)}$ are used in these illustrations. Genuine and spurious resonances are mixed together outside

the unit circles in the $\text{FPT}^{(-)}$, but still the denoising Froissart filter (DFF) is fully capable of disentangling one from the other by monitoring closely the twofold signature: pole–zero coincidences and zero-valued amplitudes. By contrast, in the $\text{FPT}^{(+)}$, genuine and spurious resonances are strictly separated from each other in two disjoint parts of the complex frequency plane. Such a startling genuine–spurious division, as a signature of signal–noise separation (SNS), is of paramount importance in all interdisciplinary applications of signal processing.

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CHAPTER 4

Reflections on Formal Density Functional Theory

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1. INTRODUCTION

Density functional theory (DFT) [1,2] has emerged as arguably the most successful and widely applicable class of electronic structure methods over the past decades. The foundations of the theory are rooted in a paper by Hohenberg and Kohn [3], which has led to many discussions over the years, in particular regarding the meaning of DFT being exact in principle. For a recent historical overview of the relation between DFT and *ab initio* quantum chemistry and extensive discussion of these issues, see a recent paper by Kutzelnigg [4]. This paper is an attempt to contribute to the discussion by considering a variety of generalizations of the established theoretical framework underlying DFT. In particular, it is demonstrated that many variations of the Hohenberg–Kohn construction can be formulated, which all yield the exact energy in principle employing a functional of density-like quantities and possibly the external molecular potential. Likewise, the widely applied Kohn–Sham formulation [5] of DFT can be viewed as but one of many possibilities, all of which are in principle exact. This enormous flexibility of in principle exact formulations is somewhat unnerving, and it is the aim of this chapter to clearly establish the existing freedom and to discuss to some extent the implications regarding the physical foundations of DFT.

In the first part of this chapter (Section 2), the Hohenberg–Kohn theorem [3] is reviewed and various extensions of the Hohenberg–Kohn construction of DFT are discussed, with a focus on the mapping between external potential, which provides knowledge of the Hamiltonian and hence all calculable properties and auxiliary density-like quantities that satisfy a one-to-one relation to the external potential. Functionals of many such auxiliary quantities provide in principle exact total electronic energies, although they are not universal, in the sense that the not explicitly known part of the energy functional will depend on the molecular external potential. Related, these nonuniversal functionals do not yield the exact ground state density at stationarity, even for exact functionals. It is argued that in practice it is very hard to distinguish between universal and nonuniversal functionals, in particular in applications to molecular systems with singular Coulomb potentials. Next, other generalizations of the Hohenberg–Kohn construction will be considered, and it is demonstrated that the energy is an exact functional of the Hartree–Fock density, which provides a formal basis for post-Hartree–Fock density functional methods [6–8], for example, and in turn the Hartree–Fock energy itself is a functional of the associated electron density [9,10]. In the final part of this section, it is shown that if one considers the possibility (and potential) of nonuniversal density functionals, further generalizations can be made, and one can decompose the density functional into an explicitly known part as a functional of the external potential, or the nuclear framework, while treating the remainder as a

density functional. This allows, for example, a simple treatment of van der Waals interactions within a formally exact DFT framework.

The second part of this chapter (Section 3) considers DFT in a Kohn–Sham framework [5], and it considers the orbital-dependent kinetic energy contribution from a constrained search perspective. This section then primarily focuses on the treatment of exact exchange in a Kohn–Sham framework. It is argued that one can obtain the exact Hartree–Fock result from an exact exchange Kohn–Sham method (see also [9,10]). This is difficult to achieve in a conventional Kohn–Sham framework in which the orbitals satisfy a one-electron Schrödinger equation with a local multiplicative potential, which imposes an additional constraint [11] (for recent discussions, see [12–14]). To achieve exact Hartree–Fock results within a conventional Kohn–Sham framework, one therefore needs to incorporate an unknown correction to the kinetic energy. Alternatively, kinetic energy and exchange energy can both be treated through an orbital-dependent functional, and this leads to the conventional Hartree–Fock equations. Pursuing the analysis, one can formulate Hartree–Fock-like density functionals for the exact correlated energy [9,10,15,16]. Moreover, one can postulate more general orbital-dependent functionals, in which part of the energy is described as an explicitly known functional dependent on orbitals, while the remaining not explicitly known part depends on the density. The resulting generalized Kohn–Sham equations will contain a specific type of nonlocal potential, depending on the orbital-dependent part of the functional. This approach has been discussed long ago [17,18] in the context of rationalizing hybrid density functional methods that include a fraction of exact Hartree–Fock exchange.

This chapter concludes (Section 4) with a discussion of the meaning of the Hohenberg–Kohn theorem and the Kohn–Sham formulation of DFT, and the significance of universality in light of the above generalizations. This chapter is essentially self-contained, as the topic may be of wider interest and effort was put to keep the material accessible to nonexperts in the field, which includes the author.

2. THE HOHENBERG–KOHNS CONSTRUCTION OF AN EXACT DENSITY FUNCTIONAL AND ITS EXTENSIONS

In this section, I will first review the Hohenberg–Kohn construction and the proof that shows that the energy is a functional of the density, that the minimum of this functional is the exact ground state energy, and that this minimum is reached at the exact ground state density. The steps in the proof are discussed in detail, as they will be used in subsequent generalizations of the Hohenberg–Kohn construction and theorem. The original

Hohenberg–Kohn theorem establishes that the total energy functional can be expressed as the sum of an explicitly known expression involving the external potential, $\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$, and a not explicitly known, but universal part, which describes the kinetic energy and electron repulsion energy as a functional of the density. The external potential plays a vital role in the original Hohenberg–Kohn construction and some of the implications of the fact that the energy can alternatively be considered a functional of the external potential will be discussed. In the second part of this section, a generalization of the Hohenberg–Kohn construction is discussed to a class of functionals for which the minimum is still the exact ground state energy, but this minimum is not reached for the exact ground state density, however. Moreover, the not explicitly known part of the functional depends on the external potential and is hence not universal. The potential relevance of these potentials, even in the current practice of DFT, is addressed.

In the third part of this section, density functionals are discussed, which yield the in principle exact energy not as their minimum, but for specifically the Hartree–Fock density. These functionals are denoted as post-Hartree–Fock functionals (see, e.g., [6–8]). The not explicitly known part of the functional will depend on the external potential and the functionals are hence nonuniversal. It will be shown that one can base in principle exact functionals also on different type of Hartree–Fock-like problems, involving different forms for the electron–electron interaction and their correspondingly modified density functionals, all the while preserving the property of exactness in principle.

A final extension will consider the construction of density functionals in which part of the energy is modeled in terms of the nuclear framework, for example, to model van der Waals interactions, while the remaining part of the energy can still be expressed as an exact but nonuniversal density functional.

All of the functionals discussed in this section are formally of Hohenberg–Kohn type, and they refer only the density. In Section 3, the discussion turns to functionals based on orbitals, as in Kohn–Sham theory.

2.1. Review of the Hohenberg–Kohn construction of an exact density functional

Let us first establish some notation and reiterate the well-known proof for the fundamental assertion of DFT that the electronic energy is a functional of the electron density. Consider a system of N -electrons described by a molecular Hamiltonian that consists of the usual kinetic energy operator $\hat{T} = -1/2\sum_i\nabla_i^2$, the electron–electron repulsion term $\hat{W} = \sum_{i\neq j}1/r_{ij}$, and a nuclear–electronic attraction potential of the form $v^{\text{Ne}}(\mathbf{r}) = -\sum_{\alpha}Z_{\alpha}/|\mathbf{r} - \mathbf{R}_{\alpha}|$, with nuclei of charge Z_{α} located at positions $\mathbf{R}_{\alpha}$. A particular form of the external potential is used here, but the important point is that it is a local or

multiplicative operator and that it is explicitly known. The (molecular) Hamiltonian is then defined as

$$\hat{H} = \hat{T} + \hat{V}^{\text{Ne}} + \hat{W}, \quad (1)$$

where $\hat{V}^{\text{Ne}} = \sum_i v^{\text{Ne}}(\mathbf{r}_i)$.

In addition, a family of auxiliary Hamiltonians is introduced, which have the same form for the kinetic energy and electron–electron repulsion interaction, but for which the auxiliary external potential operator will be considered to be variable although it is multiplicative: $\hat{V}_a = \sum_i v_a(\mathbf{r}_i)$, where $v_a(\mathbf{r})$ is a function over the three-dimensional space, $\mathbf{r} \in \mathbb{R}^3$. Hence, a family of Hamiltonians is considered,

$$\hat{H}_a = \hat{T} + \hat{V}_a + \hat{W}, \quad (2)$$

each characterized by a different auxiliary external potential $v_a(\mathbf{r})$. In order to avoid complications of mathematical rigor with the Hohenberg–Kohn theorem [3], as addressed by Lieb [19] and Eschrig [20] and summarized in a recent paper by Kutzelnigg [21], the discussion is restricted to auxiliary external potentials that give rise to bound state problems, for example, consisting of the usual nuclear–electronic attraction potential $v^{\text{Ne}}(\mathbf{r})$, plus a “small” perturbation, that is, $v_a(\mathbf{r}) = v^{\text{Ne}}(\mathbf{r}) + \Delta_a(\mathbf{r})$. Moreover, it is assumed that this family of Hamiltonians has a nondegenerate ground state. In practice, this might be accomplished by choosing a molecular system with a nondegenerate ground state and a large energy gap to the first excited state and then admitting small changes in the external potential, which will lead to small changes in the electron density. This restricted type of variability is all that is needed to discuss the issues below and to avoid a number of complications. Of course, it is not claimed that this is a mathematically rigorous treatment, but it has the virtue of simplicity. It is well possible that the arguments can be made more rigorous using the Legendre transformation formulation of DFT [19,20].

Restricting ourselves to this class of Hamiltonians, the proof of the Hohenberg–Kohn theorem that the electronic energy is a functional of the density consists of two steps (see also [22]).

- (1) If $|\Psi_a\rangle$ is the nondegenerate ground state of $\hat{H}_a$ and $|\Psi_b\rangle$ is the nondegenerate ground state of $\hat{H}_b$ with an external potential $v_b(\mathbf{r})$ that differs from $v_a(\mathbf{r})$ by more than a constant, then the wave functions $|\Psi_a\rangle$ and $|\Psi_b\rangle$ are *essentially* different, that is, they differ by more than an overall phase factor. The proof follows by contradiction. If it were true that $|\Psi_a\rangle = |\Psi_b\rangle = |\Psi\rangle$, then

$$(\hat{H}_b - \hat{H}_a)|\Psi\rangle = (\hat{V}_b - \hat{V}_a)|\Psi\rangle = (E_b - E_a)|\Psi\rangle. \quad (3)$$

This implies that $|\Psi\rangle = 0$, whenever $\hat{V}_b - \hat{V}_a \neq C \equiv (E_b - E_a)$, while it may be nonzero only on contours where $\hat{V}_b - \hat{V}_a = (E_b - E_a)$. This

type of behavior gives rise to discontinuous derivatives and is in conflict with continuity properties of the wave function for “reasonably well-behaved” potentials (for instance, potentials not containing infinite barriers, etc.; see, e.g., [22]). Hence, not surprisingly, ground state wave functions are essentially different for Hamiltonians that correspond to different external potentials. To my surprise, this step is actually somewhat problematic for Hamiltonians that contain a magnetic field [23,24].

- (2) If the ground state wave functions $|\Psi_a\rangle$ and $|\Psi_b\rangle$ are essentially different and the ground states of $\hat{H}_a$ and $\hat{H}_b$ are nondegenerate, it follows that also the one-electron density $\rho_a(\mathbf{r}) = \langle \Psi_a | \hat{\delta}(\mathbf{r}) | \Psi_a \rangle \equiv \rho[\Psi_a]$ is different from the corresponding $\rho_b(\mathbf{r}) \equiv \rho[\Psi_b]$.

Proof:

$$(\langle \Psi_b | \hat{H}_a | \Psi_b \rangle - \langle \Psi_a | \hat{H}_a | \Psi_a \rangle) + (\langle \Psi_a | \hat{H}_b | \Psi_a \rangle - \langle \Psi_b | \hat{H}_b | \Psi_b \rangle) > 0 \quad (4)$$

due to the satisfaction of the variational principle, the assumption of non-degeneracy of the respective ground states, and the fact that the wave functions $|\Psi_a\rangle$ and $|\Psi_b\rangle$ are essentially different. The expectation values of the $\hat{T}$ and $\hat{W}$ operators mutually cancel and the remaining energy difference is evaluated as

$$\begin{aligned} & \int v_a(\mathbf{r})[\rho_b(\mathbf{r}) - \rho_a(\mathbf{r})]d\mathbf{r} + \int v_b(\mathbf{r})[\rho_a(\mathbf{r}) - \rho_b(\mathbf{r})]d\mathbf{r} \\ &= \int [\rho_b(\mathbf{r}) - \rho_a(\mathbf{r})][v_a(\mathbf{r}) - v_b(\mathbf{r})]d\mathbf{r} > 0, \end{aligned} \quad (5)$$

and it therefore follows that the densities cannot be identical.

To establish that the energy is a functional of the density, the following argument is made. First, the external potential determines the ground state wave function and the ground state energy through a solution of Schrödinger’s equation. Second, by the Hohenberg–Kohn theorem, if the external potential changes, the density changes, and there are no two essentially different potentials that yield the same ground state density. Hence, there is a one-to-one mapping between external potentials and densities, or, more precisely, between external potentials and v -representable densities, densities that correspond to ground states of some external potential. Using the above construction, one can partition the energy for the Hamiltonian $\hat{H}_a$ as follows:

$$\langle \Psi_a | \hat{H}_a | \Psi_a \rangle = \int v_a(\mathbf{r})\rho_a(\mathbf{r}) + \langle \Psi_a | \hat{T} + \hat{W} | \Psi_a \rangle, \quad (6)$$

where the sum of kinetic and electron repulsion energy can be considered a functional of $\rho_a(\mathbf{r})$, that is, one defines

$$E^{\text{TW}}[\rho_a] = \langle \Psi_a | \hat{T} + \hat{W} | \Psi_a \rangle = \langle \Psi_a | \hat{H}_a | \Psi_a \rangle - \int v_a(\mathbf{r}) \rho_a(\mathbf{r}) d\mathbf{r}. \quad (7)$$

Using this functional $E^{\text{TW}}[\rho_a]$, one can define a functional form for the original energy, involving the explicitly known nuclear–electron potential $v^{\text{Ne}}(\mathbf{r})$ as

$$E[\rho] = \int v^{\text{Ne}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E^{\text{TW}}[\rho]. \quad (8)$$

This functional by construction reaches its minimum for the true ground state energy, and the corresponding density at the stationary point is the true ground state density. This establishes the Hohenberg–Kohn variational principle, which forms the foundation of DFT. The functional $E^{\text{TW}}[\rho]$ is universal, because it is completely independent of the known external potential $v^{\text{Ne}}(\mathbf{r})$. This is a somewhat confusing issue as $\rho(\mathbf{r})$, when varied, implicitly contains knowledge about the auxiliary external potential, but, and this is the important point, not the actual potential $v^{\text{Ne}}(\mathbf{r})$. At the minimum energy point, the density is exact, or stated differently, the auxiliary potential related to the minimum energy density is precisely the known external potential $v^{\text{Ne}}(\mathbf{r})$. Given the imposed restrictions on the allowed variations of the external potential and densities (small deviations from the target v^{Ne} potential), strictly speaking this only proves a modest version of the Hohenberg–Kohn theorem, in particular it indicates that a local functional exists, focusing on small deviations from the exact ground state density corresponding to the target external potential. Even this very modest version of the grander original (but mathematically more cumbersome) Hohenberg–Kohn theorem suffices for the analysis below. A weak point of the current analysis is that it is restricted to v -representable densities. An elegant way to avoid this problem is the constrained search approach by Levy [25] and Lieb [19], which replaces the rather intangible v -representability constraint on admissible densities by the mathematically convenient N -representability constraint. In the remainder of this chapter, the Hohenberg–Kohn construction is followed, and implicitly the densities considered are assumed to be v -representable, or the variations considered are over v -representable densities only. Not much thought has been given to see if the arguments below could be based on the constrained search approach, alleviating this limitation. It is appropriate to point out that many of the conclusions reached here focus on the mapping between density and external potential. It would require a substantial rethinking of the main threads of the paper, if the arguments were to be based on the constrained search construction of density functional rather than the Hohenberg–Kohn construction as discussed below.

It is of interest to reflect further on the essentials of the Hohenberg–Kohn theorem and on the depth of the statement that the energy is a functional of the density. First, one of the cornerstones of the Hohenberg–Kohn construction is the fact that the auxiliary energy $\langle \hat{H}_a \rangle$ is a functional of the external potential $v_a(\mathbf{r})$, for a given number of electrons, as it serves to completely define the Hamiltonian $\hat{H}_\alpha = \hat{T} + \hat{V}_\alpha + \hat{W}$, and from this we can in principle obtain the ground state energy, as well as other ground state properties, and even all excited state properties (within the clamped nucleus approximation), corresponding to this auxiliary Hamiltonian. It may be worthwhile to emphasize this ingredient of the Hohenberg–Kohn construction: All calculable properties defined implicitly by the N -electron Hamiltonian $\hat{H}_\alpha = \hat{T} + \hat{V}_\alpha + \hat{W}$ are a functional of the external potential $v_a(\mathbf{r})$. In particular, we may consider the most commonly employed external potential in chemistry, which is determined through a set of nuclear charges Z_α and nuclear positions $\mathbf{R}_\alpha$, yielding the Coulomb potential due to the nuclei: $v^{\text{Ne}}(\mathbf{r}) = \sum_\alpha -Z_\alpha/|\mathbf{r} - \mathbf{R}_\alpha|$. From the statement that all calculable properties are a functional of the external potential and the number of electrons, it then follows that the ground state energy, excited state energies, and all other ground and excited state properties are a function of the number of electrons and the specification of the nuclear framework $\{Z_\alpha, \mathbf{R}_\alpha\}$. In particular, *molecular mechanics, which parameterizes the ground state energy as a function of the nuclear framework, is in principle exact*. There exists an exact force field for *each* electronic state with a given number of electrons. This force field is in principle universal in the sense that it only depends on the $\{Z_\alpha, \mathbf{R}_\alpha\}$, the number of electrons, and the ordinal number of state of the system (ground state, first excited state, and so forth). This statement, that the external potential and number of electrons determines all calculable properties, is a basic ingredient of the Hohenberg–Kohn construction. In fact, in molecular mechanics, there is the advantage that one does not have to consider the mathematically defined but rather unphysical auxiliary potentials of DFT and one only requires the energy functional for the physically significant $v^{\text{Ne}}(\mathbf{r})$. A somewhat unattractive prospect, in light of the above in essence trivial point, is that every future paper employing molecular mechanics would justifiably include a sentence in the introduction that “molecular mechanics is employed in which the only fundamental unknown is the force field, but this is in principle exact,” following the current folklore regarding DFT applications within the quantum chemistry community.

Let us leave rhetoric behind and return to the definition of the functional of the kinetic energy – electron repulsion energy

$$E^{\text{TW}}[\rho_a] = \langle \Psi_a | \hat{T} + \hat{W} | \Psi_a \rangle = \langle \Psi_a | \hat{H}_a | \Psi_a \rangle - \int v_a(\mathbf{r}) \rho_a(\mathbf{r}) d\mathbf{r}. \quad (9)$$

Taking the functional derivative with respect to the external potential, one finds

$$\begin{aligned} \frac{\delta E^{\text{TW}}}{\delta v_a(\mathbf{r}')} &= \frac{\delta \langle \Psi_a | \hat{H}_a | \Psi_a \rangle}{\delta v_a(\mathbf{r}')} - \int \delta(\mathbf{r} - \mathbf{r}') \rho_a(\mathbf{r}) d\mathbf{r} - \int v_a(\mathbf{r}) \frac{\delta \rho_a(\mathbf{r})}{\delta v_a(\mathbf{r}')} d\mathbf{r} \\ &= \rho_a(\mathbf{r}') - \rho_a(\mathbf{r}') - \int v_a(\mathbf{r}) \frac{\delta \rho_a(\mathbf{r})}{\delta v_a(\mathbf{r}')} d\mathbf{r} = - \int v_a(\mathbf{r}) \frac{\delta \rho_a(\mathbf{r})}{\delta v_a(\mathbf{r}')} d\mathbf{r}, \end{aligned} \quad (10)$$

where the derivative of the expectation value is analogous to the Hellmann–Feynman theorem. The functional derivative of E^{TW} with respect to the density yields

$$\begin{aligned} \frac{\delta E^{\text{TW}}[\rho_a]}{\delta \rho_a(\mathbf{r}')} &= \frac{\delta}{\delta \rho_a(\mathbf{r}')} [\langle \Psi_a | \hat{H}_a | \Psi_a \rangle - \int \rho_a(\mathbf{r}) v_a(\mathbf{r}) d\mathbf{r}] \\ &= 0 - \int v_a(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} = -v_a(\mathbf{r}'), \end{aligned} \quad (11)$$

which is precisely the external potential needed to generate the particular density ρ_a by solving the Schrödinger equation. This equation is then consistent with the fact that the functional derivative of the total electronic energy

$$E[\rho_a] = \int v^{\text{Ne}}(\mathbf{r}) \rho_a(\mathbf{r}) d\mathbf{r} + E^{\text{TW}}[\rho_a] \quad (12)$$

with respect to the density vanishes precisely at the ground state density:

$$\frac{\delta E}{\delta \rho_a(\mathbf{r})} = v^{\text{Ne}}(\mathbf{r}) - v_a(\mathbf{r}) = 0, \quad \text{or} \quad v_a(\mathbf{r}) = v^{\text{Ne}}(\mathbf{r}) \text{ at stationarity.} \quad (13)$$

This concludes the discussion of the original Hohenberg–Kohn construction. We next consider extensions, which serve to put the Hohenberg–Kohn theorem in a broader perspective.

2.2. Nonuniversal density-like functionals satisfying a variational principle

The original Hohenberg–Kohn asserts that the energy is a functional of the density and that minimization of this functional with respect to the density will yield the exact ground state density. This leads to the question, whether the exact ground state energy might also be a functional of other (density-like) quantities, and whether a variational principle might still hold, although this might not yield the exact ground state density. Upon examining the proof of the Hohenberg–Kohn theorem, the crucial aspect is establishing a one-to-one correspondence between a “density-like” quantity and the auxiliary external

potential. It transpires that it is straightforward to construct generalizations of the Hohenberg–Kohn theorem. I will consider a particular example to demonstrate the point, without aiming to achieve full generality. Consider using instead of the Coulomb interaction between electrons, the Yukawa potential, $\hat{W}^\lambda = \sum_{i \neq j} e^{-\lambda r_{ij}} / r_{ij}$ and define the family of Hamiltonians

$$H_a^\lambda = \hat{T} + \hat{V}_a + \hat{W}^\lambda. \quad (14)$$

Through the scalar parameter λ , this defines a continuous one-parameter family of Hamiltonians for every external potential while the original Coulombic Hamiltonian is recovered for $\lambda = 0$. For a given fixed value of λ , one can trace the steps in the Hohenberg–Kohn argument and establish that there is a one-to-one correspondence between the Yukawa-based density $\rho_a^\lambda(\mathbf{r})$ and the auxiliary external potential $v_a(\mathbf{r})$. The construction only depends on the variational principle (which is equally valid, of course) and the requirement that the Yukawa-based ground state wave function changes with external potential, which invokes the same continuity argument as in the original Hohenberg–Kohn proof. Hence, there exists a one-to-one mapping between $\rho_a^\lambda(\mathbf{r})$ and the external potential and therefore to the *original* Coulombic Hamiltonian $H_a^0 = \hat{T} + \hat{V}_a + \hat{W}^0$. The ground state energy for the Coulomb Hamiltonian ($\lambda = 0$) is therefore a functional of $\rho_a^\lambda(\mathbf{r})$. Since this construction may appear to be rather far fetched and only serves to prove that more general “density functionals” exist, it may be good to explicitly trace the steps in the construction.

- (1) For a given external potential $v_a(\mathbf{r})$, solve the Yukawa Schrödinger equation corresponding to $\hat{H}_a^\lambda$ and obtain $\rho_a^\lambda(\mathbf{r})$.
- (2) Also solve the Schrödinger equation for the Hamiltonian $\hat{H}_a^0$, and the same auxiliary potential $v_a(\mathbf{r})$, yielding $|\Psi_a\rangle, \rho_a^0(\mathbf{r})$. Define the energy functional

$$E_\lambda^{\text{TVW}}[\rho_a^\lambda] = \int v^{\text{Ne}}(\mathbf{r}) [\rho_a^0(\mathbf{r}) - \rho_a^\lambda(\mathbf{r})] d\mathbf{r} + \langle \Psi_a | \hat{T} + \hat{W}^0 | \Psi_a \rangle, \quad (15)$$

which we note now depends explicitly on the molecular potential $v^{\text{Ne}}(\mathbf{r})$. This functional is hence explicitly *not* a universal functional of the density.

- (3) By construction, the total energy expression

$$E^\lambda[\rho_a^\lambda] = \int v^{\text{Ne}}(\mathbf{r}) \rho_a^\lambda(\mathbf{r}) d\mathbf{r} + E_\lambda^{\text{TVW}}[\rho_a^\lambda] \quad (16)$$

equals the original energy

$$E[\rho_a^0] = \int v^{\text{Ne}}(\mathbf{r}) \rho_a^0(\mathbf{r}) d\mathbf{r} + E^{\text{TW}}[\rho_a^0] \quad (17)$$

at corresponding densities, that is, $\rho_a^0(\mathbf{r}) \leftrightarrow v_a(\mathbf{r}) \leftrightarrow \rho_a^\lambda(\mathbf{r})$

This functional $E^\lambda[\rho_a^\lambda]$ can be varied over the auxiliary density $\rho_a^\lambda(\mathbf{r})$, and by construction it has a minimum at the Yukawa density for the target external potential $v^{\text{Ne}}(\mathbf{r})$, and the value of the functional at this minimum yields the exact ground state energy. This generalization has many features in common with the original Hohenberg–Kohn construction although it differs substantially in the treatment of the energy contribution due to the target external potential, which has turned into something that has a complicated functional dependence on the density-like variability $\rho^\lambda(\mathbf{r})$, as can be seen from the explicit form in Eq. (15). The construction using the Yukawa potential is only one example. By modifying the electron–electron interaction and possibly the kinetic energy, many different functionals for the total energy can be obtained that all express the original energy as a functional of a density that corresponds to a different type of Hamiltonian (different value of λ in the Yukawa case). From this formal theoretical perspective, the original Hohenberg–Kohn functional, based on the exact density, is but one of many possibilities.

To many practitioners in the field, this construction will not classify as a DFT at all, as the density corresponding to the ground state energy is not exact and the density functional is not universal. From a formal point of view, however, one might simply call the above *nonuniversal* density functionals to indicate the distinction. The total electronic energy is *always* a nonuniversal functional of the density but the part due to the molecular external potential is explicitly known. The distinction is perhaps not as large as one might think. The nuclear–electron attraction potential is encoded in the behavior of the electron density near the nucleus, and in the restricted form of the Hohenberg–Kohn construction in which we employ $v_a(\mathbf{r}) = v^{\text{Ne}}(\mathbf{r}) + \Delta_a(\mathbf{r})$, every auxiliary density implicitly contains knowledge on the molecular external potential $v^{\text{Ne}}(\mathbf{r})$, and the difference between universal and nonuniversal functionals loses its significance. In the practice of quantum chemistry or solid state physics, all densities are obtained for external potentials that have precisely the above form, that is, they are singular at the nuclear positions, and it might even be very hard to distinguish such nonuniversal density functional schemes from proper Hohenberg–Kohn schemes as in practice one does not obtain, or even know, the exact density. More explicitly, practical DFT might unintentionally model nonuniversal functionals $E^{\text{TVW}}[\rho]$. In fact, this possibility is not so hard to test. One could perform DFT and high-quality ab initio calculations for truly arbitrary external potentials. If the results from DFT calculations sharply deviate from the ab initio results for such arbitrary potentials, this would be consistent with the fact that indeed current functionals implicitly model potentials of the v^{Ne} type. Pushing the argument further, the results from DFT regarding total energies might be better than the values for the nuclear attraction energy itself, indicating that the error in the energy due to the error in the density is substantial, and this is compensated by using

“nonuniversal” density functionals. This argument is perhaps not very convincing as one might also attribute this hypothetical higher accuracy for the total energy to the satisfaction of the variational principle, while the nuclear attraction energy is a first-order property, which is expected to have a larger error, also in (variational) wave function-based theories. One can make a final argument that suggests that nonuniversal functionals play a role, even in the current versions of DFT. The above generalization of the Hohenberg–Kohn theorem recognizes that many different exact energy functionals exist if one relaxes the condition that at stationarity the density should be exact. This greater variety of functionals might make it easier to design approximate functionals, as the precise form of the functional might be less critical and optimizing some undetermined parameters might bring it closer to *one* particular member of the family of exact functionals. This argument would rationalize the existence in practice of many different DFT functionals and Kohn–Sham potentials that all lead to results of comparable high accuracy. Nonuniversal functionals can indeed be different, yet exact.

2.3. Functionals of the Hartree–Fock density

There are additional possibilities to construct in principle exact density functionals. For example, one might ask if the exact energy is perhaps a functional of the (exact, basis set free) Hartree–Fock density. For a given Hamiltonian $\hat{H}_a = \hat{T} + \hat{V}_a + \hat{W}$, one solves for the single determinant wave function $|\Phi_a\rangle$ that minimizes the energy and which yields the density $\rho_a^{\text{HF}}(\mathbf{r})$. If the Hartree–Fock determinant is different for two essentially different external potentials, then it follows from the variational principle associated with the Hartree–Fock method that the associated densities are also different (step 2 in the Hohenberg–Kohn proof continues to hold). The one-to-one correspondence between Hartree–Fock density and external potential and a fortiori, the full Hamiltonian is then established and it follows that the energy is a functional of the Hartree–Fock density [9,10]. The fact that the Hartree–Fock determinants are different for different external potentials is not hard to establish, following essentially the same line of proof as for the Hohenberg–Kohn theorem. Suppose that $|\Phi_a\rangle = |\Phi_b\rangle = |\Phi\rangle$ and satisfies the Hartree–Fock equations

$$\begin{aligned} (\hat{T} + \hat{V}_a + \hat{V}^{\text{HF}}[\Phi])|\Phi\rangle &= E_a^0|\Phi\rangle \\ (\hat{T} + \hat{V}_b + \hat{V}^{\text{HF}}[\Phi])|\Phi\rangle &= E_b^0|\Phi\rangle, \end{aligned} \tag{18}$$

where $\hat{V}^{\text{HF}}[\Phi]$ is the nonlocal Hartree–Fock potential (Coulomb + exchange). Subtracting these equations, we are led to analogous equations as before: $(\hat{V}_b - \hat{V}_a)|\Phi\rangle = (E_b^0 - E_a^0)|\Phi\rangle$, which violates continuity

conditions if the external potentials differ by more than a constant. Hence, this contradiction shows that the Hartree–Fock determinants corresponding to different external potentials are essentially different and all of the Hohenberg–Kohn machinery can be used to establish that the exact total energy is a functional of the Hartree–Fock density. The above also demonstrates that the Hartree–Fock energy itself, corresponding to Hamiltonian $\hat{H}_a$, is a functional of the external potential and hence of the Hartree–Fock density. One simply replaces the exact energy from the Schrödinger equation by the Hartree–Fock energy in the construction of the functional. We will return to this point in a later section. It also follows that the correlation energy ($E^{\text{exact}} - E^{\text{HF}}$) is a functional of the Hartree–Fock density [9,10]. This observation can be used to rigorously justify the construction of post-Hartree–Fock functionals [6–8]. It should be noted that post-Hartree–Fock density functionals have to recover from the fact that the density is not exact, and hence the exact Hartree–Fock correlation energy functional includes effects to correct for an inexact treatment of the nuclear–electron attraction term. It is therefore of the nonuniversal type, although surely for molecular systems the v^{Ne} potential is encoded in the Hartree–Fock density near the nuclei, and the distinction between universal and nonuniversal functionals therefore becomes skin-deep if the approach is applied to molecular systems defined by v^{Ne} -type potentials.

The post-Hartree–Fock approaches are quite different from the variational approaches considered before. The methodology would proceed by first solving the Hartree–Fock equations, obtaining a density, and subsequently plugging the density in the energy functional to obtain the exact energy “in principle.” The functional is not required to be at a minimum for the Hartree–Fock density. From a practical perspective, these methods are perhaps a bit more cumbersome than self-consistent DFT methods as analytical energy gradients and second derivatives require more computational effort than in conventional DFT approaches. On the other hand, the procedure does not require a potential or functional derivative of the density, and it appears that the only criterion to gauge the accuracy of the approach would be the computed energy.

The above post-Hartree–Fock treatment can be combined with changes in the Hamiltonian, for example, replacing the electron–electron interaction with the Yukawa potential. Nothing essential changes in the formal proofs and so the exact total energy is a functional also of the Yukawa–Hartree–Fock density, $E = E[\rho^{\lambda, \text{HF}}]$. The Yukawa family of Hamiltonians is just an example and further generalizations are easily constructed if other families of electron–electron interactions (or kinetic energy operators) are taken into consideration. It is well known that for certain molecular systems, for example, transition metal complexes, Hartree–Fock densities can be quite erroneous. It is possible that densities based on Yukawa or similar potentials are better behaved as the long-range behavior of the electron–electron

interaction is damped. One cannot a priori exclude therefore that it might be easier in practice to construct accurate energy functionals based on Yukawa–Hartree–Fock or similar types of densities for specific classes of molecular systems.

2.4. Nonuniversal functionals of the density containing an explicit external potential-dependent part

By considering extensions of the Hohenberg–Kohn construction to density functionals that explicitly depend on the external potential, further generalizations are possible, without obfuscating the formal exactness of the result. For example, one might parameterize van der Waals interactions in a force field-like manner, where the van der Waals interaction depends on the nuclear charges and nuclear positions. This might formally be represented as a contribution $E^{\text{vdW}}[v^{\text{Ne}}]$, which explicitly depends on the external potential, not on the (auxiliary) density. Defining

$$E^{\text{TW/vdW}}[\rho] = E^{\text{TW}}[\rho] - E^{\text{vdW}}[v^{\text{Ne}}], \quad (19)$$

it is straightforward to establish a construction that indicates the functional is in principle exact. The complete generalized Hohenberg–Kohn expression for the energy would be given by

$$E = \int v^{\text{Ne}}(\mathbf{r})\rho(\mathbf{r})\mathbf{d}\mathbf{r} + E^{\text{TW/vdW}}[\rho] + E^{\text{vdW}}[v^{\text{Ne}}]. \quad (20)$$

The above construction would have the exact energy as its minimum, and the exact density would be obtained there. For a given external potential, the above change is a trivial modification, as it only changes the energy functional by a constant. None of the explicit dependence on the density is changed. For different external potentials, the “constant” shift is different and therefore this extension of the Hohenberg–Kohn defines a nonuniversal functional of the density. As was argued before, in practice the density implicitly contains knowledge about the molecular external potential and the nonuniversality of the functional is formally of limited importance. One can further argue that in current practice, density functionals typically do not describe van der Waals interactions, and therefore they might be considered to model $E^{\text{TW/vdW}}[\rho]$ rather than $E^{\text{TW}}[\rho]$. Of course, recognizing this fact might be of help in improving density functional approximations, and the above approach has been used in applications [26,27].

The above treatment of van der Waals interactions can be combined in essentially the same way with the Yukawa-based construction of DFT (which would incidentally quickly damp long-range interactions, already described

by the explicit van der Waals formula) or with post-Hartree–Fock methods leading to further generalizations of the Hohenberg–Kohn construction.

3. GENERALIZATIONS OF THE KOHN–SHAM DENSITY FUNCTIONAL FORMULATION: INCLUSION OF EXACT EXCHANGE

In this section, we will consider orbital-dependent formulations of DFT of the Kohn–Sham type, and as in the previous section our interest is in generalizations of the original formulation, which preserve the formal exactness of the construction. The flow of logic in this section is somewhat convoluted (even for the author). Let me therefore give an outline of what is to follow. We start with a description of the Kohn–Sham formulation [5] of DFT, introducing an orbital-dependent form of the kinetic energy. Rather than focusing on the Kohn–Sham noninteracting system, a constrained search view is taken on this kinetic energy functional [17,18,25], and the connection is made subsequently to the traditional Kohn–Sham formulation leading to a one-electron Schrödinger equation with a local multiplicative potential. Considerable effort is taken to derive the stationarity equations in the appropriate way, using the external potential as the variable, not the orbitals themselves.

Next, we consider the formal application of Kohn–Sham theory to obtain the *exact* Hartree–Fock energy, which was established before to be a functional of the density. It is shown that this is a nontrivial problem, and the analysis further sheds some light on the treatment of kinetic energy in the Kohn–Sham framework. There is an easier way to achieve exact Hartree–Fock results in a DFT framework, and this is to treat kinetic energy and exchange together on the same footing, treating them both as an orbital-dependent part of the density functional and following a very similar constrained search approach as in Kohn–Sham theory to this combined quantity [10,17]. This simply yields the usual Hartree–Fock equations, and one might argue that by this alternate construction, Hartree–Fock is simply reclassified as a DFT. The procedure is general, and it is shown next that this can be turned into an exact DFT with the Hartree–Fock model replacing the Kohn–Sham noninteracting system [9,10,15,16]. Formally, this is a rather small step, but it provides an exact treatment of exchange and it solves the self-interaction problem in DFT. Continuing the generalization, it is shown that the Hohenberg–Kohn functional $E^{\text{TW}}[\rho]$ can be decomposed into an essentially arbitrary but explicitly orbital-dependent part, which can always be defined to be a functional of the density using the constrained search minimization principle, and the remainder, likewise a functional of the density. This general class of exact density functional approaches has equal formal validity as the Kohn–Sham formulation, and in principle yields

exact energies and densities employing universal functionals. Very similar generalizations have been discussed a decade ago in the context of hybrid DFT [17,18] (for a recent comprehensive review see Ref. [12]). Finally, the orbital-dependent formulation can be further generalized to include non-universal functionals of the density, following a similar line of thought as taken in the previous section. This is discussed only briefly.

3.1. Review of Kohn–Sham theory as a constrained search formulation of the kinetic energy functional

In Kohn–Sham theory, the kinetic energy as a functional of the density is approximated by the minimum of the orbital-dependent kinetic energy form $\Sigma_j \langle \varphi_j | \hat{T} | \varphi_j \rangle$ over all orthonormal set of (occupied) orbitals that yield a particular density $\rho_a(\mathbf{r}) = \Sigma_j |\varphi_j(\mathbf{r})|^2$. The orbitals are auxiliary quantities and are only determined up to a rotation amongst themselves. One can associate a Slater determinant $|\Phi\rangle$ with the set of orbitals $\{\varphi_i\}$, and this is then determined up to an overall phase factor, as usual. The kinetic energy functional can therefore be described as the minimum of the kinetic energy $\langle \Phi | \hat{T} | \Phi \rangle$ under the constraint that the density of the determinant corresponds to $\rho_a(\mathbf{r})$. The minimum value of this orbital-dependent, or determinant dependent, kinetic energy only depends on the input density $\rho_a(\mathbf{r})$ and is hence a functional of the density. The above definition adheres to the constraint search definition of the kinetic energy [25]. The connection to the traditional definition of the Kohn–Sham kinetic energy, which introduces a noninteracting system with a local multiplicative potential, can be derived if one defines a suitable computational scheme to obtain the functional in practice. To obtain the above kinetic energy corresponding to a particular density, one might minimize the following functional, which includes undetermined Lagrange multipliers to enforce the constraints on the orbitals, which are considered to be real in what follows. Hence,

$$L_T[\{\varphi_i\}; \rho_a] = -\frac{1}{2} \sum_j \int \varphi_j^*(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r}) d\mathbf{r} + \int \mu(\mathbf{r}) \left[\sum_j |\varphi_j(\mathbf{r})|^2 - \rho_a(\mathbf{r}) \right] d\mathbf{r} - \sum_{ij} \varepsilon_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right), \quad (21)$$

where a continuous Lagrangian multiplier field $\mu(\mathbf{r})$ is introduced to insure that the orbitals sum up to the density for all $\mathbf{r}$, if the functional is required to be stationary with respect to variations in $\mu(\mathbf{r})$, while the discrete Lagrange multipliers ε_{ij} insure orthonormality of the orbitals at stationarity with respect to the ε_{ij} . The subscript T indicates that the functional refers to the kinetic energy. The stationary condition for the orbitals deriving from the functional $L_T[\{\varphi_i\}; \rho_a]$

can be expressed in *canonical* form (see, e.g., the text-book approach in Szabo and Ostlund for a discussion of the canonical Hartree–Fock method [28])

$$-\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + \mu(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}), \quad (22)$$

and it follows that the orbitals should satisfy a one-electron Schrödinger equation with a local multiplicative potential $\mu(\mathbf{r})$. This condition only suffices to show that the kinetic energy functional is stationary, it is not necessarily a minimum. Eq. (22) also implies that the density is noninteracting v -representable, which is typically invoked also in the traditional Kohn–Sham formulations although it can be avoided in the constraint search formulations in the ensemble formulation [29]. Defining the external potential operator $\hat{V}_s = \sum_i \mu(\mathbf{r}_i)$, the associated Slater determinant $|\Phi\rangle$ is required to satisfy a Schrödinger equation for noninteracting electrons of the form

$$(\hat{T} + \hat{V}_s)|\Phi\rangle = E_s|\Phi\rangle. \quad (23)$$

In the original formulation of the Kohn–Sham procedure [5], the Hohenberg–Kohn theorem is invoked to show that the total ground state energy for the above noninteracting Schrödinger equation is a functional of the density, and hence also the kinetic energy corresponding to this ground state is a functional of the density. The functional is usually denoted as $T_s[\rho] = E_s[\rho] - \int v_s(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$. In order for the definitions of the constraint search formulation and the Kohn–Sham definition of the kinetic energy functional to agree, it is necessary that the Kohn–Sham formulation yields a minimum for the kinetic energy expression rather than just a stationary point.

In actual calculations, DFT is usually carried out in the Kohn–Sham framework, and the total energy functional is defined as

$$E^{\text{KS}}[\rho] = T_s[\rho] + \int v^{\text{Ne}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F^{\text{KS}}[\rho], \quad (24)$$

in which the density is written as the sum over orbitals $\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2$, and the Kohn–Sham functional $F^{\text{KS}}[\rho] = E^{\text{TW}}[\rho] - T_s[\rho]$ is a universal functional of ρ . The orbital-dependent form of the kinetic energy, implicit in the definition of $T_s[\rho]$, provides a fairly accurate zeroth-order description of the kinetic energy. Invoking stationarity with respect to variation in the density leads to one-electron equations for the orbitals that can be conveniently solved on a computer. It is essential that the potential in the resulting one-electron equations is local multiplicative, otherwise the resulting description of kinetic energy would not be valid, as indicated above. In most approximations, the functional $F^{\text{KS}}[\rho]$ is explicitly given as a functional of $\rho(\mathbf{r})$, and then this condition is automatically fulfilled.

In order to facilitate the subsequent discussion of the treatment of exact exchange, it is worthwhile to be more explicit about the relation between the constraint search formulation and the one-electron Schrödinger equation for the Kohn–Sham noninteracting system. In particular, the derivation of the one-electron Kohn–Sham equations starting from Eq. (24) requires a careful treatment.

Returning to the constrained search formulation of Kohn–Sham theory, given the external potential $\mu(\mathbf{r})$, the orbitals satisfy the equation $-1/2\nabla^2\varphi_i(\mathbf{r}) + \mu(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$, the density is given by $\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2$, and the Kohn–Sham energy $E^{\text{KS}}[\rho] = T_s[\rho] + \int V^{\text{Ne}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F^{\text{KS}}[\rho]$ is to be minimized with respect to the density. Because the density is in one-to-one correspondence with the Lagrangian multiplier field, we can say alternatively that the energy is to be minimized with respect to the Lagrange multiplier field $\mu(\mathbf{r})$. The consideration of variations with respect to the Lagrange multiplier field is easier than to consider variations in the density. In the following, we will continue assuming that the orbitals are real, to facilitate the algebra. Taking the functional derivative with respect to $\mu(\mathbf{r})$ and using the chain rule to obtain explicit expressions in terms of orbitals one obtains,

$$\frac{\partial E^{\text{KS}}}{\partial \mu(\mathbf{r})} = 2 \int \left[\sum_i -\frac{1}{2} \nabla^2 \varphi_i(\mathbf{r}') + \left(V^{\text{Ne}}(\mathbf{r}') + \frac{\delta F^{\text{KS}}}{\delta \rho(\mathbf{r}')}(\mathbf{r}') \right) \varphi_i(\mathbf{r}') \right] \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} d\mathbf{r}', \quad (25)$$

where we used, for example,

$$\begin{aligned} \frac{\delta F^{\text{KS}}[\rho]}{\delta \mu(\mathbf{r})} &= \int d\mathbf{r}'' \int d\mathbf{r}' \frac{\delta F^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r}'')}(\mathbf{r}'') \sum_i \frac{\delta \rho(\mathbf{r}'')}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \\ &= \int d\mathbf{r}'' \int d\mathbf{r}' \frac{\delta F^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r}'')}(\mathbf{r}'') \delta(\mathbf{r}' - \mathbf{r}'') \sum_i 2\varphi_i(\mathbf{r}'') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \\ &= 2 \sum_i \int d\mathbf{r}' \frac{\delta F^{\text{KS}}[\rho]}{\delta \rho(\mathbf{r}')}(\mathbf{r}') \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \end{aligned} \quad (26)$$

and

$$\begin{aligned} \frac{\partial T_s[\rho]}{\partial \mu(\mathbf{r})} &= \sum_i \int \frac{\delta \sum_j \langle \varphi_j | \hat{T} | \varphi_j \rangle}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} d\mathbf{r}' \\ &= 2 \int \sum_i -\frac{1}{2} \nabla^2 \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} d\mathbf{r}' \end{aligned} \quad (27)$$

and similar manipulations. The functional derivative of the orbitals with respect to the Lagrangian multiplier field (or the potential in the one-electron Schrödinger equation) is a well-known expression given by [12]

$$\frac{\delta\varphi_i(\mathbf{r}')}{\delta\mu(\mathbf{r})} = \sum_{k \neq i} \varphi_k(\mathbf{r}') \frac{\varphi_k(\mathbf{r})\varphi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_k}, \quad (28)$$

and it is important to note that

$$\int \varphi_i(\mathbf{r}') \frac{\delta\varphi_i(\mathbf{r}')}{\delta\mu(\mathbf{r})} d\mathbf{r}' = 0, \quad (29)$$

which expresses that the change in the perturbed orbital is orthogonal to $\varphi_i(\mathbf{r})$ to preserve normalization in first order. Substituting $-1/2\nabla^2\varphi_i(\mathbf{r}) = -\mu(\mathbf{r})\varphi_i(\mathbf{r}) + \varepsilon_i\varphi_i(\mathbf{r})$ in the functional derivative, Eq. (25), we obtain

$$\frac{\delta E^{\text{KS}}}{\delta\mu(\mathbf{r})} = 0 = 2 \int \sum_i \left[-\mu(\mathbf{r}') + V^{\text{Ne}}(\mathbf{r}') + \frac{\delta F^{\text{KS}}}{\delta\rho(\mathbf{r}')} + \varepsilon_i \right] \varphi_i(\mathbf{r}') \frac{\delta\varphi_i(\mathbf{r}')}{\delta\mu(\mathbf{r})} d\mathbf{r}'. \quad (30)$$

Due to the orthogonality condition [Eq. (29)], it follows that the equation is satisfied if

$$-\mu(\mathbf{r}') + V^{\text{Ne}}(\mathbf{r}') + \frac{\delta F^{\text{KS}}}{\delta\rho(\mathbf{r}')}(\mathbf{r}') = 0. \quad (31)$$

In other words, the Lagrangian multiplier field is precisely the traditional Kohn–Sham external potential. These equations hence lead to the usual Kohn–Sham one-electron equations [substituting the expression for $\mu(\mathbf{r})$ in Eq. (22)]

$$-\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + \left[V^{\text{Ne}}(\mathbf{r}) + \frac{\delta F^{\text{KS}}}{\delta\rho(\mathbf{r})}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}). \quad (32)$$

The equations have to be solved self-consistently as the potential depends on the density.

The above appears to be a complicated way to derive the Kohn–Sham equations, but it indicates how one can deal with functional derivatives of orbitals, densities, and the Lagrange-multiplier field consistently to obtain the correct result. It also shows that underlying all of these derivatives is the derivative with respect to the external potential (i.e., the Lagrange multiplier field). It follows that also in the constrained search formulation of kinetic

energy the orbitals are required to satisfy a Kohn–Sham one-electron equation with a local multiplicative potential. The reader may take notice that if the explicit orbital derivative of the Kohn–Sham energy expression [Eq. (24)] is taken, the same result is obtained. This procedure is mathematically less careful, but it works because taking the explicit orbital derivatives leads to a local potential, such that the required stationarity of purely the kinetic energy functional with respect to orbital variations while yielding a particular density, is automatically satisfied also.

Let me emphasize that one should not take the functional derivative with respect to one particular orbital, as this implies a change in the external potential and this in turn involves all orbitals. This is clearly discussed in the literature [30] and is also referred to as the dual formulation of Kohn–Sham DFT [24]. For a recent discussion of the subtleties involved in taking functional derivatives of orbital-dependent functionals, see also Ref. [12]. In principle, these subtleties are there already for the simplest case of the original Kohn–Sham equations, although as mentioned, one does arrive at the correct result even if one proceeds following the improper path, using orbital derivatives directly. In our subsequent derivations, one would be led astray if derivatives are taken with respect to orbitals directly, and the above procedure is recommended.

3.2. Application of the Kohn–Sham formalism to the exact Hartree–Fock energy

Here, Kohn–Sham theory will be applied to obtain the exact Hartree–Fock energy rather than the exact energy from the Schrödinger equation, and the energy functional is naturally expressed in terms of orbitals, not in terms of the density. Let us establish first that this is a well-posed problem.

As was argued before, the Hartree–Fock energy is a functional of the density. This functional is most easily thought of as being constructed by varying the external potential. A particular choice of $v_a(\mathbf{r})$ leads by solving the Hartree–Fock equations, that is, minimizing $\langle \Phi_a | \hat{H}_a | \Phi_a \rangle$, where $\hat{H}_a = \hat{T} + \hat{V}_a + \hat{W}$ and $|\Phi_a\rangle$ is a single determinant, to a particular density $\rho_a(\mathbf{r})$, and a set of canonical orbitals $\{\varphi_i(\mathbf{r})\}$. The energy can be decomposed as

$$E_a^{\text{HF}} = \langle \hat{T} \rangle_a + \langle \hat{V}_a \rangle + E_a^H + E_a^X, \quad (33)$$

where the dependence of the components of the energy on the choice of auxiliary external potential is made explicit by the subscript a . In the above, E_a^H indicates the Hartree or Coulomb energy and E_a^X denotes the Hartree–Fock exchange energy.

It transpires that one can identify the exchange energy as a function of external potential, or of the corresponding Hartree–Fock density as

$E^X[\rho_a] = E_a^{\text{HF}} - \langle T \rangle_a - \langle \hat{V}_a \rangle - E_a^H$, and in terms of orbitals it is given explicitly by

$$\begin{aligned} E^X[\{\varphi_i\}] &= E^X[\Phi] = -\frac{1}{2} \sum_{i,j \in \text{occ}} \int \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\equiv -\frac{1}{2} \sum_{i,j} \langle ij | ji \rangle, \end{aligned} \quad (34)$$

while $\sum_i \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}) = \rho_a(\mathbf{r})$. It is to be noted that this exchange energy functional is exact by construction. Likewise, the kinetic energy $\langle T \rangle_a$ by construction is a functional of the auxiliary external potential and hence of the density. The Hohenberg–Kohn Hartree–Fock energy functional as a function of the density is defined by replacing the auxiliary potential energy term $\langle \hat{V}_a \rangle$ by the true potential energy $\langle \hat{V}^{\text{Ne}} \rangle$, yielding

$$E^{\text{HK-HF}}[\rho_a] = \langle \hat{T} \rangle[\rho_a] + \langle \hat{V}^{\text{Ne}} \rangle[\rho_a] + E^H[\rho_a] + E^X[\rho_a]. \quad (35)$$

Optimizing this functional following the Hohenberg–Kohn prescription will yield the exact Hartree–Fock energy, and the density corresponding to the minimum is $\rho^{\text{HF}}(\mathbf{r})$, corresponding to an external potential $v_a(\mathbf{r}) = v^{\text{Ne}}(\mathbf{r})$. This is all precisely analogous to previous Hohenberg–Kohn descriptions for the exact energy, as discussed in Section 1.

The above prescription can also be followed within a Kohn–Sham density functional scheme and appears to be particularly simple in this context as all terms of the functional are known in terms of orbitals, in particular the Hartree–Fock and Kohn–Sham form of the kinetic energy are identical. Therefore, following the Hohenberg–Kohn construction, *one would expect to obtain the exact Hartree–Fock energy from a Kohn–Sham exact exchange calculation.*

Within the framework of conventional Kohn–Sham theory, however, the above statement is surprising. The orbitals of the Kohn–Sham determinant are imposed to satisfy a one-electron Schrödinger equation corresponding to a multiplicative potential. This acts as a constraint and the energy of a single determinant for which the orbitals satisfy a local Kohn–Sham equation is higher than the unconstrained Hartree–Fock energy. This is well established in the literature on work on the so-called optimized effective potential [11] (for recent insightful work see Refs [13,14]). In this context, it is perhaps worthwhile to quote a paragraph (page 9) in a recent paper by Görling [12], which deals in detail with the subject: “... it was shown that minimization of the total energy expression does not lead to the KS equations for the orbitals [in case of exact exchange]. However, if in addition the orbitals are also required to be eigenfunctions of one-particle Schrödinger equations with a local multiplicative potential, the [optimized] effective potential v_{oepr} , then

minimization leads to the Kohn–Sham equation.” Another quote from this paper (same page) reads: “Therefore the exchange-only Kohn–Sham total energy has to be larger or at best equal to the Hartree–Fock energy. In practice it turns out that the two energies are almost identical.” Consulting the recent reference [13], this energy difference is 0.6 mH for the Be atom and 1.7 mH for the Neon atom, implying it appears to be chemically significant for these small systems, and the difference is likely to grow with the size of the system.

It is hard to see anything wrong with the above formal Hohenberg–Kohn Hartree–Fock construction, and it would spell major trouble for DFT if the exact Hartree–Fock energy would not be a functional of the density, as all steps for the existence of the proof are analogous to the Hohenberg–Kohn construction for the exact energy. Likewise, Kohn–Sham theory is expected to be a particular realization of the Hohenberg–Kohn construction and is likewise expected to be in principle exact, also for Hartree–Fock theory. On the other hand, if orbitals are required to satisfy a one-electron Schrödinger equation with a multiplicative potential, this is well established (see above) to yield a real constraint, and the optimal energy for such a determinant is higher than the Hartree–Fock limit in general. There is no doubt about this, at least if the equations are solved numerically “exactly,” and not in a finite basis set [12–14].

To resolve this conundrum requires that we reinvestigate the construction of the Hartree–Fock–Kohn–Sham functional. The Hohenberg–Kohn Hartree–Fock energy functional is given by

$$E^{\text{HK-HF}}[\rho_a] = \langle \hat{T} \rangle_a + \langle \hat{V}^{\text{Ne}} \rangle[\rho_a] + E^H[\rho_a] + E^X[\rho_a]. \quad (36)$$

However, in this functional the kinetic energy refers to the stationary Hartree–Fock orbitals, which satisfy the nonlocal Hartree–Fock equations. This kinetic energy is a functional of the density, by its construction through the external potential and solving the respective Hartree–Fock equations, but it is *not* the Kohn–Sham definition of kinetic energy. In order to obtain the kinetic energy as a functional of the density as it is used in the Kohn–Sham equation, one would have to evaluate the corresponding noninteracting form of the kinetic energy (obtaining orbitals that correspond to the same density but satisfying a Schrödinger equation with a local potential), and we can hence write

$$\begin{aligned} E^{\text{KS-HF}}[\rho_a] &= T_s[\rho_a] + \langle \hat{V}^{\text{Ne}} \rangle + E^H[\rho_a] + E^X[\rho_a] + \left(\langle \hat{T} \rangle_a - T_s[\rho_a] \right) \\ &= T_s[\rho_a] + \langle \hat{V}^{\text{Ne}} \rangle + E^H[\rho_a] + E^{\text{TX}}[\rho_a], \end{aligned} \quad (37)$$

where we have defined an effective Hartree–Fock kinetic exchange energy functional, $E^{\text{TX}}[\rho]$, which will have a complicated form in general. In order to obtain the exact Hartree–Fock energy within a conventional Kohn–Sham

framework requires a density functional component for the kinetic energy correction, and hence the Hartree–Fock Kohn–Sham functional is not simply the Hamiltonian expectation value of the Kohn–Sham determinant. It will be clear that the exact Kohn–Sham functional for the Hartree–Fock energy is not known explicitly in practice, and this is due to the definition of the kinetic energy in the Kohn–Sham framework. It is intriguing that in practice the form for the kinetic energy term, $-1/2\sum_i \int \varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})d\mathbf{r}$, appears to be exactly the same in Kohn–Sham theory and in Hartree–Fock theory, while they refer to different functionals of the density: $T_s[\rho_a]$, $\langle T \rangle[\rho_a]$. In Kohn–Sham theory, this “implicit” use of $T_s[\rho]$ is accomplished by taking functional derivatives with respect to the external potentials. It is understood that one cannot take the derivative with respect to one particular orbital, as this implies a change in the external potential and this in turn involves all orbitals. It transpires that the definition of $T_s[\rho]$ is not as simple as one might think. The solution of the Kohn–Sham equation using a multiplicative potential is implicitly used to define $T_s[\rho]$. Let us note that these issues are already there for the case of the Kohn–Sham kinetic energy functional, as discussed before, although here a straightforward treatment of taking explicit orbital derivatives leads, to some extent fortuitously, to the proper result.

There is a much simpler way to obtain the exact Hartree–Fock energy, and this is to consider the functional $E^{\text{HK-HF}}[\{\varphi_a\}] = \langle \Phi | \hat{T} | \Phi \rangle + \langle V^{\text{Ne}} \rangle + \langle \Phi | \hat{W} | \Phi \rangle$, as a functional of the orbitals (or the determinant), and to minimize this energy expression directly as a functional of the orbitals. This is nothing but Hartree–Fock theory of course, and it gives rise to one-electron equations that involve the nonlocal exchange operator from Hartree–Fock theory

$$\frac{\delta E^x}{\delta \varphi_i(\mathbf{r})} = -2 \sum_j \varphi_j(\mathbf{r}_2) \frac{1}{|\mathbf{r} - \mathbf{r}_2|} \varphi_i(\mathbf{r}_2) d\mathbf{r}_2 \varphi_j(\mathbf{r}) = 2 \left(\hat{K}^x[\Phi] \varphi_i \right)(\mathbf{r}). \quad (38)$$

The question arises if this type of functional derivative might be used immediately in a Kohn–Sham-like theory, by generalizing the definition of the orbital-dependent kinetic energy operator. This is discussed next.

3.3. Kohn–Sham exchange theory

Below, an alternative mathematically straightforward procedure is described to deal with exchange energy in a DFT framework. Following very much the same logic as in the beginning of this section, one can treat the kinetic energy and exchange energy together. In the resulting “Kohn–Sham exchange” (KSX) theory, the sum of the kinetic energy and exchange energy as a functional of the density is approximated by the minimum of the orbital-dependent definition $E_{\text{TX}}[\{\varphi_i\}] = \sum_i \langle \varphi_i | \hat{T} | \varphi_i \rangle - 1/2 \sum_{i,j} \langle ij | ji \rangle$ over all

orthonormal set of orbitals that yield a particular density $\rho_a(\mathbf{r}) = \sum_j |\varphi_j(\mathbf{r})|^2$. Since this minimum only depends on the input density, it is a functional of $\rho_a[\mathbf{r}]$. As before, the orbitals will only be defined up to a unitary transformation, and it is more appropriate to speak of the single determinant $|\Phi\rangle$ constructed from the orbitals and which yields the density $\rho_a[\mathbf{r}]$. To obtain this kinetic/exchange energy corresponding to a particular density, one can minimize the functional

$$L_{\text{TX}}[\rho_a] = -\frac{1}{2} \sum_j \int \varphi_j^*(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \sum_{j,i} \langle ij | ji \rangle + \int \mu(\mathbf{r}) \left[\sum_j |\varphi_j(\mathbf{r})|^2 - \rho_a(\mathbf{r}) \right] d\mathbf{r} - \sum_{i,j} \varepsilon_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right), \quad (39)$$

where, as before, a continuous Lagrangian multiplier field $\mu(\mathbf{r})$ is introduced to insure that the orbitals sum up to the density if the functional is required to be stationary with respect to variations in $\mu(\mathbf{r})$, while the discrete Lagrange multipliers ε_{ij} insure orthonormality of the orbitals at stationarity with respect to the ε_{ij} . The stationary condition for the orbitals deriving from the functional $L_{\text{TX}}[\rho_a]$ can be expressed in canonical form as

$$-\frac{1}{2} \nabla^2 \varphi_i(\mathbf{r}) + [\hat{K}^X[\Phi] \varphi_i](\mathbf{r}) + \mu(\mathbf{r}) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (40)$$

and it follows that the orbitals should satisfy a one-electron Schrödinger equation that contains the usual Hartree–Fock exchange operator $\hat{K}^X$ corresponding to the orbitals, in addition to a local multiplicative potential. As was demonstrated before, the total Hartree–Fock-like energy is a functional of the density, following a Hohenberg–Kohn construction, and therefore so is the kinetic exchange component

$$E^{\text{TX}}[\rho_a] = E^{\text{HF}}[\rho_a] - E^H[\rho_a] - \int v_a(\mathbf{r}) \rho_a(\mathbf{r}) d\mathbf{r} = E^{\text{TX}}[\{\varphi_i\}] = \sum_i \langle \varphi_i | \hat{T} | \varphi_i \rangle - \frac{1}{2} \sum_{i,j} \langle ij | ji \rangle, \quad (41)$$

where the latter form is valid (only) if the (canonical) orbitals satisfy the nonlocal one-electron Schrodinger equation of the type of Eq. (40).

The KSX Hartree–Fock functional is then given by

$$E^{\text{KSX-HF}} = E^{\text{TX}}[\rho] + \langle V^{\text{Ne}} \rangle + E^H[\rho] = \sum_i \langle \varphi_i | \hat{T} | \varphi_i \rangle - \frac{1}{2} \sum_{i,j} \langle ij | ji \rangle + \int V^{\text{Ne}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E^H[\rho], \quad (42)$$

which appears to simply the Hartree–Fock expression for the energy, but the constraint on the orbitals is implicit. If we now consider this energy as a functional of the Lagrange-multiplier field as before, we obtain for the stationarity condition

$$\begin{aligned} \frac{\delta E^{\text{KSX-HF}}}{\delta \mu(\mathbf{r})} = 0 = 2 \int \left[\sum_i -\frac{1}{2} \nabla^2 \varphi_i(\mathbf{r}') + (\hat{K}^X[\Phi] \varphi_i)(\mathbf{r}') \right. \\ \left. + [V^{\text{Ne}}(\mathbf{r}') + V^H(\mathbf{r}')] \varphi_i(\mathbf{r}') \right] \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} d\mathbf{r}' \end{aligned} \quad (43)$$

and substituting using Eq. (40), one finds for the stationarity condition

$$\frac{\delta E^{\text{KSX-HF}}}{\delta \mu(\mathbf{r})} = 2 \int \left[-\mu(\mathbf{r}') + V^{\text{Ne}}(\mathbf{r}') + V^H(\mathbf{r}') + \varepsilon_i \right] \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} d\mathbf{r}' = 0 \quad (44)$$

which, invoking the orthogonality condition, Eq. (29), to remove the dependence on the orbital energy, shows that the Lagrange multiplier field can simply be taken as the sum of the nuclear–electron attraction and the Hartree potential, in other words, the local multiplicative part of the Fock operator. This implies in turn that Eq. (40) at the minimum reduces to the conventional Hartree–Fock equations.

This solution may appear to be somewhat disingenuous. Rather than creating a Kohn–Sham theory of the Hartree–Fock energy, the Hartree–Fock method is essentially declared to be a DFT. The argument is made that this is indeed a small step to take, if one views the original Kohn–Sham kinetic energy functional from a constrained search perspective and turns this into a constrained search kinetic–exchange functional.

3.4. Generalizations of the Kohn–Sham exchange formalism to an exact density functional theory

The ideas can be generalized, and the exchange kinetic energy functional can be combined with the original Hohenberg–Kohn functional for the energy, defining the correlation energy functional $E^C[\rho] = E^{\text{TW}}[\rho] - E^{\text{TX}}[\rho] - E^H[\rho]$, such that the orbital-dependent functional

$$\begin{aligned} E^{\text{KSX}}[\rho] &= E^{\text{TX}}[\rho] + \langle V^{\text{Ne}} \rangle + E^H[\rho] + E^C[\rho] \\ &= \sum_i \langle \varphi_i | \hat{T} | \varphi_i \rangle - \frac{1}{2} \sum_{i,j} \langle ij | ji \rangle + \int v^{\text{Ne}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E^H[\rho] + E^C[\rho] \end{aligned} \quad (45)$$

defines an in principle exact DFT, including exact exchange [9,10,15,16]. The resulting KSX equations take the form

$$(\hat{T} + \hat{K}^X[\Phi] + \hat{V}^{\text{KSX}})|\varphi_i\rangle = \varepsilon_i^{\text{KSX}}|\varphi_i\rangle, \quad (46)$$

where $\hat{V}^{\text{KSX}}$ corresponds to a local multiplicative potential, in agreement with the treatment of $E^{\text{TX}}[\rho]$ as a functional of the density. This will be the case if $E^{\text{C}}[\rho]$ is approximated as an explicit functional of the density. This is a small step to take at this point, but the implications are that by adding a correlation correction $E^{\text{C}}[\rho]$ to the traditional Hartree–Fock energy expression, one can in principle obtain exact results for both the energy and the density.

3.5. Further generalizations to orbital-dependent Kohn–Sham formulations

The above presents but one possibility. In general, one can assign a part of the Hohenberg–Kohn functional, $E^{\text{TW}}[\rho]$, to an explicit orbital-dependent energy expression, denoted as $E^{\text{O}}[\{\varphi_i\}] \equiv E^{\text{O}}[\Phi]$, where $|\Phi\rangle$ denotes the determinant associated with the orbitals. The superscript O denotes the implicit *orbital-dependent* part of the energy. This energy expression is turned into a functional of the density, by minimizing the energy expression subject to the constraint that the orbitals yield the given density $\sum_i |\varphi_i(\mathbf{r})|^2 = \rho(\mathbf{r})$. The minimization can be carried out using the Lagrange multiplier procedure and will lead to

$$\frac{\delta E^{\text{O}}[\{\varphi_i\}]}{\delta \varphi_i(\mathbf{r})} + \lambda(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}). \quad (47)$$

The functional derivative of $E^{\text{O}}[\{\varphi_i\}]$ with respect to $\varphi_i(\mathbf{r})$ can be evaluated explicitly and will result in general into an orbital-dependent Kohn–Sham or “OKS” equation that can be represented as

$$(\hat{K}^{\text{O}}[\Phi] \varphi_i)(\mathbf{r}) + \lambda(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}). \quad (48)$$

The form of the operator $\hat{K}^{\text{O}}[\Phi]$ is explicitly known if one assumes a definite expression for $E^{\text{O}}[\{\varphi_i\}]$, and in general will depend on the orbitals, requiring a self-consistent solution therefore. The continuous Lagrange multiplier field $\lambda(\mathbf{r})$ defines a local potential. Importantly, the minimization procedure turns the energy expression into a functional of the density, and conversely if the orbitals satisfy an equation of the type of Eq. (48), the energy expression $E^{\text{O}}[\{\varphi_i\}]$ is stationary, although not necessarily a minimum. The remaining part of the full Hohenberg–Kohn $E^{\text{TW}}[\rho]$ can then formally be defined as

$$E^{\text{TW/O}}[\rho] = E^{\text{TW}}[\rho] - E^{\text{O}}[\rho] \quad (49)$$

and the OKS density functional takes the explicit form

$$E^{\text{OKS}}[\{\varphi_i\}] = E^{\text{O}}[\{\varphi_i\}] + \int v^{\text{Ne}}(\mathbf{r})\rho(\mathbf{r})\mathbf{d}\mathbf{r} + E^{\text{TW/O}}[\rho]. \quad (50)$$

The unknown part of the functional $E^{\text{TW/O}}[\rho]$ is to be modeled as an explicit function of the density, such that the functional derivatives with respect to the Lagrange multiplier field $\mu(\mathbf{r})$, which has a one-to-one correspondence to the density, can be evaluated as

$$\begin{aligned} \frac{\delta E^{\text{TW/O}}[\rho]}{\partial \mu(\mathbf{r})} &= \sum_i \int \frac{\delta E^{\text{TW/O}}[\rho]}{\delta \rho(\mathbf{r}'')} \frac{\delta \rho(\mathbf{r}'')}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \mathbf{d}\mathbf{r}'' \mathbf{d}\mathbf{r}' \\ &= 2 \sum_i \int \frac{\delta E^{\text{TW/O}}[\rho]}{\delta \rho(\mathbf{r}'')} \delta(\mathbf{r}'' - \mathbf{r}') \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \mathbf{d}\mathbf{r}'' \mathbf{d}\mathbf{r}' \\ &= 2 \sum_i \int \frac{\delta E^{\text{TW/O}}[\rho]}{\delta \rho(\mathbf{r}')} \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \mathbf{d}\mathbf{r}' \\ &\equiv 2 \sum_i \int v^{\text{TW/O}}(\mathbf{r}') \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \mathbf{d}\mathbf{r}'. \end{aligned} \quad (51)$$

Importantly, this provides a form involving the action of a local multiplicative potential. Using Eq. (48), the stationarity of the energy with respect to the Lagrangian multiplier field takes the by now familiar expression

$$\frac{\delta E^{\text{OKS}}}{\delta \mu(\mathbf{r})} = 2 \int \left[-\mu(\mathbf{r}') + V^{\text{Ne}}(\mathbf{r}') + v^{\text{TW/O}}(\mathbf{r}') + \varepsilon_i \right] \varphi_i(\mathbf{r}') \frac{\delta \varphi_i(\mathbf{r}')}{\delta \mu(\mathbf{r})} \mathbf{d}\mathbf{r}' = 0 \quad (52)$$

with the solution $\mu(\mathbf{r}) = V^{\text{Ne}}(\mathbf{r}) + v^{\text{TW/O}}(\mathbf{r})$, which combined with Eq. (48) yields

$$(\hat{K}^{\text{O}}[\Phi] \varphi_i)(\mathbf{r}) + v^{\text{Ne}}(\mathbf{r})\varphi_i(\mathbf{r}) + v^{\text{TW/O}}(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}). \quad (53)$$

Upon solving the equation self-consistently, the orbitals define a stationary value of the orbital-dependent component of the total energy $E^{\text{OKS}}[\rho]$, and of the explicitly orbital-dependent part energy $E^{\text{O}}[\{\varphi_i\}]$, as required. It is not necessarily a minimum, and this is potentially a problem, but this is no different from the situation in regular Kohn–Sham calculations. Let us note, that in analogy to regular Kohn–Sham formulations, the mathematically less careful procedure of taking explicit orbital-dependent derivatives, while employing $\delta \rho(\mathbf{r}')/\delta \varphi_i(\mathbf{r}) = 2\varphi_i(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$, will yield the same final result, Eq. (53), for essentially the same reasons as it does for traditional Kohn–Sham formulations.

The above generalization can be used to derive formally exact hybrid Hartree–Fock schemes as discussed a decade ago [17,18]. In that work also, the generalization of the adiabatic connection and the corresponding perturbation expansion of the correlation energy [10] were discussed, building on the locality of the remaining part of the potential.

The extensions of the above OKS or KSX schemes to nonuniversal density functionals, of either the Yukawa-type, as discussed in Section 2.2, or to the explicitly modified functionals, for example to include van der Waals corrections (see Section 2.4), are essentially straightforward and are happily left to the interested reader.

4. CONCLUDING REMARKS

The principal goal of the above investigations and survey of generalizations of the Hohenberg–Kohn and Kohn–Sham constructions is to assess the uniqueness of density functional theory, to provide a framework to discuss universality, and to discuss the meaning of “in principle exact” in the context of DFT. This is also an attempt to disjoin the formal properties of DFT from its practical aspects and successes. Summarizing the findings regarding generalizations of Hohenberg–Kohn constructions, the various types of in principle exact functionals are illustrated in Figure 4.1. For any molecular external potential, the Hohenberg–Kohn functional yields the exact ground state energy and the exact ground state density at its minimum. The Hohenberg–Kohn functional is unique by construction if the explicit dependence of the energy on the molecular external potential follows the most straightforward definition $\int V^{\text{Ne}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$. Various examples have been given of constructions for *nonuniversal* functionals, which for any molecular external potential yield the exact energy at their minimum, but typically not the exact density. The unknown part of the functional will then also depend on the external molecular potential. Post-Hartree–Fock functionals have also been discussed, which for any molecular potential yield the exact ground state energy for precisely the Hartree–Fock density (and the result can be generalized to other computationally well-defined densities), but they are not necessarily minima of the functionals. Finally, in Figure 4.1, a hypothetical functional is shown, which for any molecular potential is intended to yield the exact energy and exact density at its minimum but which deviates from the Hohenberg–Kohn energy for other values of the (auxiliary) density, while keeping the molecular potential fixed. No explicit mental construction of such a hypothetical functional was given, and it is not clear to me at the moment if this can actually be done, but the picture is easily imagined. The functional would be of the nonuniversal type. The discussed generalizations of the Hohenberg–Kohn

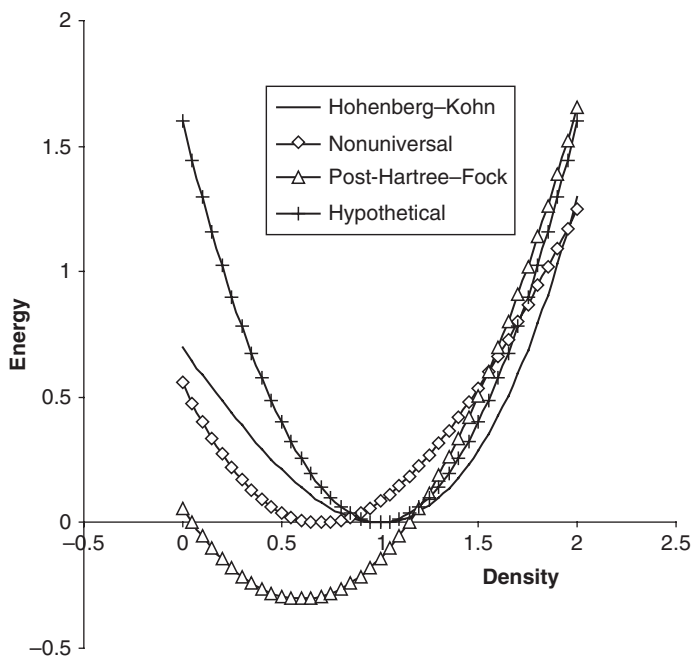


Figure 4.1 Illustrations of different, in principle exact, functionals of the density. The total energy including electron–nuclear attraction energy is plotted against “density,” depicted in one dimension. The solid line indicates the Hohenberg–Kohn functional, which defines the exact ground state energy (0) and the exact ground state density (“1”). Nonuniversal functionals yield the exact energy at their minimum but not the exact density (in the figure at ~ 0.7). Post-Hartree–Fock functionals yield the exact energy at the Hartree–Fock density (at ~ 1.2 in the figure), but this is not a minimum. The “hypothetical” functional yields exact energy and density at the minimum but is different from the Hohenberg–Kohn functional away from the minimum.

theorem are perhaps not very satisfactory to practitioners in the field as they significantly change the formal properties of the functional, in particular its universality.

The generalizations of the Kohn–Sham method are quite different in this respect, as the universal part of the original Hohenberg–Kohn density functional, denoted throughout the paper as $E^{\text{TW}}[\rho]$, can be partitioned in many different ways into an orbital-dependent part and a remainder. If the orbital-dependent part is turned into a functional of the density, for example, by minimization, the result is a universal DFT. The choice of treating kinetic energy in an orbital-dependent way, as in the Kohn–Sham framework, is perhaps the most straightforward choice, but formally there is a large array of possibilities here. From a formal point of view, the KSX formalism would be perhaps most appealing, as it avoids the problem of

spurious self-interactions, but in practice it appears to be difficult to create accurate functionals of this type, and current DFT functionals are often considered accurate precisely because they achieve an implicit cancellation between exchange and correlation contributions. Baerends and Gritsenko have raised strong arguments for this point of view [31].

The above are the essential findings of the paper, many of which are known, although perhaps not all that well disseminated. In this final section, I would like to explore the implications of these findings and draw a comparison between wave function-based methods, DFT, and molecular mechanics (see also the recent paper by Kutzelnigg [4]). There are no “exact” answers here, merely a pondering of perhaps rather “metaphysical” questions that may yield some further clarity or stir discussion. The discussion may appear to be biased toward wave function-based methods, and for this reason molecular mechanics also plays a role in the discussion. Readers may at least to some extent share my views regarding molecular mechanics but may feel my conclusions regarding DFT are pushing things too far. Let me note that I personally think it is logically more tenable to disagree with me earlier on, already at the level of molecular mechanics.

A first question one might ask is “Can we expect to find ever more accurate density functionals, for example, by exploring formal requirements, and might we even imagine finding the exact functional in due time?” To guide our thinking, we might reason by analogy. For example, would it be reasonable a priori to expect to find “the exact laws of physics”? I think many scientists would share my view, that this is actually very surprising and counterintuitive. Perhaps, if such mathematical laws indeed exist, one can contemplate plausible (or possible) structures (e.g., classical mechanics, Maxwell equations, quantum mechanics, and general relativity theory), all of which already require a lot of imagination. Another step might involve guessing elementary interactions. In our current laws of physics and chemistry, these appear to be exceedingly simple and these interactions are pairwise, at least to a great degree of accuracy. If they were not so simple, it is far less likely that these laws would ever be discovered. Let me also note that in many fields of science, such as biology or studies of mesoscopic structures, exact laws are less prevalent than in physics and chemistry. The discovery of the laws of physics that appear to have universal validity is truly extraordinary, inspiring thoughts of mystical or religious proportions. To explore the question at the top of this paragraph further, let us turn to a more mundane realm of the wide spectrum of scientific explorations. It was argued in this paper that molecular mechanics is in principle exact, in the sense that the (Born–Oppenheimer) ground state energy is a function of the details of the nuclear framework. In this case, it does not appear reasonable to expect that one will ever discover the exact universal force field. In particular, the force field would require higher body interactions, and these are hard to model, let alone describe exactly. I do not

think that the “in principle exact” of molecular dynamics plays any role in practical investigations.

So what about the exact density functional? It would seem reasonable to expect also this functional to be complicated, far more complicated than our current imaginations, I think. The fact that it is in principle exact should not be counted as a compelling argument in favor of the likelihood of finding it, in analogy with the molecular mechanics case. An argument in favor of pursuing the quest for the exact (or ever more accurate) density functional is its universality, within a particular domain of application, for example, chemistry and solid state physics governed by electronic interactions. Hence, in contrast to molecular mechanics, the unknown troublesome part of the energy functional in DFT is universal, that is, does not depend on the (molecular) external potential. This distinction appears to carry a lot of weight in the current assessment of DFT. However, the distinction disappears for the nonuniversal density functionals discussed in this chapter in the context of generalizations of the Hohenberg–Kohn construction. It was already argued that in practice one might well, unknowingly, be modeling such nonuniversal functionals, while in addition molecular densities contain implicit information about the nuclear framework, such that the non-universality of the functionals carries little or no practical importance. I am tempted to infer therefore that the “exact in principle” in the practice of chemistry has the same validity in molecular mechanics and in DFT.

There is another side to this issue, however. In the DFT community, much theoretical work is based on the fact that DFT *is* indeed in principle exact. Hence, the notion of exactness is a clear factor in the design of functionals and in particular imposes useful constraints. Most of the theoretical developments to date are based on universal formulations of DFT and in particular on Kohn–Sham theory and the associated model of non-interacting electrons in the appropriate external potential. It would appear that a consideration of nonuniversal density functionals might remove some of the constraints imposed, and it is not clear to me to what degree considerations of exactness would continue to play a role in such a more general framework. The most pertinent remark is perhaps that at present the potential exactness of DFT does have obvious merit.

The above critique of the notion “in principle exact” and a reflection on its meaning in DFT leads to the question of the status of DFT in a formal theoretical context. In particular, can DFT be regarded as a (nonempirical) first-principles computational methodology? To answer this question, it is pertinent perhaps to define first what one might mean by a first-principles computational method. The starting point in this context is Schrödinger’s equation in a nonrelativistic, clamped nucleus formulation. This is the theoretical component, and it can be considered the universal starting point for all computational methods in the current context. In most *ab initio* or wave function-based methods such as configuration interaction or

coupled cluster, a finite basis set is introduced, an excitation manifold is considered, and the resulting equations are solved numerically. *Within the confines* of the method, convergence of the computational parameters can be tested in principle, and one might even assess to what extent the Schrödinger equation (the theory) is satisfied, for example, by calculating the dispersion $\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2$ (evaluating $\hat{H}^2$ in real space). The dispersion is always greater than or equal to zero and vanishes only for the exact solution. Hence, dispersion can serve as an intrinsic measure of the accuracy of a solution and it is in principle accessible, at a somewhat tractable cost, a cost at the least far less than checking the satisfaction of the 3N-dimensional Schrödinger equation itself. Calculating the dispersion in principle requires knowledge of the four-particle reduced density matrix within the finite basis set calculation, in addition to four-body integrals of $\hat{H}^2$. The situation is clearly different in a molecular mechanics context. One may parameterize different force fields, but within the confines of molecular mechanics there is no means to test the validity of the method. The only possibility is to check results, for molecular geometries, vibrational frequencies, or energy differences between conformations, against external data, either experimental or data obtained at a higher level of theory, meaning a more robust and accurate computational methodology.

What then is the situation in DFT? Clearly, the numerical precision of density functional calculations can be tested within the confines of DFT, for example, regarding basis set convergence. Moreover, formal constraints and scaling arguments can be used to assess to some extent the formal quality of a particular density functional approximation. However, there is no internal way to rigorously test the accuracy of a density functional method, against the exact solution of Schrödinger's equation. Density functionals also need to be calibrated either against experimental results (in so far as these agree with the models used and taking into account the limitations of the clamped nucleus nonrelativistic Schrödinger equation in comparison to experiment) or against higher levels of computational methodology. They are no different in this respect from force field methods and they have an empirical component. The density functional method should not therefore be considered a first-principles computational method, if one accepts the requirement that such a method should be able to check (exact) theory within its own confines. On these grounds, it is reasonable to rank wave function-based *ab initio* methods at a higher rank in the hierarchy, even if they are less widely applicable and even if they are in their practical application less accurate than DFT methods. They do possess the possibility of internal testing of convergence and accuracy.

We can also ask the question regarding the various purposes of computations, simulations, and theoretical investigations. Obviously, computations serve a very practical purpose in that they assist the interpretations of experimental results and that the understanding gained by theoretical

considerations is often key in suggesting further experiments or potential applications. In this regard, molecular mechanics, DFT, and a wealth of other approximate simulation techniques are clearly very useful. They often yield results of sufficient accuracy to aid experimentalists and in a timely fashion. Wave function-based methods have an additional role to play, however, in the sense that their systematic convergence to the proper solution of the theoretical model considered to represent experiment allows one to unambiguously assess the validity of the model itself. This is less clear for computational methods that cannot provide such a systematic convergence.

Besides these practical considerations, there is a far less tangible argument, which nevertheless may play a role in evaluating different computational methodologies. In brief, this refers to the “beauty” factor of our science, which I suspect provides substantial motivation for many of us to pursue our hard work. There are various dimensions to the beauty factor, and no doubt part of this is quite personal. For many of us, the understanding of particular phenomena may be the quintessential scientific experience. All of science has its own aspects of beauty, and understanding is not directly related to the “accuracy” of simulations or experiment. In my mind, however, among the various branches of science, physics is exceptionally beautiful. The fact that we know that the laws of physics (e.g., the Schrödinger equation) are (to large agree) a very accurate representation of reality inspires awe in the human intellectual enterprise, uplifting the human spirit. In this sense, wave function methods pay homage to this aspect of the scientific enterprise, as they attempt to systematically solve the most fundamental laws of nature. Clearly, molecular mechanics can have fewer poetic claims in this regard, and in my opinion, also DFT is somewhat removed from this most fundamental level of science, as it does not directly address solving the Schrödinger equation, that is, the fundamental laws of nature. These are considerations that are clearly outside the realm of a scientific journal, and it is perhaps appropriate to quote the maxim “Beauty is in the eye of the beholder,” as it is unlikely there is universal agreement on the above sentiments. Nonetheless, I think it is clear that these subjective notions influence scientific explorations, and practitioners of DFT may have analogous sensibilities regarding the use of the methods of molecular mechanics, which are so far removed from the fundamental quantum world, compared to DFT.

In a related, but somewhat more down to earth context, considerations of generalizations of DFT are illuminating, because they emphasize the mathematical nature of the construction. For many practitioners in the field, DFT appears to have taken on the power of a new physics, which is based on an *observable* quantity, the electron density. In addition, in the practical construction of new functionals, physical arguments and even physical intuition often play an important role. The point of view taken in this chapter is

altogether different. Here, DFT is considered foremost a mathematical construction, and this is confirmed by the fact that there are many ways to proceed, all leading to different functionals, each of which is exact in principle. This qualifies the value of the “in principle exact” statement and the physical content of the theory. One can hence make the argument that obtaining suitable approximations to a density functional is primarily an “engineering” problem, not a deep problem in physics. The fact that many different exact functionals formally exist may actually simplify the task, and it helps to rationalize the existence of the plethora of accurate functionals in the literature, which might perhaps be viewed as approximations to different members of the extended family of exact, albeit nonuniversal, density functionals. But, in my opinion, the existence of many different exact functionals, which are not obviously all “somehow” mathematically equivalent (e.g., in the sense of Dirac’s transformation theory), also suggests that the physical content of DFT is easily overrated. I might once more draw upon the analogy with molecular mechanics: while physical ideas enter the construction of force fields, they are indirect and do not necessarily refer to the underlying fundamental laws of physics.

The above remarks are critical of the emphasis in much of formal DFT on the fact that the theory is in principle exact. The reader may have got the impression that one can turn almost any approach into an approximation to a formally exact theory (I consider my most extreme example the add-on to describe van der Waals interactions). I think such a view is probably largely correct, and it indicates that the emphasis should simply not be on this formal property: If virtually “everything” one does is formally exact, the statement ceases to have significance. While a destructive undercurrent regarding DFT may appear to have motivated this chapter, and in particular this final section, one can take a more constructive view. This chapter also indicates that there are many, many, different ways to tackle the electronic structure problem from a density functional point of view, and all of these one might formally rank on the same level: Traditional Hohenberg–Kohn/Kohn–Sham universal density functionals, yielding exact energy and density; nonuniversal density functionals containing an explicit contribution to the energy, which is dependent on the molecular external potential (the van der Waals example); nonuniversal potentials that will not yield exact densities (the Yukawa example); post-Hartree–Fock density functionals that do not need to be evaluated at their minimum; KSX theory that is a direct generalization of Hartree–Fock theory; and other orbital-dependent density functionals leading to nonlocal potentials. All of these different possibilities are valid approaches to the problem, and I have tried to argue that even present day functionals might perhaps better be viewed from this more general point of view. The generalizations include the traditional Hohenberg–Kohn and Kohn–Sham formalism, and taking a wider view on the formalism simply opens up more possibilities, which is always good from an engineering point of

view although I hasten to ascertain, nonuniversal functionals may not be aesthetically pleasing.

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CHAPTER 5

Multiple, Localized, and Delocalized/Conjugated Bonds in the Orbital Communication Theory of Molecular Systems

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1. INTRODUCTION

In this chapter, the bold-face symbol **X** represents a square or rectangular matrix, the bold-face italic *X* denotes a row vector, and the ordinary italic *X* stands for a scalar quantity corresponding to the quantum mechanical operator $\hat{X}$. The entropy/information descriptors of molecular probability

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distributions and communication channels are measured in *bits*, which correspond to the base 2 in the logarithmic (Shannon) measure of information.

The techniques and concepts of the information theory (IT) [1–8] have been shown to provide novel, efficient tools for tackling diverse problems in the theory of molecular electronic structure [9–12]. Among other developments, the IT definition of atoms-in-molecules (AIM) [9,13] has provided additional support to Hirshfeld's [14] "stockholder" division of the molecular electron distribution into atomic contributions. The information content of electronic distributions in molecules has been examined [9,15,16], the entropic origins of the chemical bond have been investigated [9,17–21], and a thermodynamic-like description of the electronic "gas" in molecular systems has been attempted [9,22]. The electron localization function [23] has been shown to explore the nonadditive part of the Fisher information [1–3] in the molecular orbital (MO) resolution [9,24], while a similar approach in the atomic orbital (AO) representation generates the so-called contra-gradiance descriptors of chemical bonds, related to the matrix representation of the electronic kinetic energy operator [25]. The molecular quantum mechanics and IT are related [11,25–27] through the Fisher (locality) measure of information [1–3], which represents the gradient content of the system wave function, thus being proportional to the average kinetic energy of electrons. The stationary Schrödinger equation marks the optimum probability amplitude of the Fisher information principle including the constraint of the fixed value of the system potential energy.

The Shannon theory of communication [4–6] has been used to probe bonding patterns in molecules within the communication theory of the chemical bond (CTCB) [9,17–21]. The key concept of this IT approach is the molecular information system, which can be constructed at alternative levels of resolving the electron probabilities into the underlying elementary "events" determining the channel inputs $A = \{a_i\}$ and outputs $B = \{b_j\}$, for example, of finding an electron on the basis-set orbital, AIM, and molecular fragment. They can be generated within both the local and the condensed descriptions of electronic probabilities in a molecule. Such molecular information networks describe the probability/information propagation in a molecule and can be characterized by the standard quantities developed in IT for real communication devices. Due to electron delocalization throughout the network of chemical bonds in a molecule, the transmission of "signals" about the electron assignment to the underlying events of the resolution in question becomes randomly disturbed, thus exhibiting the communication "noise." Indeed, an electron initially attributed to the given atom/orbital in the channel "input" A (molecular or promolecular) can be later found with a nonzero probability at several locations in the molecular "output" B .

This feature of the electron delocalization is embodied in the conditional probabilities of the outputs given inputs, $P(B|A) = \{P(a_i|b_j)\}$, which define the molecular channel. Both the *one*-electron [28,29] and the *two*-electron

[9,17–21,30,31] approaches have been devised to construct this matrix. The latter uses the simultaneous probabilities of two electrons in a molecule, assigned to the input and output, respectively, to determine the network conditional probabilities, while the former constructs the orbital pair probabilities using the superposition principle of quantum mechanics [32].

The CTCB, originally formulated within the Shannon theory, has recently been extended to cover the molecular Fisher channels in orbital resolution [28,29]. The overall IT bond-multiplicity indices and their covalent/ionic components generated for several model systems in the integral atomic resolution have been shown to generally agree with intuitive chemical expectations [9,17–21]. In the orbital resolution, both the “geometrical” and the “physical” conditional probabilities have been distinguished [31]. The former are determined by all MO resulting from the adopted basis set, occupied and virtual, while the latter involve the probability scattering via the occupied MO alone. The consecutive cascades of information systems representing the elementary orbital transformation and electron excitation stages have been applied to generate the resultant channels for an effective orbital promotion due to the system chemical bonds [31,32], and the probability-scattering perspective on atomic promotion due to orbital hybridization has been reported [21]. Several strategies for molecular subsystems have been designed [9,19,20], and the atomic resolution of bond descriptors has been proposed [33]. The relation between CTCB and the familiar valence bond (VB) theory [34] has been examined [35] and molecular similarities explored [9,36]. Moreover, the configuration-projected channels for excited states have been developed [37] and the ensemble-average channels of deterministic components have been introduced [38]. Within the *local* resolution [38–42], the Hirshfeld communication systems of stockholder AIM have been examined [30,39,40] and the numerical values of the entropy/information indices for the chemical bond in H₂ have been estimated [38,41]. The channel reduction technique [6,9,19] has been applied to separate the effects due to the AIM *promotion* (polarization) as well as the *forward* and *back* donations between bonded atoms [29]. The relation between the interorbital contributions to the entropy/information descriptors of the Shannon channel and Wiberg’s quadratic indices of the bond covalency has been established [28,29].

To summarize, this development has widely explored the use of the average communication-noise (delocalization, indeterminacy) and information-flow (localization, determinacy) indices as novel descriptors of the overall IT covalency and ionicity, respectively, of all chemical bonds in the molecular system as a whole, the *internal* bonds present in its constituent subsystems, and the *external*, interfragment bonds. It is the main purpose of this work to further extend the range of recent applications of this *one*-electron approach to molecular information systems in the orbital representation. The emphasis will be placed on illustrating the versatility of this new tool in

probing diverse bonding patterns in molecules and on how it is actually applied to tackle familiar, textbook issues in the electronic structure theory.

After the method brief summary the conditional probabilities for the open-shell configurations are developed and the relation between the off-diagonal communications and the quadratic indices of the chemical bond [42–52] is examined. Several illustrative model applications are then presented, which cover both the single (localized) bonds in hydrides and the multiple bonds in CO and CO₂, as well as the conjugated π -bonds in simple hydrocarbons (allyl, butadiene, and benzene), for which predictions from the *one*- and *two*-electron approaches are compared. The IT bond descriptors are generated for both molecules as wholes and their constituent fragments. The latter are extracted using the appropriate reductions of the channel outputs. The main goal of this analysis is to investigate the bond differentiation effects, which have been found to be poorly represented in the *two*-electron treatment [9]. The atom promotion in hydrides will also be tackled, again to compare predictions of the new *one*-electron information systems to those resulting from the previous *two*-electron cascades [21]. Finally, the information origins of the π -bond conjugation in simple hydrocarbons will be investigated in detail, by extracting the IT indices characterizing the molecular channels in the diatomic bond representation.

2. ENTROPIC DESCRIPTORS OF MOLECULAR INFORMATION CHANNELS IN ORBITAL RESOLUTION

Let us first assume, for simplicity, the molecular closed-shell ground state for $N=2n$ electrons, that is, the configuration of the n lowest (real and orthonormal), doubly occupied MO expanded as linear combinations of the appropriate (orthogonalized) basis functions $\chi = (\chi_1, \chi_2, \dots, \chi_m) = \{\chi_i\}$, $\langle \chi | \chi \rangle = \{\delta_{i,j}\} \equiv \mathbf{I}$, for example, Löwdin's symmetrically orthogonalized AO: $\phi = (\phi_1, \phi_2, \dots, \phi_n) = \{\phi_s\} = \chi \mathbf{C}$; here the rectangular matrix $\mathbf{C} = \{C_{i,s}\}$ groups the relevant expansion coefficients of the linear combinations of atomic orbitals (LCAO). The system electron density and the associated density-per-electron $p(\mathbf{r}) = \rho(\mathbf{r})/N$, the probability distribution or the *shape* factor of ρ ,

$$\rho(\mathbf{r}) = 2\phi(\mathbf{r})\phi^\dagger(\mathbf{r}) = \chi(\mathbf{r}) [2\mathbf{C}\mathbf{C}^\dagger] \chi^\dagger(\mathbf{r}) \equiv \chi(\mathbf{r}) \gamma \chi^\dagger(\mathbf{r}) = Np(\mathbf{r}), \quad (1)$$

are determined by the charge and bond-order (CBO) matrix γ in the AO representation, which represents the projection operator $\hat{P}_\phi$ onto the subspace of all occupied MO:

$$\gamma = 2\langle \chi | \phi \rangle \langle \phi | \chi \rangle \equiv 2\langle \chi | \hat{P}_\phi | \chi \rangle = \left\{ \gamma_{i,j} = 2\langle \chi_i | \hat{P}_\phi | \chi_j \rangle \equiv 2\langle i | \hat{P}_\phi | j \rangle \right\}. \quad (2)$$

It satisfies the idempotency relation:

$$(\gamma)^2 = 2\gamma. \quad (3)$$

The CBO matrix reflects the promoted, valence state of AO in the molecule, with the diagonal elements measuring the effective electron occupations of the basis functions, $\{\gamma_{i,i} = N_i = Np_i\}$, where p_i denotes the molecular probability of χ_i being occupied; they determine the molecular AO probability vector, $\mathbf{p} = \{p_i\}$.

The information system in the (condensed) orbital resolution involves the AO events χ in its input, $\mathbf{A} = \{\chi_i\}$, and output $\mathbf{B} = \{\chi_j\}$, thus representing the effective promotion of these basis functions in the molecule. In order to determine the entropy/information indices of the system chemical bonds, this channel can be probed using both the promolecular ($\mathbf{p}^0 = \{p_i^0\}$) and the molecular ($\mathbf{p}$) input probabilities, in order to extract the IT multiplicities of the *ionic* and *covalent* components, respectively. The “communication” network linking all AO inputs and outputs is determined by the conditional probability matrix, with the input (row) and the output (column) indices, respectively,

$$\mathbf{P}(\mathbf{B}|\mathbf{A}) = \left\{ P(j|i) = \frac{P_{ij}}{p_i} \right\}, \quad \sum_j P(j|i) = 1; \quad (4)$$

here the simultaneous *two*-orbital probabilities $\mathbf{P}(\mathbf{A}, \mathbf{B}) = \{P_{ij}\}$ satisfy the usual normalization:

$$\sum_i \sum_j P_{ij} = \sum_i p_i = \sum_j p_j = 1. \quad (5)$$

Both *two*-electron and *one*-electron approaches in orbital resolution have been previously adopted to generate the conditional probabilities between the specified orbital “events” in a molecule. The former conditions the probabilities of finding one electron on the specified AO in the molecular “output” on the *parameter* event of another electron being located on the given AO in the molecular “input.” The physical *one*-electron probabilities explore the dependencies between AO resulting from the occupied MO in the given electron configuration, which generate the network of chemical bonds. It is the main purpose of this work to compare these two types of communication networks for several prototype molecules and to explore the associated differences in the entropy/information bond compositions they generate. The emphasis will be placed on the *one*-electron treatment, since the other approach has been widely explored in previous works [9,17–21,30,31,33–41].

As argued elsewhere [28,29], the conditional probabilities of quantum states, embodied in the superposition principle of quantum mechanics [32], involve the squares of the moduli of the relevant expansion coefficients, which represent projections of one state onto another. For example,

a geometric conditional probability $P^g(\psi|\phi)$ of the state ψ given another state ϕ , given by the square of the corresponding overlap integral $\langle\phi|\psi\rangle$, can be expressed as the expectation value of the corresponding projection operators:

$$\begin{aligned} P^g(\psi|\phi) &= |\langle\phi|\psi\rangle|^2 = \langle\psi|\phi\rangle\langle\phi|\psi\rangle \equiv \langle\psi|\hat{P}_\phi|\psi\rangle \\ &= \langle\phi|\psi\rangle\langle\psi|\phi\rangle \equiv \langle\phi|\hat{P}_\psi|\phi\rangle = P(\phi|\psi), \end{aligned} \quad (6)$$

where $P(\psi|\psi) = P(\phi|\phi) = 1$. This conditional probability is thus determined by the expectation value in the *variable* state, say ψ , of the projection operator $\hat{P}_\phi$ onto the *parameter* (reference) state ϕ . When applied to AO, with $\phi = \chi_i$ and $\psi = \chi_j$, these probabilities can be also thought of as involving additional projection onto the whole molecular Hilbert space spanned by the adopted basis functions χ , which is equivalent to the projection onto all MO derived from them, $\phi^{o+v} = (\phi, \phi^v)$, including both the occupied (ϕ) and the virtual (ϕ^v) MO, $\hat{P}_\chi \equiv |\chi\rangle\langle\chi| = |\phi^{o+v}\rangle\langle\phi^{o+v}| \equiv \hat{P}_\phi^{o+v} = \hat{P}_\phi + \hat{P}_\phi^v = 1$,

$$P^g(j|i) = \langle i|j\rangle\langle j|i\rangle = \langle j|\hat{P}_\phi^{o+v}|i\rangle\langle i|\hat{P}_\phi^{o+v}|j\rangle. \quad (7)$$

The corresponding physical probability $P(j|i)$ in the molecular ground state [Eq. (4)] represents the dependence of the variable (output) AO χ_j on the reference (input) AO χ_i via the system of all chemical bonds generated by the occupied MO. Therefore, it similarly involves the renormalized square of the subspace projection

$$P(j|i) = \mathcal{N}_i \left| \langle i|\hat{P}_\phi|j\rangle \right|^2 = (2\gamma_{i,i})^{-1} \gamma_{i,j} \gamma_{j,i}, \quad (i,j) = 1, 2, \dots, m, \quad (8)$$

where the normalization constant $\mathcal{N}_i = (2\gamma_{i,i})^{-1}$ follows directly from Eq. (3). The conditional probabilities $\mathbf{P}(\mathbf{B}|\mathbf{A})$ then define the corresponding simultaneous probabilities $\mathbf{P}(\mathbf{A},\mathbf{B})$, for the specified pairs of the input and output AO,

$$P_{i,j} = p_i P(j|i) = (2N)^{-1} \gamma_{i,j} \gamma_{j,i}, \quad (i,j) = 1, 2, \dots, m. \quad (9)$$

It should be emphasized that the normalization constant $\mathcal{N}_i = (2\gamma_{i,i})^{-1}$ [Eq. (8)] applies only to the closed-shell configurations. Indeed, by using the idempotency relation of Eq. (3), one then directly verifies the relevant normalization condition:

$$\sum_j P(j|i) = (2\gamma_{i,i})^{-1} \sum_j \gamma_{i,j} \gamma_{j,i} = 1. \quad (10)$$

In the open-shell case, one partitions the CBO matrix into contributions originating from the closed-shell (doubly occupied) MO φ_β and the open-shell (singly occupied) MO φ_α , $\varphi = (\varphi_\alpha, \varphi_\beta)$:

$$\gamma = \langle \chi | \varphi_\alpha \rangle \langle \varphi_\alpha | \chi \rangle + 2 \langle \chi | \varphi_\beta \rangle \langle \varphi_\beta | \chi \rangle \equiv \langle \chi | \hat{P}_\varphi^\alpha | \chi \rangle + 2 \langle \chi | \hat{P}_\varphi^\beta | \chi \rangle \equiv \gamma^\alpha + \gamma^\beta. \quad (11)$$

They satisfy separate idempotency relations,

$$\begin{aligned} (\gamma^\alpha)^2 &= \langle \chi | \hat{P}_\varphi^\alpha | \chi \rangle \langle \chi | \hat{P}_\varphi^\alpha | \chi \rangle = \langle \chi | (\hat{P}_\varphi^\alpha)^2 | \chi \rangle = \langle \chi | \hat{P}_\varphi^\alpha | \chi \rangle = \gamma^\alpha, \\ (\gamma^\beta)^2 &= 4 \langle \chi | \hat{P}_\varphi^\beta | \chi \rangle \langle \chi | \hat{P}_\varphi^\beta | \chi \rangle = 4 \langle \chi | (\hat{P}_\varphi^\beta)^2 | \chi \rangle = 4 \langle \chi | \hat{P}_\varphi^\beta | \chi \rangle = 2\gamma^\beta, \end{aligned} \quad (12)$$

where we have recognized the idempotency/orthogonality of the MO projections, $\hat{P}_\varphi^\alpha \hat{P}_\varphi^\beta = \hat{P}_\varphi^\beta \delta_{\alpha,\beta}$, and the identity character of the overall AO projection: $\hat{P}_\chi \equiv |\chi\rangle\langle\chi| = 1$. Hence, taking again

$$P(j|i) = \mathcal{N}_i \left| \langle i | \hat{P}_\varphi | j \rangle \right|^2 = \left(\gamma_{i,i}^\alpha + 2\gamma_{i,i}^\beta \right)^{-1} \gamma_{i,j}^\alpha \gamma_{j,i}, \quad (13)$$

one determines the generalized normalization constant $\mathcal{N}_i = (\gamma_{i,i}^\alpha + 2\gamma_{i,i}^\beta)^{-1}$ to satisfy the sum rule for conditional probabilities in i th row of $\mathbf{P}(\mathbf{B}|\mathbf{A})$:

$$\begin{aligned} \sum_j P(j|i) &= \left(\gamma_{i,i}^\alpha + 2\gamma_{i,i}^\beta \right)^{-1} \sum_j \left(\gamma_{i,j}^\alpha + \gamma_{i,j}^\beta \right) \left(\gamma_{j,i}^\alpha + \gamma_{j,i}^\beta \right) \\ &= \left(\gamma_{i,i}^\alpha + 2\gamma_{i,i}^\beta \right)^{-1} \sum_j \left(\gamma_{i,j}^\alpha \gamma_{j,i}^\alpha + \gamma_{i,j}^\beta \gamma_{j,i}^\beta \right) \\ &= \left(\gamma_{i,i}^\alpha + 2\gamma_{i,i}^\beta \right)^{-1} \left(\gamma_{i,i}^\alpha + 2\gamma_{i,i}^\beta \right) = 1. \end{aligned} \quad (14)$$

Above, we have used the idempotency relations of Eq. (12) and realized that

$$\sum_j \gamma_{i,j}^\alpha \gamma_{j,i}^\beta = 2 \langle i | \hat{P}_\varphi^\alpha | \chi \rangle \langle \chi | \hat{P}_\varphi^\beta | i \rangle = \langle i | \hat{P}_\varphi^\alpha \hat{P}_\varphi^\beta | i \rangle = \sum_j \gamma_{i,j}^\alpha \gamma_{j,i}^\beta = \langle i | \hat{P}_\varphi^\beta \hat{P}_\varphi^\alpha | i \rangle = 0. \quad (15)$$

The conditional probabilities of Eqs (8) and (13) define the probability scattering in the AO promotion channel of the molecule, in which the “signals” of the molecular (or promolecular) electron allocations to basis functions are transmitted between the AO inputs and outputs. Such information system constitutes the basis of the *one*-electron approach in CTCB [9,28,29]. This open-shell development can be straightforwardly generalized into the case of fractional MO occupations, which result from the ensemble averaging of the above CBO contributions due to integer MO occupations.

To summarize, the conditional probability $P(j|i)$ represents the appropriately renormalized square of their mutual projection, for example, of χ_j

onto χ_i due to their involvement in all occupied MO, which embody the system chemical bonds. Hence, the diagonal conditional probability of i th AO output, given i th AO input, $P^p(i|i) = \gamma_{i,i}/2 = N_i/2$, is generally different from unity, when the orbital of one atom takes part in chemical interactions with empty or partly occupied orbitals of remaining atoms.

The off-diagonal conditional probability of j th AO output given i th AO input is thus proportional to the squared element of the CBO matrix linking the two AO, $\gamma_{j,i} = \gamma_{i,j}$. Therefore, it is also proportional to the corresponding AO contribution to the Wiberg index of the chemical bond covalency [42]. When formulated within the ordinary spin-restricted Hartree-Fock (RHF) theory of the assumed closed-shell electronic configuration, the elementary “covalent” contribution due to an interaction between orbitals χ_i and χ_j originating from atoms A and B, respectively, is measured in Wiberg’s approach by the square of the corresponding CBO matrix element coupling these two basis functions, $\mathcal{M}_{i,j} = \gamma_{i,j}^2$. Such contributions then generate the resultant interatomic index

$$\mathcal{W}^W(A, B) = \sum_{i \in A} \sum_{j \in B} \mathcal{M}_{i,j}. \quad (16)$$

Various generalized forms of such quadratic descriptors of molecular bond orders have been widely applied in both the HF and the Kohn–Sham (KS) MO theories [43–52]. In the difference approach to quadratic bond multiplicities, which combines the covalent and the ionic components of the system chemical bonds, the squares of the diagonal CBO elements, which determine the distribution of electrons among basis functions, are classified as “ionic” [46–52].

In CTCB, the entropy/information indices of the covalent/ionic components of all chemical bonds in a molecule represent the complementary descriptors of the average communication noise and the amount of information flow in the molecular information channel. Both the molecular, $p(A) \equiv p$, and the promolecular, $p(A^0) \equiv p^0 = \{p_i^0\}$, input probabilities are used to probe a scattering of the AO probabilities among basis functions, in order to extract the IT-covalent/IT-ionic composition of the overall bond multiplicity. These alternative inputs produce the corresponding molecular-output probabilities:

$$p(A) \mathbf{P}(B|A) = p \quad \text{and} \quad p^0 \mathbf{P}(B|A) = p^*(A^0) = \{p_j^*\}, \quad (17)$$

where in general $p \neq p^*$. The purely molecular communication system is devoid of any reference (history) of the chemical bond formation and generates the average noise index of the bond covalency, measured by the conditional entropy $S(B|A) \equiv S$ of the system outputs given inputs:

$$S(B|A) = - \sum_i p_i \sum_j P(j|i) \log P(j|i) \equiv S[p|p] \equiv S. \quad (18)$$

The promolecular channel refers to the initial state in this process, for example, represented by the atomic “promolecule” – a collection of non-bonded (free atoms) in their respective positions in a molecule. It gives rise to the average information-flow descriptor of the bond ionicity, representing the mutual information in the channel input and output events:

$$I(\mathbf{A}^0; \mathbf{B}) = \sum_i p_i^0 \sum_j P(j|i) \log \left[\frac{P(j|i)}{p_j^*} \right] = \sum_i p_i^0 \sum_j P(j|i) \log \left[\frac{P(j|i)}{p_i^0} \right] \equiv I[\mathbf{p}^0; \mathbf{p}^*] \equiv I. \quad (19)$$

Finally, their sum

$$N(\mathbf{A}^0; \mathbf{B}) = S + I \equiv N[\mathbf{p}^0; \mathbf{p}] \equiv N \quad (20)$$

measures the overall IT bond multiplicity in the molecular system under consideration. These complementary descriptors of two dependent sets of events are schematically represented by the corresponding areas in Figure 5.1. It follows from this diagram that in the particular case, when $\mathbf{p} = \mathbf{p}^* = \mathbf{p}^0$, $N[\mathbf{p}; \mathbf{p}] = H[\mathbf{p}]$.

For the vanishing CBO matrix element between the specified AO, the associated conditional probability vanishes, so that there is no *direct* “communication” link between these orbitals in the molecular communication system. This does not imply, however, that there is no effective chemical bond interaction in IT between these two basis functions. Indeed, such orbitals, by being simultaneously involved in the probability scattering to remaining orbitals in the chemical bond system are in fact *indirectly* communicating with themselves. Therefore, it comes as no surprise that they will exhibit finite entropy/information indices of their resultant chemical interaction in a

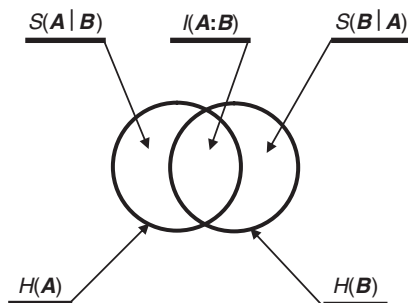


Figure 5.1 The entropy information indices characterizing two dependent probability distributions $\mathbf{p} = \mathbf{p}(\mathbf{A}) = \{p_i\}$ and $\mathbf{q} = \mathbf{q}(\mathbf{B}) = \{q_j\}$. In this diagram, the circles represent the Shannon entropies of the separate distributions, $H(\mathbf{A}) = -\sum_i p_i \log p_i = H[\mathbf{p}]$ and $H(\mathbf{B}) = -\sum_j q_j \log q_j = H[\mathbf{q}]$, the overlap area depicts their mutual information $I(\mathbf{A}; \mathbf{B}) = I[\mathbf{p}; \mathbf{q}]$, while the remaining parts of both circles denote the conditional entropies $S(\mathbf{A} | \mathbf{B}) = S[\mathbf{p} | \mathbf{q}]$ and $S(\mathbf{B} | \mathbf{A}) = S[\mathbf{q} | \mathbf{p}]$; $H[\mathbf{p}] = S[\mathbf{p} | \mathbf{q}] + I[\mathbf{p}; \mathbf{q}]$, $H[\mathbf{q}] = S[\mathbf{q} | \mathbf{p}] + I[\mathbf{p}; \mathbf{q}]$.

molecule. Therefore, the sharp Coulson/Wiberg criterion that the vanishing γ_{ij} implies no chemical interaction between χ_i and χ_j can be regarded as being oversimplified, missing a wealth of all indirect sources of the chemical bond, which add to the subtlety of this important and complex concept.

It should be finally emphasized that these entropy/information descriptors and the underlying probabilities depend on the selected basis set, for example, the canonical AO of isolated atoms or the hybrid orbitals (HO) of their promoted (valence) states, and the localized MO (LMO). We shall illustrate this dependence in the following, applicative sections of this chapter.

3. ILLUSTRATIVE APPLICATION TO LOCALIZED BONDS IN HYDRIDES

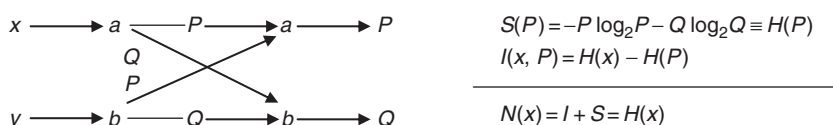
The localized bond between the given pair of atoms A and B in a molecule can be modeled as a result of a chemical interaction between the corresponding pair of the singly occupied canonical or directed (hybrid) orthonormal orbitals $a \in A$ and $b \in B$ of atomic valence shells, which gives rise to the doubly occupied (bonding) MO:

$$\varphi_b = \sqrt{P}a + \sqrt{Q}b, \quad P+Q = 1. \quad (21)$$

Its shape is determined by the complementary (conditional) probabilities $P(a|\varphi_b) = P$ and $P(b|\varphi_b) = Q$, which control the bond polarization, covering the symmetrical bond for $P = Q = 1/2$ and the limiting lone-pair (zero bond) configurations for $P = (0, 1)$. The model CBO matrix,

$$\gamma = 2 \begin{bmatrix} P & \sqrt{PQ} \\ \sqrt{PQ} & Q \end{bmatrix}, \quad (22)$$

then generates the information system shown in [Scheme 5.1](#), for the general input probability vector $\mathbf{p}^0 = (x, y = 1 - x)$. It follows from this scheme that the IT covalency of this simplest localized bond (in bits) is measured by the conditional entropy (average noise) represented by the binary entropy function $H(P) = -P \log_2 P - Q \log_2 Q$, reaching the highest value for the symmetric bond configuration, $H(P = 1/2) = 1$, and vanishing for the lone-pair configurations, $H(P = 0) = H(P = 1) = 0$, which mark the ion-pair configurations A^+B^-



Scheme 5.1 The two-orbital information system modeling the localized bond and its entropy/information descriptors (in bits).

and A^-B^+ , respectively, relative to the initial orbital occupations $N^0 = (1, 1)$ corresponding to $p^0 = (1/2, 1/2)$ in the atomic promolecule. Accordingly, the complementary IT ionicity index, determining the channel (mutual) information capacity $I(x=1/2, P) = 1 - H(P)$, reaches the highest value for these two limiting electron-transfer configurations, $I(x=1/2, P=0, 1) = 1$. This component identically vanishes for the symmetric bond, $I(x=1/2, P=1/2) = 0$ [9]. Both components yield the conserved overall bond index $N(x=1/2) = 1$, in the whole range of bond polarizations: $P \in [0, 1]$.

Therefore, this simple model transparently accounts for the competition between the bond covalency and ionicity, while preserving the overall 1 bit measure describing the resultant bond multiplicity of this single chemical bond.

This localized bond model can be naturally extended into the familiar scenario of r -localized bonds in simple hydrides XH_r , for example, CH_4 , NH_3 , or H_2O , for $r = 4, 3, 2$, respectively. A single σ -bond $X-H_\alpha$, $X = C, N, O$, $\alpha = 1, \dots, r$, can be regarded as resulting from the chemical interaction of a pair of the orthonormal orbitals: the bonding sp^3 hybrid h_α of the central atom, directed toward the hydrogen ligand H_α , and the $1s_\alpha \equiv H_\alpha$ orbital of the latter. The localized bond $X-H_\alpha$ then originates from the doubly occupied bonding MO:

$$\varphi_\alpha = \sqrt{P}h_\alpha + \sqrt{Q}H_\alpha, \quad P+Q=1. \quad (23)$$

The corresponding CBO matrix $\gamma^{HO/AO} = \{\gamma_{\alpha,\beta}\}$ in this minimum basis set of valence-shell orbitals $\chi^{HO/AO} = (h_1, \dots, h_r, H_1, \dots, H_r)$, which combine the HO of the central atom X and the AO of ligands, with the bonding α -hybrids placed before the remaining nonbonding β -hybrids, then include the following nonvanishing elements [see Eq. (16)]:

(1) for each pair of the chemically mixed orbitals of the preceding equation

$$\gamma_{h_\alpha, h_\alpha} = 2P, \quad \gamma_{H_\alpha, H_\alpha} = 2Q, \quad \gamma_{h_\alpha, H_\alpha} = \gamma_{H_\alpha, h_\alpha} = 2\sqrt{PQ}; \quad (24a)$$

(2) for each of $4r$ nonbonded hybrids $\{h_\beta\}$ describing the lone electronic pair

$$\gamma_{h_\beta, h_\beta} = 2. \quad (24b)$$

The corresponding nonvanishing conditional probabilities of Eq. (8), which determine the communication network in this orbital representation, thus read

$$P(h_\alpha|h_\alpha) = P, \quad P(H_\alpha|H_\alpha) = Q, \quad P(h_\alpha|H_\alpha) = Q, \quad P(H_\alpha|h_\alpha) = P, \quad P(h_\beta|h_\beta) = 1. \quad (25)$$

Therefore, the electron probability is not scattered by the lone-pair β -hybrids. As a result, they introduce the exactly vanishing contribution to the entropy-covalency index S , but their nonbonding (n) contribution I_n to the complementary index of the information ionicity I_n does not vanish. Hence, the average communication-noise descriptor counts only the bonding (b) interactions in the molecule, $S = S_b$, while the information flow index generally contains both the bonding and the nonbonding components: $I = I_b + I_n$.

The assumed initial (valence state) configurations of electrons in the three central atoms,

$$\begin{aligned} [C^v]^{\text{HO}} &\equiv [h_1^1 h_2^1 h_3^1 h_4^1] = [s^1 p_x^1 p_y^1 p_z^1] \equiv [C^v]^{\text{AO}}, \\ [N^v]^{\text{HO}} &\equiv [h_1^1 h_2^1 h_3^1 h_4^2] = [s^{5/4} p_x^{5/4} p_y^{5/4} p_z^{5/4}] \equiv [N^v]^{\text{AO}}, \\ [O^v]^{\text{HO}} &\equiv [h_1^1 h_2^1 h_3^1 h_4^2] = [s^{3/2} p_x^{3/2} p_y^{3/2} p_z^{3/2}] \equiv [O^v]^{\text{AO}}, \end{aligned} \quad (26)$$

and the ground-state configuration of all hydrogens $[H^0] = [H^1]$ then generate the following HO probabilities in the input of the valence-state information channels for $N=8$ valence electrons:

$$\begin{aligned} p_{\text{HO}}^v(\text{CH}_4) &= \left[\frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right], \\ p_{\text{HO}}^v(\text{NH}_3) &= \left[\frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{4}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right], \\ p_{\text{HO}}^v(\text{H}_2\text{O}) &= \left[\frac{1}{8}, \frac{1}{8}, \frac{1}{4}, \frac{1}{4}, \frac{1}{8}, \frac{1}{8} \right]. \end{aligned} \quad (27)$$

They give rise to the following molecularly promoted output probabilities:

$$\begin{aligned} p_{\text{HO}}(\text{CH}_4) &= p_{\text{HO}}^*(\text{CH}_4) = \left[\frac{P}{4}, \frac{P}{4}, \frac{P}{4}, \frac{P}{4}, \frac{Q}{4}, \frac{Q}{4}, \frac{Q}{4}, \frac{Q}{4} \right], \\ p_{\text{HO}}(\text{NH}_3) &= p_{\text{HO}}^*(\text{NH}_3) = \left[\frac{P}{4}, \frac{P}{4}, \frac{P}{4}, \frac{1}{4}, \frac{Q}{4}, \frac{Q}{4}, \frac{Q}{4} \right], \\ p_{\text{HO}}(\text{H}_2\text{O}) &= p_{\text{HO}}^*(\text{H}_2\text{O}) = \left[\frac{P}{4}, \frac{P}{4}, \frac{1}{4}, \frac{1}{4}, \frac{Q}{4}, \frac{Q}{4} \right]. \end{aligned} \quad (28)$$

In Table 5.1, we have listed the resulting entropy/information indices in the sp^3 -HO representation for the model chemical bonds in the valence shells of the three hydrides under consideration. It follows from the bonding (b) indices

Table 5.1 Entropy/information indices in the HO representation, relative to the valence states of Eq. (26), of localized chemical bonds in three illustrative hydrides

	CH ₄	NH ₃	H ₂ O
$S = S[p_{\text{HO}} p_{\text{HO}}] = S_b$	$H(P)$	$3/4 H(P)$	$1/2 H(P)$
$I = I[p_{\text{HO}}^v p_{\text{HO}}] = I_b + I_n$	2	2	2
I_n	0	$1/2$	1
$N[p_{\text{HO}}^v p_{\text{HO}}] = I + S$	$2 + H(P)$	$2 + 3/4 H(P)$	$2 + 1/2 H(P)$
$N_b = S_b + I_b$	$2 + H(P)$	$3/2 + 3/4 H(P)$	$1 + 1/2 H(P)$

reported in this table that in this model $S_b(X-H) = 1/4H(P)$ bits of entropy covalency and $I_b(X-H) = 1/2$ bits of information ionicity per single localized bond $X-H$, $X=C, N, O$, as well as $I_n(X) = 1/2$ bits of information ionicity per single lone pair of electrons on $X = N, O$, characterize the electronic structure of the valence shell of all these hydrides. They give rise to the overall IT index of $N_b(X-H) = 1/2 + 1/4 H(P)$ per bond, which reaches the maximum value of $N_b^{\max}(X-H) = 3/4$ for the symmetric MO of Eq. (23), when $P = Q = 1/2$, that is, $H(1/2) = 1$. With increasing polarization of the $X-H$ bond, when $P > Q$, this resultant entropic index is lowered, with increasing relative contribution from the IT ionicity component, which measures the degree of determinicity (localization) of the system probability scattering. For example, the polarized MO characterized by $P = 3/4$ ($Q = 1/4$) gives $S_b(X-H) = 0.20$, $I_b(X-H) = 1/2$, and hence $N_b^{\max}(X-H) = 0.70$ bits per localized chemical bond, relative to the assumed valence state of the central atom.

One also observes that due to the constant lone-pair ionicity I_n , the total bond index from the HO channel in water molecule, $N^{\max}(\text{O}-H) = 5/4$, exceeds 1 bit value characterizing a single symmetric chemical bond in Scheme 5.1. For the same reason, $N^{\max}(\text{N}-H) = 0.92$ is higher than its bonding part $N_b^{\max}(\text{N}-H) = 0.75$.

Expressing in Eq. (23) the sp^3 hybrids of the central atom in terms of AO and calculating the corresponding ground-state CBO matrix $\gamma^{\text{AO}} = \{\gamma_{ij}\}$ gives the associated conditional probability matrices $\mathbf{P}(\chi^{\text{AO}}|\chi^{\text{AO}}) = \{P(j|i)\}$ for these model hydrides in the AO representation $\chi^{\text{AO}} = [(s, p_x, p_y, p_z), (H_1, \dots, H_r)] \equiv (\chi^X, \chi^H)$. For example, in the most symmetric CH_4 case, when all hybrids are bonding, these probabilities can be summarized as follows:

$$\begin{aligned} P(j|i) &= P\delta_{ij}, \quad (i, j) \in \chi^X; & P(j|i) &= Q\delta_{ij}, \quad (i, j) \in \chi^H; \\ P(j|i) &= \frac{Q}{4}, \quad i \in \chi^X, j \in \chi^H; & P(j|i) &= \frac{P}{4}, \quad i \in \chi^H, j \in \chi^X. \end{aligned} \quad (29)$$

The molecular AO probabilities, $\mathbf{p}^{\text{AO}} = \{p_i\}$, similarly read: $p_i = P/4$, $i \in \chi^X$, and $p_i = Q/4$, $i \in \chi^H$. This molecular information channel in AO representation gives the entropy covalency,

$$S_b = S[\mathbf{p}^{\text{AO}}|\mathbf{p}^{\text{AO}}] = H(P) + 4PQ, \quad (30)$$

of all four bonds in methane, which reaches the maximum value $S_b^{\max} = 2$ for the symmetric MO, when $P = Q = 1/2$. Obviously, the estimate of the overall information ionicity $I_b = I[\mathbf{p}^{0, \text{AO}}; \mathbf{p}^{*, \text{AO}}]$ depends on the initial (promolecular) reference distribution $\mathbf{p}^{0, \text{AO}}$. The following choices of the ground-state configurations of carbon atom can be made: the spherically symmetrized open-shell configuration $[\bar{C}^0] = [s^2 p_x^{2/3} p_y^{2/3} p_z^{2/3}]$ and two choices of the nonspherical configurations $[C_1^0] = [s^2 p_x^2]$ and $[C_2^0] = [s^2 p_x^1 p_y^2]$. The corresponding expressions for I_b ,

$$I_b[\bar{C}^0] = 0.945P + Q, \quad I_b[C_1^0] = 0.708P + Q, \quad I_b[C_2^0] = 0.906P + Q, \quad (31)$$

give rise to the following bond-ionicity indices in the symmetrical MO, when $P = Q = 1/2$,

$$I_b[\bar{C}^0] = 0.97, \quad I_b[C_1^0] = 0.85, \quad I_b[C_2^0] = 0.95. \quad (32)$$

They generate the associated overall bond indices in the communication theory:

$$N_b[\bar{C}^0] = 2.97, \quad I_b[C_1^0] = 2.85, \quad I_b[C_2^0] = 2.95, \quad (33)$$

which compare favorably with the 3-bit value predicted from the HO expressions of Table 5.1. However, the bond covalent/ionic compositions are different in the AO representation compared to the corresponding HO representation predictions of Table 5.1. Each C—H bond now exhibits 1/2 of the (dominating) entropy-covalency contribution to the overall indices $N(\text{C—H}) = (0.74, 0.71, 0.74)$, for the three promolecular references, respectively, to be compared with the $N(\text{C—H}) = 0.75$ value predicted in the table, with 1/4 entropy-covalency component.

A similar analysis carried out for the ammonia and water molecules, which exhibit the lone pairs of electrons, gives for the symmetric combination of AO in the bonding MO and the reference heavy-atom configurations $[N^0] = [s^2 p_x^1 p_y^1 p_z^1]$ and $[O^0] = [s^2 p_x^{4/3} p_y^{4/3} p_z^{4/3}]$:

$$\begin{aligned} S(\text{NH}_3) &= 1.89, & I(\text{NH}_3) &= 0.90, & N(\text{NH}_3) &= 2.79, \\ S(\text{H}_2\text{O}) &= 1.41, & I(\text{H}_2\text{O}) &= 1.15, & N(\text{H}_2\text{O}) &= 2.56. \end{aligned} \quad (34)$$

The above N -predictions per bond, $N^{\text{AO}}(\text{N—H}) = 0.93$ and $N^{\text{AO}}(\text{O—H}) = 1.28$, are similar to those resulting from the corresponding HO channels, $N(\text{N—H}) = 0.92$ and $N(\text{O—H}) = 1.25$, but the predicted bond composition is again different. In the AO channels, the entropy covalency per bond, $S(\text{N—H}) = 0.63$ and $S(\text{O—H}) = 0.71$, dominates the overall index per single bond, in contrast to the bond composition resulting from the corresponding HO information system.

4. ATOM PROMOTION IN HYDRIDES

It has been shown recently [21,29] that the entropy/information indices of CTCB can be used to describe the polarization/promotion processes of the mutually closed atoms, from their ground states in the promolecule $[X^0]$ to their valence states $[X^v]$ in the molecule. The latter can exhibit both the orbital hybridization and/or the changes in orbital populations, due to effective electron excitations in molecular environment. In the previous study, the *two*-electron conditional probabilities resulting from the consecutive cascade of the elementary orbital-mixing and electron-excitation

subchannels has been used to generate such entropy/information descriptors of atomic electronic structure. Here, we shall use the *one*-electron open-shell communicational links defined by Eq. (13) to characterize the promotion of the heavy atoms in hydrides of the preceding section to their respective valence-state configurations of Eq. (26).

The sp^3 valence state gives rise to the identical valence-state probabilities of AO, $\chi = (s, p_x, p_y, p_z)$, in the atom as a whole: $p_x^v(\chi) = (1/4, 1/4, 1/4, 1/4)$. Again, the numerical values of the IT-ionic descriptors depend on the assumed promolecular reference, which determines the initial state of the atom promotion. In order to examine this dependence on the promotion origin, the three initial configurations of carbon defined in Section 3 will be examined: $\{[\bar{C}^0], [C_1^0], [C_2^0]\}$. For oxygen, we similarly examine two non-spherical references, $[O_1^0] = [s^2 p_x^2 p_y^2]$ and $[O_2^0] = [s^2 p_x^2 p_y^1 p_z^1]$, besides the previously introduced spherical atom configuration $[O^0] \equiv [\bar{O}^0]$. Finally, only the spherical reference $[N^0] \equiv [\bar{N}^0]$ will be considered for nitrogen, as representing the true ground-state configuration in accordance with the familiar Hund's rule of atomic physics.

The effective information channels can be derived from the corresponding CBO matrices γ^α and γ^β of Eq. (11), due to projections onto the doubly occupied, lone-pair hybrids $\{h_\beta\}$ and the singly occupied hybrids $\{h_\alpha\}$, respectively. Only the latter are chemically active, to form bonds with hydrogens, so that their number determines the chemical *valence* of the promoted atom. The relevant CBO data read as follows:

$$\gamma_C^\alpha = \gamma_C = \mathbf{I} = \{\delta_{i,j}\}, \quad \gamma_C^\beta = \mathbf{0};$$

$$\gamma_N^\alpha = \frac{1}{4} \begin{bmatrix} 3 & 1 & -1 & 1 \\ 1 & 3 & 1 & -1 \\ -1 & 1 & 3 & 1 \\ 1 & -1 & 1 & 3 \end{bmatrix}, \quad \gamma_N^\beta = \frac{1}{2} \begin{bmatrix} 1 & -1 & 1 & -1 \\ -1 & 1 & -1 & 1 \\ 1 & -1 & 1 & -1 \\ -1 & 1 & -1 & 1 \end{bmatrix}, \quad \gamma_O = \frac{1}{4} \begin{bmatrix} 5 & -1 & 1 & -1 \\ -1 & 5 & -1 & 1 \\ 1 & -1 & 5 & -1 \\ -1 & 1 & -1 & 5 \end{bmatrix};$$

$$\gamma_O^\alpha = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{bmatrix}, \quad \gamma_O^\beta = \begin{bmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{bmatrix}; \quad \gamma_O = \frac{1}{2} \begin{bmatrix} 3 & 0 & 0 & -1 \\ 0 & 3 & -1 & 0 \\ 0 & -1 & 3 & 0 \\ -1 & 0 & 0 & 3 \end{bmatrix}. \quad (35)$$

These matrices generate the following open-shell conditional probability matrices $\mathbf{P}_X(\chi|\chi)$ of Eq. (13):

$$\mathbf{P}_C(\chi|\chi) = \mathbf{I}, \quad \mathbf{P}_N(\chi|\chi) = \frac{1}{28} \begin{bmatrix} 25 & 1 & 1 & 1 \\ 1 & 25 & 1 & 1 \\ 1 & 1 & 25 & 1 \\ 1 & 1 & 1 & 25 \end{bmatrix}, \quad \mathbf{P}_O(\chi|\chi) = \frac{1}{10} \begin{bmatrix} 9 & 0 & 0 & 1 \\ 0 & 9 & 1 & 0 \\ 0 & 1 & 9 & 0 \\ 1 & 0 & 0 & 9 \end{bmatrix}. \quad (36)$$

They are seen to be strongly diagonally dominated, thus producing mainly populational (ionic) promotion of AO, with only marginal orbital-mixing (covalent) component. This observation is indeed confirmed by the numerical results listed in Table 5.2.

The carbon represents the limiting case, in which the covalent contribution exactly vanishes, marking the purely deterministic (diagonal) propagation of electron AO probabilities in the valence state. The overall IT index of the carbon promotion reproduces that resulting from the previous analysis using the information cascade [21], but these two approaches are seen to focus on the complementary aspects of the atom promotion process. The present (*one*-electron) treatment emphasizes its ionic (localization) facet, while the previous (*two*-electron) cascade development has focused on its covalent (delocalization) aspect.

It should be further observed that in the quantum mechanics, the two valence configurations of the carbon atom in Eq. (26), $[C^v]^{HO} = [h_1^1 h_2^1 h_3^1 h_4^1]$ and $[C^v]^{AO} = [s^1 p_x^1 p_y^1 p_z^1]$, are physically equivalent, since the two sets of singly occupied orbitals generate the same Slater determinant for the carbon atom as a whole. Therefore, it is not the IT-covalent component, which distinguishes the atomic valence state from its initial stage in the promotion process, but rather the associated IT-ionic descriptor of this process, stressing the deterministic aspect of the probability propagation in the atom promotion channel. This is exactly what the unit propagator $P_C(\chi|\chi) = I$ in Eq. (36) implies. One thus concludes that the present *one*-electron treatment correctly describes this atomic promotion as being of the purely ionic origin.

The new, *one*-electron information channels for the orbital promotion in the remaining atoms predict some entropy covalency in the promotion of

Table 5.2 Entropy/information indices of the heavy-atom promotion in hydrides, from the atomic ground-state configuration $[X^0]$ to the valence state $[X^v]$ of Eq. (26)

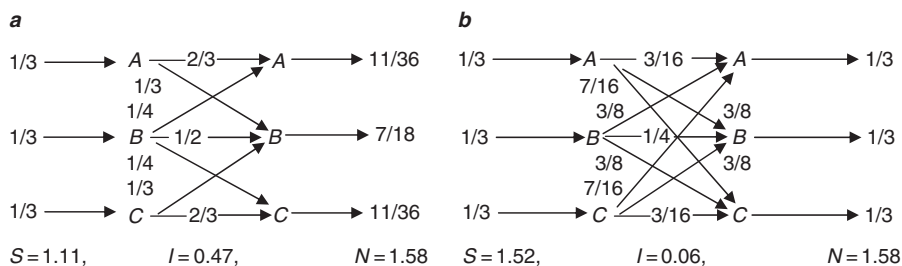
Index	$[X^0]$	$[C^v]$	$[N^v]$	$[O^v]$
S	—	0.00	0.66	0.47
$I[X^0]$	$[\bar{X}^0]$	1.79	1.28	1.51
	$[X_1^0]$	1.00	—	1.27
	$[X_2^0]$	1.50	—	1.48
$N[X^0]$	$[\bar{X}^0]$	1.79	1.94	1.98
	$[X_1^0]$	1.00	—	1.74
	$[X_2^0]$	1.50	—	1.95

nitrogen and oxygen, as indeed implied by the physical nonequivalence of the AO and HO for the unequal occupations of hybrids in the valence states of Eq. (26). The nitrogen promotion involves a relatively higher contribution from this orbital-mixing (noise) component, as indeed implied by the more numerous nonvanishing communicational connections in the conditional probability matrix of Eq. (36). However, the ionic contribution still dominates the overall indices $N[X^0] = S + I[X^0]$, about 2 bits each, of the atom promotion $[X^0] \rightarrow [X^v]$, thus demonstrating the mainly deterministic aspect of this process.

5. ONE- AND TWO-ELECTRON APPROACHES TO CONJUGATED π -BONDS IN HYDROCARBONS

The communication system of Scheme 5.1, common to both the *one*- and *two*-electron treatments, describes the *localized* σ - or π -bonds, for example, in H_2 and ethylene, respectively. However, these two approaches should generate different information channels for *delocalized* bonds in polyatomic systems, thus predicting different bond alternation patterns and the covalent/ionic composition of the overall IT bond multiplicity and its diatomic contributions. The *two*-electron probability propagation systems have been shown to give rise to only a minor differentiation of π -bonds in simple hydrocarbons, for example, between the nearest neighbors and the alternative pairs of more distant atoms in the carbon chain of allyl, butadiene, and benzene [9,19,20,52]. The technique of the channel output reduction, namely, combining several output events into a single, condensed (reduced) event, that is, by adding the associated columns of the conditional probability matrix, has been singled out as particularly convenient tool for extracting the internal and external bonds of molecular fragments [9,19]. Indeed, such manipulation hides the effects of the intrafragment communications, thus missing the entropy/information contributions due to internal bonds of the reduced fragment(s) in question. This technique has also been used recently to extract the effects due to the atom promotion, and the forward and back donations in the *three*-orbital model of the multiple bond [29].

In this section, we shall compare the performance of the new (*one*-electron) and the former (*two*-electron) information systems for the π -electron systems in allyl, butadiene, and benzene, generated in the condensed AO resolution of the Hückel theory. We shall focus on differences in the resulting ionic/covalent compositions of both overall bond descriptors and the entropy/information indicators of diatomic interactions in these prototype molecular systems. The effects due to bond conjugation will be addressed in Section 7.



Scheme 5.2 The *one*-electron (panel a) and *two*-electron (panel b) information channels of π -electrons in allyl. In panel a only the nonvanishing communication links are indicated. Below each diagram the corresponding overall bond indices (in bits) are reported.

In [Scheme 5.2](#) we have compared the two information systems for π -electrons in the carbon chain (A—B—C) of allyl. It follows from these diagrams that the two channels preserve the overall IT bond order of about $3/2$ bits, determined by the Shannon input (output) entropies. This is in a qualitative agreement with the chemical estimate of roughly 1.5 π -bond in this molecular system. The *one*-electron channel is more diagonally dominated, thus being more deterministic in character, giving rise to more information ionicity in the system. Indeed, there is distinctly more probability scattering (noise) in the *two*-electron channel, which thus generates more entropy covalency. This is reflected by numerical results reported in the scheme, with the *two*-electron channel exhibiting only a marginal level of IT ionicity, thus predicting almost purely covalent π -interactions in this radical carbon chain.

The diatomic IT descriptors of π -bonds in the carbon chain of allyl can be extracted by appropriate reductions of the two channels shown in [Scheme 5.2](#). It should be recalled that the *input* reduction determines the sources of the chemical bonds, while the *output* reduction defines the actual bonds being counted [\[9,19\]](#). Since we are interested in full AO origins of all bonds in the system, only the output-reduced information systems will be considered, giving rise to the overall bond indices missing contributions from the internal bonds in the condensed subset of orbitals. Therefore, the diatomic bond indices can be obtained as differences between the corresponding bond descriptors of the unreduced channel of [Scheme 5.2](#) and its reduced analog characterizing the information system with the diatomic fragment (X + Y) being considered as a single, combined unit in the output of the condensed channel. The results of such manipulations are reported in [Table 5.3](#).

Table 5.3 The overall and diatomic entropy/information indices $\mathcal{M} = S, I, N$ of π -bonds in allyl

Index	One-electron channel			Two-electron channel		
	A, B, C	$[A, B], C$	$[A, C], B$	A, B, C	$[A, B], C$	$[A, C], B$
$S(A, B, C)$	1.112	0.576	0.945	1.524	0.880	0.907
$I(A, B, C)$	0.473	0.312	0.019	0.061	0.039	0.011
$N(A, B, C)$	1.585	0.888	0.964	1.585	0.918	0.918
$S[X-Y]$	—	0.536	0.167	—	0.644	0.617
$I[X-Y]$	—	0.161	0.454	—	0.023	0.050
$N[X-Y]$	—	0.697	0.621	—	0.667	0.667

The IT-descriptors of the output-reduced fragment $[X, Y]$ determine the diatomic interactions: $\mathcal{M}[X-Y] = \mathcal{M}(X, Y, Z) - \mathcal{M}([X, Y], Z)$.

A reference to this table again shows that the two unreduced approaches give rise to dramatically different bond compositions, while preserving the overall IT bond index. The *one*-electron channel exhibits a substantial degree of determinism in the probability scattering, of approximately 1/3 of the overall bond multiplicity. The same trend is reflected in diatomic indices predicted within these two approaches. The *one*-electron treatment additionally produces a relatively sharp differentiation between a covalently strong, nearest-neighbor bond $A-B$ and the covalently weak bond $A-C$ between the terminal carbon atoms, with both interactions exhibiting a substantial IT-ionic contribution. This is in contrast to predictions from the *two*-electron channel, which gives practically the same, almost purely covalent, interactions in each case. Clearly, the former results are in a better agreement with the chemical expectations, thus again demonstrating the advantage of using the *one*-electron chemical bond-projected dependencies between AO in modeling the molecular information channels.

In Table 5.4, we report similar results for π -bonds in the carbon chain $M = (A, B, C, D)$ of butadiene. It should be observed that the descriptors $\mathcal{M} = S, I, N$ of the equal terminal π -bonds in this molecular system, $\mathcal{M}[A-B] = \mathcal{M}[C-D]$, can be estimated from the corresponding data of the unreduced (A, B, C, D) channel and the output-reduced channel $([A-B], [C-D])$: $\mathcal{M}[X-Y] = 1/2 [\mathcal{M}(A, B, C, D) - \mathcal{M}([A, B], [C, D])]$. One again observes that the unreduced *one*-electron channel generates a relatively high mutual-information ionicity, roughly a half of the system entropy covalency, while preserving the overall IT bond order, of effectively two π -bonds in the system, of its *two*-electron analog. In the latter case, the bond appears almost purely covalent. As also observed in allyl, the diatomic covalency from the *one*-electron approach identifies the terminal bonds to be much stronger and covalently dominated, compared to the remaining diatomic π -interactions in

Table 5.4 The entropy/information analysis of the π -bond alternation in butadiene

Index	<i>One-electron channel</i>					<i>Two-electron channel</i>				
	$A, B,$ C, D	$[A, B],$ $[C, D]$	$[B, C],$ A, D	$[A, C],$ B, D	$[A, D],$ B, C	$A, B,$ C, D	$[A, B],$ $[C, D]$	$[B, C],$ A, D	$[A, C],$ B, D	$[A, D],$ B, C
$S(A, B, C, D)$	1.361	0.469	1.166	1.181	1.166	1.944	0.948	1.472	1.472	1.472
$I(A, B, C, D)$	0.639	0.531	0.334	0.319	0.334	0.056	0.052	0.028	0.028	0.028
$N(A, B, C, D)$	2.000	1.000	1.500	1.500	1.500	2.000	1.000	1.500	1.500	1.500
$S[X-Y]$	—	0.446	0.195	0.181	0.195	—	0.498	0.473	0.473	0.473
$I[X-Y]$	—	0.054	0.305	0.319	0.305	—	0.002	0.027	0.027	0.027
$N[X-Y]$	—	0.500	0.500	0.500	0.500	—	0.500	0.500	0.500	0.500

the molecule, which are dominated by their ionic component. This is in a general agreement with both the chemical intuition and the corresponding covalent indices of Wiberg [Eq. (16)]: $\mathcal{M}_{A,B}=0.80$, $\mathcal{M}_{A,C}=0$, $\mathcal{M}_{B,C}=\mathcal{M}_{A,D}=0.27$. This bonding pattern is in sharp contrast to the *two*-electron treatment, which predicts all diatomic interactions to be practically equal and almost purely covalent.

Similar overall trends characterize the IT bond indices of π -bonds in the carbon ring of benzene, $M=(1, 2, \dots, 6)$, as reflected by the unreduced results reported in Table 5.5. This relative ionicity of the *one*-electron channel, compared to its *two*-electron analog, also transpires from the corresponding conditional probabilities of these two communication systems:

(1) *one*-electron network:

$$P(i|i)=0.50, \quad P(i+1|i)=0.22, \quad P(i+2|i)=0.00 \quad P(i+3|i)=0.06;$$

(2) *two*-electron network:

$$P(i|i)=0.10, \quad P(i+1|i)=0.16, \quad P(i+2|i)=0.20, \quad P(i+3|i)=0.19.$$

Indeed, the *one*-electron probabilities are seen to be more deterministic (diagonally dominated), compared to a more noisy pattern exhibited by the *two*-electron probability distribution. Both descriptions generate the same overall IT bond-multiplicity index of $N=2.585$ bits, which is lower than 3 bits measure describing three localized (separate) σ -bonds in cyclohexatriene. This demonstrates a natural tendency of these bonds to alternate, in order to maximize the overall bond order. In benzene, it has been compromised by much stronger σ -bonds, which are responsible for the regular hexagon structure of the benzene ring [53], thus preventing the π -bonds to achieve their full bonding capacity when the bond alternation is allowed.

Table 5.5 Comparison of the entropy/information descriptors of the overall and diatomic π -bonds in benzene

Probability, index	One-electron channel				Two-electron channel			
	1, ... 6	[1, 2]	[1, 3]	[1, 4]	1, ... 6	[1, 2]	[1, 3]	[1, 4]
$S(1, \dots, 6)$	1.696	1.482	1.555	1.609	2.551	2.221	2.226	2.226
$I(1, \dots, 6)$	0.889	0.770	0.697	0.643	0.034	0.031	0.026	0.026
$N(1, \dots, 6)$	2.585	2.252	2.252	2.252	2.585	2.252	2.252	2.252
$S[i-j]$	—	0.214	0.141	0.087	—	0.330	0.325	0.325
$I[i-j]$	—	0.119	0.192	0.246	—	0.003	0.008	0.008
$N[i-j]$	—	0.333	0.333	0.333	—	0.333	0.333	0.333

Only the reduced fragment $[i, j]$, in square brackets, is indicated in the output-reduction scheme.

The covalent components of diatomic interactions between carbons in the relative *ortho*-, *meta*-, and *para*-positions in the ring are again seen to be strongly differentiated in the *one*-electron information systems, with the simultaneous increase in the ionic complement, to preserve the overall diatomic interaction of 1/3 of a bit. This trend in the IT covalency index agrees with that exhibited by the quantum mechanical quadratic bond multiplicities of Wiberg [Eq. (16)]: $\mathcal{M}_{1,2}=0.44$, $\mathcal{M}_{1,3}=0$, $\mathcal{M}_{1,4}=0.11$. Again, in the *two*-electron treatment, these three types of chemical interactions, almost purely IT covalent, remain practically indistinguishable.

It thus follows from this comparison that the new *one*-electron communication channels, probing the dependencies between basis functions resulting from their participation in all chemical bonds in the molecule, give quite satisfactory description of chemical bonds in these molecules, much closer to both the accepted chemical intuition and the bond multiplicities from the MO approaches, than that resulting from the *two*-electron CTCB. Moreover, the new treatment appears to be much simpler computationally, by requiring only the 1-density matrix to diagnose the bonding patterns in the molecule.

6. MODEL MULTIPLE BONDS

In order to verify the applicability of the *one*-electron approach to the multiple chemical bonds, in this section, we shall illustrate its performance in CO and CO₂, modeling the localized and delocalized multiple-bond systems, respectively. Since we are mainly interested in the information indices of the main orbital-mixing effects, the mutual overlap of the valence AO on different atoms will be neglected. In other words, the symmetrically orthogonalized valence-shell AO are again assumed throughout. An example of such an analysis of the forward and back donations in the 3-AO problem has been reported elsewhere [29]. By assumption, the bond is directed along z-axis.

In CO containing $N=10$ valence electrons, the equivalent sp_z -hybridization on both constituent atoms is assumed, with the bonding (h_b) and nonbonding (h_n) hybrids pointing toward and away from the bond partner, respectively. These four σ -type basis functions supplemented by the remaining four π -type orbitals, (p_x , p_y) on each atom, form the minimum basis set of valence-shell orbitals:

$$\chi(\text{CO}) = (h_b^C, h_n^C, p_x^C, p_y^C, h_b^O, h_n^O, p_x^O, p_y^O) \equiv (b^C, n^C, x^C, y^C; b^O, n^O, x^O, y^O).$$

Their assumed electron configurations in the atomic valence states, $[\text{C}^v] = [h_b^0 h_n^2 p_x^1 p_y^1]$ and $[\text{O}^v] = [h_b^2 h_n^2 p_x^1 p_y^1]$, give the following initial probabilities

of AO in the associated valence state “promolecule”: $\mathbf{p}^0 = [0, 1/5, 1/10, 1/10; 1/5, 1/5, 1/10, 1/10]$. The doubly occupied MO include three bonding combinations,

$$\sigma_1 = \sqrt{P}b^C + \sqrt{Q}b^O; \quad \pi_\beta = \sqrt{T}\beta^C + \sqrt{U}\beta^O, \quad \beta = x, y; \quad P+Q=T+U=1, \quad (37)$$

and two lone-pair hybrids: $\sigma_2 = n^C$ and $\sigma_3 = n^O$. They give rise to the following nonvanishing CBO matrix elements in the assumed basis-set representation:

$$\begin{aligned} \gamma_{b,b}^C &= 2P, \quad \gamma_{b,b}^O = 2Q, \quad \gamma_{n,n}^C = \gamma_{n,n}^O = 2, \quad \gamma_{x,x}^C = \gamma_{y,y}^C = 2T, \quad \gamma_{x,x}^O = \gamma_{y,y}^O = 2U, \\ \gamma_{b,b}^{C,O} &= \gamma_{b,b}^{O,C} = 2\sqrt{PQ}, \quad \gamma_{x,x}^{C,O} = \gamma_{y,y}^{C,O} = \gamma_{x,x}^{O,C} = \gamma_{y,y}^{O,C} = 2\sqrt{TU}, \end{aligned} \quad (38)$$

and the associated molecular probabilities of AO: $\mathbf{p} = [P/5, 1/5, T/5, T/5; Q/5, 1/5, U/5, U/5] = \mathbf{p}^*$.

Using Eq. (8), one generates from the above bond orders the nonvanishing conditional probabilities:

$$\begin{aligned} P(b^C|b^C) &= P(b^O|b^C) = P, \quad P(b^O|b^C) = P(b^O|b^O) = Q, \quad P(n^C|n^C) = P(n^O|n^O) = 1, \\ P(x^C|x^C) &= P(y^C|y^C) = P(x^C|x^O) = P(y^C|y^O) = T, \\ P(x^O|x^C) &= P(y^O|y^C) = P(x^O|x^O) = P(y^O|y^O) = U. \end{aligned} \quad (39)$$

This probability-scattering channel gives rise to the following conditional probability (S) and mutual-information (I) descriptors:

$$S[\mathbf{p}|\mathbf{p}] = \frac{1}{5}H(P) + \frac{2}{5}H(T), \quad I[\mathbf{p}^0:\mathbf{p}] = \log_2 5 = 2.32. \quad (40)$$

Therefore, for the maximum-covalency case, when $P=Q=T=U=1/2$, $S=0.6$, and hence $N=2.92$. It thus follows from these model predictions that this multiple bond is strongly information ionic, reflecting the presence of two lone electron pairs in the system and rather localized character of the orbital-mixing pattern, which implies a relatively deterministic (localized) probability scattering in the communication channel. The overall index is predicted to be close to 3 bits (triple) bond multiplicity attributed to carbon monoxide by chemists.

One similarly models the valence-electron configuration in carbon dioxide, for $N=16$, by again assuming the sp_z -hybridization on each constituent atom, with both carbon hybrids now being involved in forming the localized σ -bonds with the corresponding oxygen ligands O_1 and O_2 : $\chi(\text{CO}_2) = (b_1^C, b_2^C, x^C, y^C; b_1^O, n_1^O, x_1^O, y_1^O; b_2^O, n_2^O, x_2^O, y_2^O)$. The doubly occupied MO now include four localized σ -orbitals, including two lone-pair hybrids,

$$\sigma_n = \sqrt{Q}b_n^C + \sqrt{P}b_n^O, \quad n = 1, 2, \quad \sigma_3 = n_1^O, \quad \sigma_4 = n_2^O; \quad P+Q=1,$$

and four delocalized π -orbitals, two bonding (b) and two nonbonding (n):

$$\pi_{\beta}^b = \sqrt{W}\beta_1^O + \sqrt{V}\beta^C + \sqrt{W}\beta_2^O, \quad \pi_{\beta}^n = \frac{1}{\sqrt{2}}(\beta_1^O - \beta_2^O),$$

$$\beta = x, y; \quad V + 2W = 1. \quad (41)$$

They generate the following nonvanishing CBO matrix elements: diagonal, $\gamma_{b,b}^C = 2Q$, $\gamma_{b,b}^O = 2P$, $\gamma_{n,n}^O = 2$, $\gamma_{\beta,\beta}^C = 2V$, $\gamma_{\beta,\beta}^O = 2W + 1$, and off-diagonal, $\gamma_{b,b}^{C,O} = \gamma_{b,b}^{O,C} = 2\sqrt{PQ}$, $\gamma_{\beta,\beta}^{C,O} = \gamma_{\beta,\beta}^{O,C} = 2\sqrt{VW}$, $\gamma_{\beta,\beta}^{O,O} = \gamma_{\beta,\beta}^{O,O} = 2W - 1$. Hence the molecular probabilities of orbitals:

$$p = \left[\frac{Q}{8}, \frac{Q}{8}, \frac{V}{8}, \frac{V}{8}; \frac{P}{8}, \frac{1}{8}, \frac{2W+1}{16}, \frac{2W+1}{16}; \frac{P}{8}, \frac{1}{8}, \frac{2W+1}{16}, \frac{2W+1}{16} \right].$$

For estimating the mutual-information component, the following “promolecular” valence-state probabilities for $[C^v] = [b_1^2 b_2^2]$ and $[O^v] = [b_1^1 b_2^1 x^2 y^2]$ are assumed:

$$p^0 = \left[\frac{1}{8}, \frac{1}{8}, 0, 0; \frac{1}{16}, \frac{1}{16}, \frac{1}{8}, \frac{1}{8}; \frac{1}{16}, \frac{1}{16}, \frac{1}{8}, \frac{1}{8} \right].$$

These bond-order data determine the following nonvanishing conditional probabilities of the molecular information channel: (i) diagonal, $P(b^C|b^C) = Q$, $P(\beta^O|\beta^O) = V$, $P(b^O|b^O) = P$, $P(n^O|n^O) = 1$, $P(\beta^C|\beta^C) = (2W + 1)/2$ and (ii) off-diagonal, $P(b^O|b^C) = P$, $P(\beta^O|\beta^C) = W$, $P(b^C|b^O) = Q$, $P(\beta^C|\beta^O) = 2VW/(2W + 1)$, $P(\beta^O|\beta^O) = (2W - 1)^2/[2(2W + 1)]$.

For the maximum-covalency channel, determined by $P = Q = V = 2W = 1/2$, this AO communication system gives the following output probabilities for the promolecular input:

$$p^* = \left[\frac{3}{32}, \frac{3}{32}, \frac{1}{24}, \frac{1}{24}; \frac{3}{32}, \frac{1}{16}, \frac{5}{48}, \frac{5}{48}; \frac{3}{32}, \frac{1}{16}, \frac{5}{48}, \frac{5}{48} \right].$$

The information distribution in this molecular network is described by the following IT indices:

$$S[p|p] = 0.83, \quad I[p^0:p^*] = 2.68, \quad N[p^0:p] = 3.45. \quad (42)$$

As in CO case, the bonds are strongly ionic, a clear manifestation of a small amount of the communication noise being generated in this relatively deterministic system, that is, a relatively high percentage of the channel input information being preserved in the channel output. The overall index, although lower than the intuitive, chemical estimate $N = 4$, clearly indicates the presence of the multiple bonds, approximately 3.5, which in the

assumed approximations can be regarded as qualitatively satisfying result. Moreover, it should be observed that this overall IT bond order misses contributions due to AO overlap and atomic promotions to valence states. A lowering of the overall bond multiplicity of conjugated π -bond system, relative to that characterizing separate localized bonds, has also been observed in benzene (Section 6). This phenomenon will be investigated in more detail in Section 7.

7. π -BOND CONJUGATION

In chemistry of interest also are the entropy/information indices describing the conjugation of the localized bonds into delocalized ones. This effect can be best illustrated using the representative π -electron systems of Section 5. Consider, for example, the simplest case of allyl, with the consecutive numbering of $2p_z = z$ orbitals in the π -electron system, described in the Hückel approximation by the two occupied canonical MO:

$$\begin{aligned}\varphi_1 &= \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} (z_1 + z_3) + z_2 \right] (\text{doubly occupied}), \\ \varphi_2 &= \frac{1}{\sqrt{2}} (z_1 - z_3) (\text{singly occupied}).\end{aligned}\quad (43)$$

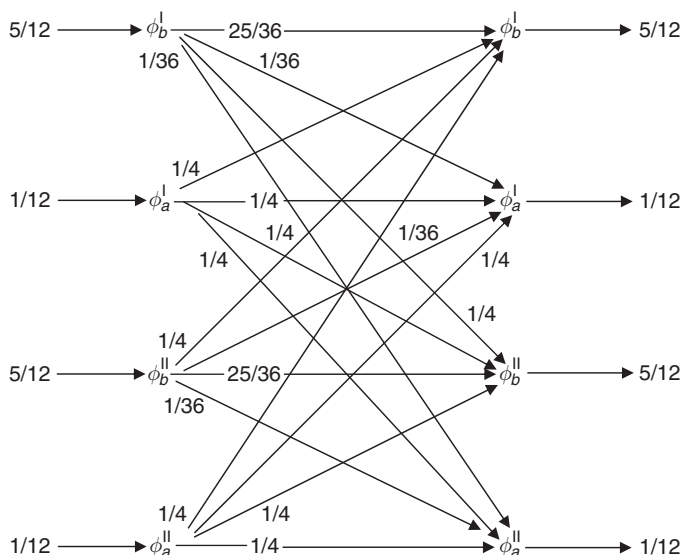
Expressing these functions in terms of the four diatomic MO (LMO), of bonds between nearest neighbors, bonding (b) and antibonding (a),

$$\begin{aligned}\phi_b^{\text{I}} &= \frac{1}{\sqrt{2}} (z_1 + z_2), & \phi_a^{\text{I}} &= \frac{1}{\sqrt{2}} (-z_1 + z_2), \\ \phi_b^{\text{II}} &= \frac{1}{\sqrt{2}} (z_2 + z_3), & \phi_a^{\text{II}} &= \frac{1}{\sqrt{2}} (-z_2 + z_3),\end{aligned}\quad (44)$$

gives

$$\varphi_1 = \frac{1}{\sqrt{2}} (\phi_b^{\text{I}} + \phi_b^{\text{II}}), \quad \varphi_2 = \frac{1}{2} (\phi_b^{\text{I}} - \phi_a^{\text{I}} - \phi_b^{\text{II}} - \phi_a^{\text{II}}).\quad (45)$$

Generating next the CBO matrix in this LMO representation ($\phi_b^{\text{I}}, \phi_a^{\text{I}}, \phi_b^{\text{II}}, \phi_a^{\text{II}}$) allows one to construct, using Eq. (13), the associated communication channel shown in Scheme 5.3. The effective occupations of these four basis functions in allyl determine their equilibrium probabilities in the molecule, $\mathbf{p} = [5/12, 1/12, 5/12, 1/12]$, while the promolecular input probabilities $\mathbf{p}^0 = [1/2, 0, 1/2, 0]$, with only the two bonding MO having



Scheme 5.3 The π -electron communication system of allyl in the LMO representation, for determining the effects due to bond conjugation.

(the same) nonvanishing probability of being occupied, generate the output probability $p^* = [17/36, 1/36, 17/36, 1/36]$.

These probabilities generate the following entropy information descriptors:

$$S[p|p] = 1.29, \quad I[p^0 : p^*] = 0.16, \quad N[p^0; p] = 1.45. \quad (46)$$

Therefore, the bond-conjugation process in allyl, with the two localized bonds sharing AO of the middle carbon atom, is predominantly IT covalent (orbital mixing and delocalizational) in character, with only a marginal mutual-information (orbital occupation and localization) component. The lowering of the overall bond order $N = 1.45$, compared to the chemical intuitive estimate of $3/2$ of the localized π -bond in the carbon chain, is reflected by a small, but finite occupations of the antibonding LMO in p^* . This explains why in this representation the overall bond index is somewhat diminished, relative to that obtained in the AO representation (Table 5.3). However, this lowering of the resultant bond multiplicity relative to the $3/2$ level is predicted to be relatively small. This closeness between the overall bond-conjugation index and that reported in Table 5.3 testifies that most of the π -bonding in allyl can be accounted for only through the coupling between the localized bonds. This LMO $\rightarrow$ MO transition generates mostly IT-covalent (noise) component and little of the IT-ionic (information flow) contribution.

Butadiene involves the conjugation of two localized π -bonds, which do not share any AO, defined by the following LMO for the consecutive numbering of atoms in the carbon chain:

$$\begin{aligned}\phi_b^I &= \frac{1}{\sqrt{2}}(z_1 + z_2), & \phi_a^I &= \frac{1}{\sqrt{2}}(-z_1 + z_2), \\ \phi_b^II &= \frac{1}{\sqrt{2}}(z_3 + z_4), & \phi_a^II &= \frac{1}{\sqrt{2}}(-z_3 + z_4).\end{aligned}\quad (47)$$

In the Hückel approximation, the delocalized bonds are determined by the two (doubly occupied) canonical MO:

$$\begin{aligned}\varphi_1 &= a(z_1 + z_4) + b(z_2 + z_3), & \varphi_2 &= b(z_1 - z_4) + a(z_2 - z_3), & 2(a^2 + b^2) &= 1; \\ a &= \frac{1}{2}\sqrt{1 - \frac{1}{\sqrt{5}}} = 0.3717, & b &= \frac{1}{2}\sqrt{1 + \frac{1}{\sqrt{5}}} = 0.6015.\end{aligned}\quad (48)$$

They can be equivalently expressed in terms of the LMO of Eq. (47):

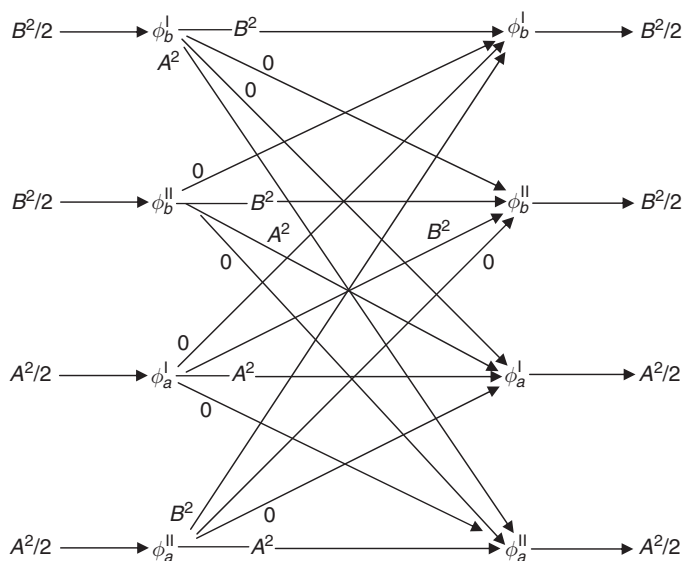
$$\begin{aligned}\varphi_1 &= \frac{B}{\sqrt{2}}(\phi_b^I + \phi_b^{II}) + \frac{A}{\sqrt{2}}(\phi_a^I - \phi_a^{II}), \\ \varphi_2 &= \frac{B}{\sqrt{2}}(\phi_b^I - \phi_b^{II}) - \frac{A}{\sqrt{2}}(\phi_a^I + \phi_a^{II}), & A^2 + B^2 &= 1, \\ A &= b - a, & B &= a + b.\end{aligned}\quad (49)$$

Calculating the bond orders in the LMO representation and using Eq. (8) give the communication channel shown in Scheme 5.4. The relevant promolecular and molecular probabilities of these four basis functions ($\phi_b^I, \phi_b^{II}, \phi_a^I, \phi_a^{II}$) read as follows: $\mathbf{p}^0 = [1/2, 1/2, 0, 0]$ and $\mathbf{p} = \mathbf{p}^* = [B^2/2, B^2/2, A^2/2, A^2/2]$. The resulting entropy/information indices of chemical bonds in this channel,

$$S[\mathbf{p}|\mathbf{p}] = 0.30, \quad I[\mathbf{p}^0 : \mathbf{p}^*] = 1, \quad N[\mathbf{p}^0; \mathbf{p}] = 1.30, \quad (50)$$

predict only a minor conditional-entropy (noise) contribution, due to mixing of LMO into MO, and a relatively substantial information-flow component. Therefore, such conjugation of the two neighboring bonds, which do not share a common AO, is predominantly IT ionic, indicating a strongly deterministic (localized) probability propagation in the information channel of Scheme 5.4: $A^2 = 0.053 \ll B^2 = 0.947$.

Moreover, a relatively large difference between the above entropy covalency and its value for the full AO resolution (Table 5.4) indicates that most of the bond covalency (orbital-mixing contribution) has been properly accounted for already in the two localized bonds, so that only a small remainder was left to be recovered at the bond-conjugation stage. In other



Scheme 5.4 The π -bond conjugation channel for butadiene.

words, in this case, the π -bond delocalization is relatively small compared to that in allyl. However, a high value of the conjugation-ionicity contribution in butadiene indicates that this spread in the electron probability is strongly localized (deterministic).

In the Hückel theory, the three occupied MO, which determine the delocalized π -bonds in benzene, can be also expressed in terms of the localized basis set of a single Kekulé structure, for example, that including the diatomic LMO of Eq. (47) supplemented by the corresponding orbitals for the (5–6) bond:

$$\phi_b^{\text{III}} = \frac{1}{\sqrt{2}} (z_5 + z_6), \quad \phi_a^{\text{III}} = \frac{1}{\sqrt{2}} (-z_5 + z_6). \quad (51)$$

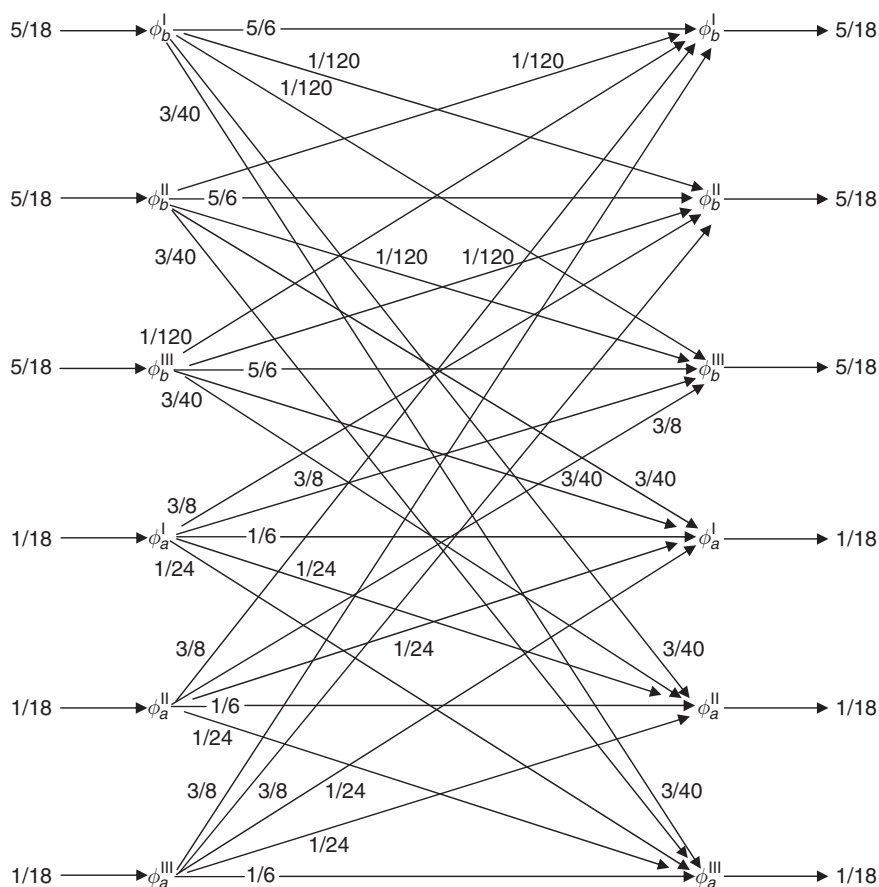
In this LMO basis set $(\phi_b^{\text{I}}, \phi_b^{\text{II}}, \phi_b^{\text{III}}, \phi_a^{\text{I}}, \phi_a^{\text{II}}, \phi_a^{\text{III}})$, the occupied canonical MO read as follows:

$$\begin{aligned} \varphi_1 &= \frac{1}{\sqrt{6}} (z_1 + z_2 + z_3 + z_4 + z_5 + z_6) = \frac{1}{\sqrt{3}} (\phi_b^{\text{I}} + \phi_b^{\text{II}} + \phi_b^{\text{III}}), \\ \varphi_2 &= \frac{1}{2} (z_1 + z_2 - z_4 - z_5) = \frac{1}{2\sqrt{2}} [2\phi_b^{\text{I}} - (\phi_b^{\text{II}} + \phi_b^{\text{III}} + \phi_a^{\text{II}} - \phi_a^{\text{III}})], \\ \varphi_3 &= \frac{1}{\sqrt{12}} (z_1 - z_2 - 2z_3 - z_4 + z_5 + 2z_6) = \frac{1}{\sqrt{24}} [3(\phi_b^{\text{III}} - \phi_b^{\text{II}}) + (\phi_a^{\text{II}} + \phi_a^{\text{III}} - 2\phi_a^{\text{I}})]. \end{aligned} \quad (52)$$

The diagonal elements of the CBO matrix generate the molecular probabilities of LMO, $\mathbf{p} = [5/18, 5/18, 5/18, 1/18, 1/18, 1/18]$, while the corresponding promolecular probabilities reflect the double occupations of the bonding-localized orbitals: $\mathbf{p}^0 = [1/3, 1/3, 1/3, 0, 0, 0]$. The conditional probabilities determining the bond-conjugation channel for benzene (Scheme 5.5) can be obtained from the CBO matrix elements in the LMO representation by using Eq. (8). It gives rise to the output probabilities $\mathbf{p}^* = [17/60, 17/60, 17/60, 1/20, 1/20, 1/20]$ corresponding to input $\mathbf{p}^0$.

The IT indices describing the bond conjugation in benzene,

$$S[\mathbf{p}|\mathbf{p}] = 1.06, \quad I[\mathbf{p}^0 : \mathbf{p}^*] = 1.30, \quad N[\mathbf{p}^0; \mathbf{p}] = 2.36, \quad (53)$$



Scheme 5.5 The π -bond conjugation channel for benzene; only nonvanishing conditional probabilities are shown in the diagram.

indicate that in this process the covalent and ionic components are of comparable magnitude, giving rise to the effective bond multiplicity much below 3 bits level characterizing three separate π -bonds in cyclohexatriene or in a single Kekulé structure.

The same effect of diminishing the overall bond index in the LMO representation, compared to the corresponding AO value, has been observed in butadiene and allyl. This is because some of the bonding effects are already included in the localized-bond promolecule. The largest lowering of the covalent component observed in butadiene indicates that the initial local bonds of the corresponding promolecule are roughly preserved after conjugation, with only a minor mixing effect being detected between the occupied bonding LMO of one bond with the antibonding LMO of the other bond. This relatively minor transformation of LMO in butadiene is also reflected by its high IT-ionic component, indicating a strongly deterministic probability propagation in [Scheme 5.4](#). The LMO mixing in benzene is seen to result in a relatively higher noise component, reflecting a strongly covalent LMO $\rightarrow$ MO information transformation. It thus gives rise to a more substantial delocalization of π -electrons, enforced by the equal (stronger) σ -bonds, which prevent the π -bond alternation. As a result of this LMO conjugation, only a fraction of the initial bonding, already accounted for in the LMO promolecule, is left in the molecule, and the newly created bond order is seen to be close to that generated in the full AO resolution.

In other words, the entropy/information descriptors of the bond-conjugation channels directly reflect only the transformation of all LMO, bonding and antibonding, into the occupied MO. Their covalent/ionic composition summarizes the overall proportions between the information dissipated in the form of a noise and the information preserved (transmitted) in the channels of [Schemes 5.3–5.5](#). The differences between these bond indices and their analogs in the full AO resolution reflect how strong the bond conjugation effects really are: the more these indices differ from one another, the lower the conjugation effect, that is, the more of the resultant bond effects of the AO representation being already accounted for in the localized bonds.

8. CONCLUDING REMARKS

Until recently, a wider use of CTCB in probing the molecular electronic structure has been hindered by the original *two*-electron conditional probabilities, which blur a diversity of chemical bonds. We have demonstrated in the present work that the new *one*-electron approach, based on the quantum mechanical superposition principle, to a large extent remedies this problem. The off-diagonal conditional probabilities it generates are proportional to the quadratic bond indices of the MO theory, and hence

the strong interorbital communications correspond to strong bond order contributions. These physical dependencies between basis functions, due to their overall involvement in all chemical bonds in the system under consideration, have been generalized to the open-shell configurations. This facilitated a discussion of the promotion effects in bonded atoms. The extra computation effort in the *one*-electron IT analysis, in addition to the standard computations of the molecular electronic structure, is negligible since all quantum mechanical computations in orbital approximation determine the CBO data for the adopted basis set.

In this overview, we have also illustrated how versatile this IT approach to chemical bonds really is. Indeed, by an appropriate selection of the basis set and a judicious choice of the channel output reduction scheme, one can focus this communication entropy/information probe on specific effects/mechanisms of interest for chemists. For example, both the global and the molecular fragment interactions can be described at both resultant (AO) and intermediate (HO, LMO) levels of resolving the electronic events in the molecular communication system. Both single and multiple bonds have been diagnosed in CTCB and the bonded-atom promotion has been tackled.

It has been demonstrated elsewhere [29] that the forward and back donations in molecules can be also adequately described in terms of the entropy/information indices of molecular information systems. This analysis has complemented the related treatment using the natural orbitals for chemical valence [54,55], determined by the so-called external eigenvalue problem [50,56–58] of the interatomic part of the displacement of the CBO matrix relative to its promolecular analog: $\Delta\gamma = \gamma - \gamma^0$.

This development is very much in the spirit of Eugene Wigner's statement, often quoted by Walter Kohn, that the understanding in science requires understanding from several different points of view. The CTCB provides such an alternative probabilistic perspective on the chemical bond problem, which complements the familiar MO interpretation. Yet another, information-distance approach [9,15,16] has uncovered the striking similarity between the entropy deficiency (missing information) [7,8] and the density difference $\Delta\rho = \rho - \rho^0$ distributions in molecular systems. All these tools enrich our understanding of the complex phenomenon of the chemical bonding, which – to paraphrase yet another famous citation, from Samuel Beckett – is one of old, good problems that never die out.

Finally, although it was not the purpose of this chapter to review all diverse and numerous applications of IT ideas and techniques in physics, biology, and chemistry, and in the theory of molecular structure in particular, let us just mention a few such developments. In physics, IT plays the unifying role by facilitating a derivation of its basic laws from the common extreme physical information principle [11] using the Fisher information measure [1–3]. It has been applied to problems in chemical kinetics [59], to issues of the electron localizability and transferability in molecules [60–62], and in the

“surprisal” analysis and synthesis of the molecular electron density [63–65]. The IT concepts have been used in the field of the Compton profiles and momentum densities [10,12,66], in density functional theory [67–70], and to describe the electron correlation [71–73]. In the field of molecular structure theory, they have been successfully used in topological descriptors of chemical structure formulated in the molecular graph theory [74–76].

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CHAPTER 6

Quantum Mechanical Methods for Loss-Excitation and Loss-Ionization in Fast Ion–Atom Collisions

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1. INTRODUCTION

Regarding energetic heavy ion–atom collisions, the literature has witnessed a remarkable resurgence of interest and activity in the development and wide applications of quantum mechanical theories. This was and still is vigorously coupled to investigations with a similar intensity in the accompanying field of related measurements. The reasons for the resurgence of interest in high-energy ion–atom collisions are multifaceted and become evident by enquiring as to who might be in need of atomic cross sections, collision rates, and other related observables from this field. Versatile information and data bases on high-energy ion–atom collisions are of paramount importance in many top-priority branches of science and technology. It suffices to mention here accelerator-based physics, the search for new sources of energy, controlled thermonuclear fusion, weak as well as strong lasers (laser-assisted fast ion–atom collisions), plasma research, astrophysics of upper atmosphere, the Earth's environment, solar-terrestrial relations, space research, particle transport physics, medical storage ring accelerators with radio-therapeutic ions, and so on.

All these interdisciplinary fields are in need of knowledge about a large variety of cross sections and collisional rates for different kinds of fast ion–atom collisions, such as single ionization, excitation, charge exchange, and various combinations thereof. These include two-electron transitions, for example, double ionization, excitation, or capture as well as simultaneous electron transfer and ionization or excitation and the like, as thoroughly analyzed in Refs [1–3]. Moreover, the physics of high-energy ion–atom collisions is not restricted to providing only its rich data bases to the neighboring branches. Most importantly, experience and expertise from heavy-particle energetic ion–atom collisions through translational research often play pivotal roles both in design of many important measurements and in interpretation of obtained experimental results in these multidisciplinary fields. There are many examples to support this fact by going from basic via applied research to technology, for example, high-temperature fusion energy research and technology (charge exchange spectroscopy for plasma diagnostics), ionosphere research (recombination and absorption processes and solar continuous spectrum), hadron radiotherapy in medicine (usage of energetic ions to help treat deep-seated tumors by reliance on the concept of optimally deposited radiation dose through the Bragg peak at the targeted lesions), and so on.

In the present study, we shall focus on electron loss collisions between two hydrogen-like atomic systems. These processes are very important for an overall energy balance in various plasmas as well as for more accurate and realistic determination of stopping powers of ions passing through matter. Energy deposition of particle beams is very different for partially and completely stripped ions while slowing down in any given traversed medium. Ionizing power of projectiles decreases with their reduced charge state. By an interplay of electron loss and electron capture, charge state of an ion changes

thousand times during its passage through matter, and this occurs mainly at the end of the ion path (the so-called range) before being stopped near the Bragg peak. These charge-state-changing processes must be taken into account for a more reliable estimate of energy loss of ions in matter.

The standard high-energy Bethe–Bloch formula for stopping power of ions includes only the channels of ionization and excitation but ignores electron loss and electron capture. However, when ions slow down considerably near the Bragg peak (viewed on the traversed pathlength scale), capture dominates ionization, since this area corresponds precisely to the Massey resonance peak, as seen on the energy scale. In the vicinity of the Massey and Bragg peaks, in their respective scales, a dressed/clothed ion is just as likely to lose one of its attendant electrons as it is to capture an electron from the traversed matter. Hence a frequently changing charge state of the ion along its path through matter.

Different charged particles spend different times in their states of reduced or effective charge, and this leads to different ranges, that is, to the emergence of the range distribution. This can be adequately modeled by including the missing channels of electron loss and capture in the description of deceleration processes in matter. Clearly, such a mechanistic approach would largely outperform the conventional introduction of an empirical effective charge of the ionic projectile through the so-called Barkas effect. The said distribution of ranges is customarily called straggling. Usually, straggling is explained by the statistical fluctuation of ion energy loss per collision, and this naturally calls for convolution of stopping powers by a Gaussian, Landau, or Vavilov probability distribution. However, as our argument plausibly indicates, straggling is also due to the fact that the ion charge state changes several thousand times along its path through electron loss and capture processes (thus turning, e.g., an α -particle (He^{2+}) into He^+ and He and vice versa). Such charge state changes occur almost entirely in the last few millimeters of the ion range.

The mentioned basic concepts and phenomena from atomic collisions can be treated accurately by employing the first principles of physics through quantum mechanical methods as analyzed in the present work. This should advantageously obviate the need for the customary reliance upon fitting and other phenomenological formulae in particle transport physics while modeling energy losses of heavy ions passing through matter.

2. SIMULTANEOUS PROJECTILE IONIZATION AND TARGET EXCITATION AND/OR IONIZATION

A collision known as electron loss (projectile ionization) with one- and two-electron transitions is symbolized as:

$$(\text{Z}_\text{P}, e_1)_{i_1} + (\text{Z}_\text{T}, e_2)_{i_2} \rightarrow \text{Z}_\text{P} + e_1(\kappa_1) + (\text{Z}_\text{T}, e_2), \quad (1)$$

where κ_1 is the momentum vector of the ejected electron e_1 relative to its parent nucleus Z_T . Unlike the entrance channel, where the target $(Z_T, e_2)_{i_2}$ is in a bound state specified by the set of the quantum numbers i_2 (usually the ground state, $i_2 = 1s$), we use the symbol (Z_T, e_2) in the exit channel of process (1) without the subscript for a postcollisional state of the target. This corresponds to those experimental data that do not detect the final, postcollisional state of the target by a coincidence measurement. To properly match the latter situation, theoretical models for process (1) should sum up over all the possibilities or channels for the final target states. These include two different classes of processes for production of the Z_P nuclei, one with single- and the other with double-electron transitions. The first obvious example that comes to mind in the class of one-electron transitions is electron loss with the target left unaffected by collision:

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow Z_P + e_1(\kappa_1) + (Z_T, e_2)_{i_2}. \quad (2)$$

However, this is not the only way for a hydrogen-like projectile to lose its electron via one-electron transitions. An alternative way, which is still within the same class, is through electron capture from projectile $(Z_P, e_1)_{i_1}$ by target $(Z_T, e_2)_{i_2}$:

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow Z_P + (Z_T; e_2, e_1)_{i_2, f_1} \quad (3)$$

where f_1 and $f_2 = i_2$ are the final state of electrons e_1 and e_2 . This belongs to the category of one-electron transitions, since the target electron e_2 in the created helium-like system $(Z_T; e_2, e_1)_f$ with $f \equiv \{i_2, f_1\}$ is conceived as occupying the same hydrogen-like orbital after and before collision (the frozen-core approximation for two-electron atoms/ions). Whenever process (3) is not differentiated experimentally from projectile ionization, as is usually the case, then this capture mechanism should also be included as one of the ways to produce the Z_P nuclei via one-electron transitions. We will include this channel in our analysis and computations, especially because capture dominates over excitation and ionization at lower energies ($E < 25 \text{ keV/amu}$), particularly below the Massey peak. Therefore, a more complete terminology would be to rename “electron loss” as “production of the Z_P nuclei” in the case at hand, which is a collision between two hydrogen-like atomic systems $(Z_P, e_1)_{i_1}$ and $(Z_T, e_2)_{i_2}$.

Likewise, the more general class with two-electron transition is usually restricted to only two processes that are simultaneous electron loss with target excitation, that is, loss-excitation (LE):

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow Z_P + e_1(\kappa_1) + (Z_T, e_2)_{f_2}; \quad f_2 \neq i_2, \quad (4)$$

as well as simultaneous electron loss with target ionization, that is, loss-ionization (LI):

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow Z_P + e_1(\boldsymbol{\kappa}_1) + Z_T + e_2(\boldsymbol{\kappa}_2), \quad (5)$$

where $\boldsymbol{\kappa}_2$ is the momentum of the emitted electron e_2 relative to its parent nucleus Z_T . Again, this does not exhaust all the two-electron processes for projectile $(Z_P, e_1)_{i_1}$ to rid itself of its electron e_1 by colliding with $(Z_T, e_2)_{i_2}$. An alternative two-electron process for production of the Z_P nuclei is through simultaneous capture to bound and continuum states. Here, projectile electron e_1 is captured by the target into a bound state. At the same time, the target electron e_2 is captured by the projectile nucleus into a continuum state, and this is recognized as the usual electron capture to continuum (ECC) in the field of the projectile:

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow Z_P + e_2 + (Z_T, e_1)_{f_1}. \quad (6)$$

We shall refer to this two-center exchange-type process as simultaneous electron capture to bound and continuum states, or shortly, bound-and-continuum capture (BCC). This should not be confused with the standard electron exchange effect, in which the ECC pathway is replaced by the ordinary capture to a bound state of the projectile according to:

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow (Z_P, e_2)_{f_2} + (Z_T, e_1)_{f_1}. \quad (7)$$

There are other types of two-electron processes resulting in the production of the Z_P nuclei. For example, simultaneous capture of the projectile electron by the target and excitation of the target electron, or for short, transfer-excitation of target (TET):

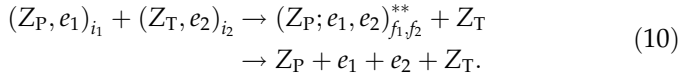
$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow Z_P + (Z_T; e_2, e_1)_{f_2, f_1}^{**}; \quad f_2 \neq i_2. \quad (8)$$

Here, the word “transfer” comes from using the synonym “electron-transfer” for electron capture. Recall that the usual term “transfer-excitation” (TE) refers to process,

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow (Z_P; e_1, e_2)_{f_1, f_2}^{**} + Z_T; \quad f_1 \neq i_1. \quad (9)$$

in which nuclei Z_P and Z_T exchange their role relative to reaction (8). In other words, in the TE process for collisions between two hydrogen-like atomic systems, it is the projectile that captures the target electron and creates the helium-like system $(Z_P; e_1, e_2)_f^{**}$ in a doubly excited state $f \equiv \{f_1, f_2\}$. In process (8), electron e_1 from $(Z_P, e_1)_{i_1}$ is transferred to the target, while the original electron e_2 in the target is simultaneously excited ($f_2 \neq i_2$). Therefore, the TET in process (8) is indeed a scattering with two-electron transitions. The target doubly excited state $(Z_T; e_2, e_1)_{f_2, f_1}^{**}$ is metastable and prone to decay via the Auger or radiative transitions, as in the usual TE

process (9) involving projectiles [2–8]. Note that the Z_P nuclei could also be produced through a higher order process involving the projectile TE process in the first step, which is followed subsequently by a two-electron decay:



Although they are interesting and important to study, processes (6)–(10) will not be examined in the present work. In this study on electron loss phenomena, we will be concerned mainly with first-order perturbation methods that are expected to be valid at intermediate and high impact energies.

3. ADIABATIC HYPOTHESIS FOR RESONANCE MASSEY PEAK

In general, the main electron loss (1), (2), (5), and charge exchange (4) are important for applications in plasma physics, astrophysics, particle transport physics, fusion research, and medicine (hadron radiotherapy). Related experimental data for electron loss provided by a number of measurements over the years in the field of atomic collisions [9–50] can serve as an invaluable testing ground for various theoretical methods. The same applies to electron transfer between two hydrogen-like atomic systems, and some of the rich literature both on experiment and on theory has recently been reviewed [2,3]. These collisional problems are instructive as they involve the four most important channels in ion–atom collisions via electron capture, electron loss, excitation, and ionization. Interplay of these four channels is such that electron loss, ionization, and excitation are dominant at high energies, whereas electron capture provides the major contribution at lower impact energies.

When an energetic ion beam (bare or dressed nuclei)¹ passes through general matter (including tissue), it loses its energy not only by ionizing and exciting the encountered particles but also by capturing electrons from (and/or losing electrons to) the traversed matter. For singly charged light ions, for example, H^+ and He^+ , electron transfer between neutral and singly ionized states does not give an appreciable contribution until these ions slow down to such an extent that their impact velocity v matches the classical orbiting velocity v_e from the outer electrons of the traversed matter. This is the velocity matching condition $v \approx v_e$ as a signature of resonance which gives the maximum of cross section $Q_{ij}(E)$. Massey [51] was the first to attribute this resonance effect to the so-called adiabatic condition of the

¹ “Dressed” or “clothed” nuclei is the term used for partially stripped projectiles that are atomic ions possessing one or more electrons such as hydrogen-like, helium-like, or higher charge state incident particles.

underlying general inelastic collisions of positive ions with atomic target systems, and not only charge exchange. In particular, electron transfer between multiply charged states can also become significant, but in this case the maximum cross sections occur at values of v larger than v_c . Assuming that the so-called adiabatic parameter a is constant, the Massey adiabatic criterion has been validated experimentally for both single- and double-electron transitions in ion-atom collisions [10,12,15].

Resonant reactions/processes are those in which the total *internal* energy of the system is nearly the same before and after the inelastic collision under study. In other words, a cross section for a collision will attain its resonance when the internal energy defect ΔE is very close to zero, $\Delta E \approx 0$. Here, the resonance defect ΔE is the change in the internal energy of the system caused by the given reaction. Specifically, if A and B are the initial and final states ($A \neq B$) of the whole colliding system with the corresponding internal (electronic) energies E_i^A and E_f^B , it follows:

$$\Delta E = E_i^A - E_f^B. \quad (11)$$

If in an inelastic encounter, a positively charged ion of impact velocity v strikes an atomic (or molecular) target over its typical dimension, say a , the collision time will be of the order of a/v . In other words, constant a is a distance over which the colliding particles interact with each other. For a very slow collision ($v \ll 1$), the ion beam spends considerable time $a/v \gg 1$ in the vicinity of the target, the state of which, therefore, will fluctuate between A and B with the energy uncertainty ΔE of the order of the rhs of Eq. (11). The corresponding linear frequency of fluctuation between these two states is:

$$\Delta\nu = \frac{\Delta E}{h}, \quad (12)$$

where h is the Planck's constant. The associated uncertainty in time is of the order of the collision time:

$$\Delta t = \frac{a}{v}. \quad (13)$$

Thus, for low-energy collisions ($v \ll 1$), or equivalently, $\Delta t \gg 1$, we have:

$$\frac{\Delta v}{\Delta t} \gg 1. \quad (14)$$

This inequality marks the *beginning* of the fulfilment of the adiabatic condition at the very outset of low values of v , where the scattering aggregates start to adjust themselves with the tendency of avoiding any transition $A \rightarrow B$ as manifested by the ensuing small cross sections. Large collision time at low impact velocities yields a large number of the said fluctuations

of the system between being mainly in state A and mainly in state B. This, in turn, reduces the chance of the system finding itself in the final state B. Consequently, smaller cross sections are expected whenever inequality (14) is satisfied.

On the other hand, (14) is at variance with the uncertainty principle:

$$\frac{\Delta\nu}{\Delta t} \geq 1. \quad (15)$$

However, as v is gradually augmented, cross sections $Q_{if}(E)$ increase rapidly, since more and more momentum can be exchanged between the scattering aggregates. Moreover, any significant increase in v automatically weakens the inequality (14), and by implication, this brings the system closer and closer to the fulfilment of the uncertainty principle (15).

Cross sections cannot increase indefinitely, since at the opposite side of the velocity scale, large values of v shorten the interaction time Δt thus leading again to small $Q_{if}(E)$. Hence, at least one maximum must occur between the low and the high edge of impact energies E . If two or more Massey peaks are present in the total cross sections, this would signify the existence of two or more competitive processes, each contributing with its own maximum. This is the case, for example, with excitation in the H(1s) – H(1s) collisions [52–109].

The particular value $v_{\max}$ of v representing the peak location of $Q_{if}(E)$ can be determined at the corresponding point in time $\Delta t_{\max}$ which is set to mark the onset of the applicability of the uncertainty principle:

$$\frac{\Delta\nu}{\Delta t_{\max}} \approx 1, \quad \Delta t_{\max} = \frac{a}{v_{\max}}. \quad (16)$$

This turning point toward the validity of (14) is called the adiabatic hypothesis (or the adiabatic rule) of Massey [51], and it actually symbolizes the *end* of the validity of the adiabatic condition (14). Impact velocity $v_{\max}$ extracted from (14) is:

$$v_{\max} = a \frac{|\Delta E|}{h}. \quad (17)$$

Thus, when an incident positively charged ionic particle approaches a given target gradually and so slowly that as a result no appreciable perturbation is produced, no transition will be incurred either by the act of collision and, consequently, the cross sections will be negligibly small. For a considerable chance of transition $A \rightarrow B$ with sizeable cross sections, we ought to have the uncertainty principle fulfilled via Eq. (14) or at least in its minimal form (17).

As an illustration of the adiabatic rule (17), consider double capture (DC) by protons from the ground state of helium. In this case, $\Delta E = A - I = 64.4 \text{ eV}$,

where A and I are the electron affinity and ionization potential. The experimentally measured cross sections of Fogel et al. [15] have a distinct maximum at 35 keV. This gives the numerical value $a \equiv a_{\text{DC}} \approx 1.58 \text{ \AA}$ for the adiabatic parameter. The value of parameter a deduced from the experimental data for cross sections measured by Stedford and Hasted [10] in the case of single capture (SC) in the same $\text{H}^+ - \text{He}(1s^2)$ collision is $a \equiv a_{\text{SC}} \approx 8 \text{ \AA}$. This finding $a_{\text{DC}} \approx 5.06 a_{\text{SC}}$ from the Massey adiabatic hypothesis is reasonable, since it is physically plausible that a process involving two-electron transfer necessitates a noticeably closer approach of protons to helium than in the case of the associated one-electron transfer.

4. ELECTRON LOSS PROCESSES AND STOPPING POWERS OF HEAVY IONS

Returning to the mentioned four competitive processes in ion-atom collisions, it should be recalled that the well-known Bethe-Bloch formula for energy losses includes only the channels of ionization and excitation but ignores charge transfer and projectile ionization, as emphasized in Section 1. This limitation is most severe for obtaining the adequate maximum of cross sections as a function of the impact energy (Massey peak), or equivalently, for predicting the maximum of stopping power as a function of the projectile's traversed pathlength. Considering how serious this omission could be, particularly in hadron radiotherapy, it suffices to state that the main clinical aspect and advantage of ion beams in treating deep seated tumors depends chiefly on an adequate modeling of the area precisely around the Bragg peak, which provides the dominant dose to the targeted tissue.

Stopping power is the energy loss per unit of the traversed pathlength z , as denoted by $S(E) = -dE/dz$. The functional dependence of S versus z gives the Bragg curve, which shows the density of ionization or specific ionization. Specific ionization is the number of ions per unit length. Close to the end of ion path, the Bragg curve attains its maximum called the Bragg peak and for an α -particle this would correspond to about 6000 ion paths per millimeter of air taken as the reference traversed medium. As such, the Bragg curve is extremely useful not only because it yields a measure of the ionization density, but also because it gives the energy loss per millimeter of path. Heavy ions deposit most of their energy at the Bragg peak.

Ionization of atoms or molecules from the traversed medium is accompanied by loss of energy of an ion beam in collisions with electrons. Every individual ion path corresponds to about 32 eV. Thus, an ion loses a very small amount of energy in each individual collision with electrons. However, the energy loss of ions accumulates through many collisions. A large number of collisions of heavy projectiles with electrons leads effectively to the production of ions from the medium along the incident

beam. Ionic projectiles deviate only slightly from the initial direction due their heavy masses compared to that of electrons.

Dependence of stopping power S on z stems from the fact that each z corresponds to one value of the impact energy E . For a given traversed medium, the so-called range R_0 is the maximum depth reachable for a fixed E with the definition $R_0 = \int_0^E dE' / S(E')$. Therefore, at the distance $z = R_0$, the projectile loses all its energy. Evidently, the greater the initial energy E of a given ion, the larger the number of collisions necessary to dissipate the energy E and, hence, the longer the ion range R_0 .

It should be noted that the Massey and Bragg peaks are mutually equivalent in the sense that they are both produced by the same physical mechanism (resonance). They are mirror images of each other in their respective abscissae. The Massey peak represents the maximum of ionization cross section as a function of impact energy, whereas the Bragg peak is the maximum of the stopping power (based on ionization) versus the traversed pathlength.

5. CHANNEL SCATTERING STATES AND PERTURBATIONS

In dealing with the main processes (1), (2), (4), and (5), it is convenient to introduce the following composite labels for the quantum numbers and momenta of initial and final states:

$$\begin{aligned} i &= \{i_1, i_2\}; & i_1 &= \{n_1 l_1 m_1\}; & i_2 &= \{n_2 l_2 m_2\}, \\ f &= \{\kappa_1, f_2\}; & f_2 &= \{n l m, \kappa_2\}; & 1 &\leq n \leq \infty. \end{aligned} \quad (18)$$

We shall also consider a subset $\{f'_2\}$ of the whole set $\{f_2\}$ in which case the following notation will be used:

$$f'_2 = \{n' l' m', \kappa_2\}; \quad \{f'_2\} \subset \{f_2\}; \quad 1 \leq n' \leq M'; \quad M' < \infty. \quad (19)$$

Regarding the corresponding bound and free energies, we write:

$$\begin{aligned} E_i &= E_{i_1} + E_{i_2}; & E_f &= E_{\kappa_1} + E_{f_2} \\ E_{i_1} &= -\frac{Z_P^2}{2n_1^2}; & E_{i_2} &= -\frac{Z_T^2}{2n_2^2} \\ E_{f_2} &= \{E_n, E_{\kappa_2}\}; & E_n &= -\frac{Z_T^2}{2n^2} \\ E_{\kappa_1} &= \frac{\kappa_1^2}{2}; & E_{\kappa_2} &= \frac{\kappa_2^2}{2}; & \kappa_j &= |\mathbf{\kappa}_j| \quad (j=1, 2). \end{aligned} \quad (20)$$

The full Hamiltonian for electron loss process (1) is defined by

$$H = H_0 + V, \quad (21)$$

with H_0 being the total kinetic energy operator:

$$H_0 = -\frac{1}{2\mu_i} \nabla_{r_i}^2 - \frac{1}{2a} \nabla_{s_1}^2 - \frac{1}{2b} \nabla_{x_2}^2 \quad (22)$$

where $\mu_i = (M_P + 1)(M_T + 1)/(M_P + M_T + 2)$, $a = M_P/(M_P + 1)$, and $b = M_T/(M_T + 1)$. Here, r_i is the position vector between the centers of mass of the (Z_T, e_2) and (Z_P, e_1) systems. Further, s_1 and x_2 are the position vectors of the projectile and target electrons e_1 and e_2 relative to their parent nuclei Z_P and Z_T , respectively. In (21), V is the complete interaction potential:

$$V = \frac{Z_P Z_T}{R} - \frac{Z_P}{s_1} - \frac{Z_P}{s_2} - \frac{Z_T}{x_1} - \frac{Z_T}{x_2} + \frac{1}{r_{12}}. \quad (23)$$

The unperturbed Hamiltonian H_i for the two noninteracting hydrogen-like systems $(Z_P, e_1)_{i_1}$ and $(Z_T, e_2)_{i_2}$ in the entrance channel is:

$$H_i = H_0 - \frac{Z_P}{s_1} - \frac{Z_T}{x_2} \quad (24)$$

and the corresponding perturbation interaction is defined by $H - H_i$ so that:

$$V_i \equiv H - H_i = \frac{Z_P Z_T}{R} - \frac{Z_P}{s_2} - \frac{Z_T}{x_1} + \frac{1}{x_{12}}. \quad (25)$$

The first and the last terms in Eq. (25) are the internuclear and interelectronic potentials $V_{PT} = Z_P Z_T / R$ and $V_{12} = 1/x_{12} = 1/|\mathbf{x}_1 - \mathbf{x}_2|$, respectively. The unperturbed scattering state Φ_i of the entrance channel is:

$$\Phi_i = \varphi_{i_1}(s_1) \varphi_{i_2}(x_2) e^{i\mathbf{k}_i \cdot \mathbf{r}_i}, \quad (26)$$

where $\mathbf{k}_i = \mu_i \mathbf{v}$ is the initial wave vector, μ_i and $\mathbf{v}$ is the corresponding vector of the relative velocity.² Further, $\varphi_{i_1}(s_1)$ and $\varphi_{i_2}(x_2)$ are the initial bound-state wave functions of the systems $(Z_P, e_1)_{i_1}$ and $(Z_T, e_2)_{i_2}$, respectively.

The unperturbed final state in the exit channel is defined by:

$$\Phi_f = \varphi_{\mathbf{k}_1}^-(s_1) \varphi_{f_2}(x_2) e^{i\mathbf{k}_f \cdot \mathbf{r}_i}, \quad (27)$$

where $\mathbf{k}_f$ is the final wave vector. Here, $\varphi_{\mathbf{k}_1}^-(s_1)$ is the Coulomb wave for the electron e_1 in the Z_P field:

$$\varphi_{\mathbf{k}_1}^-(s_1) = \tilde{N}^-(\xi) e^{i\mathbf{k}_1 \cdot \mathbf{s}_1} {}_1F_1(-i\xi, 1, -i\kappa_1 s_1 - i\mathbf{k}_1 \cdot \mathbf{s}_1), \quad (28)$$

² Relative velocity $\mathbf{v}$ can equivalently be considered as the impact velocity of projectile $(Z_P, e_1)_{i_1}$ if the target $(Z_T, e_2)_{i_2}$ is taken to be at rest.

where $\tilde{N}^-(\xi) = (2\pi)^{-3/2} \Gamma(1+i\xi) e^{\pi\xi/2}$ and $\xi = Z_P/\kappa_1$ and $\Gamma(1+i\xi)$ is the gamma function. The wave function $\varphi_{\kappa_1}^-(s_1)$ is normalized to the κ_1 -scale via $\langle \varphi_{\kappa_1}^- | \varphi_{\kappa'_1}^- \rangle = \delta(\kappa_1 - \kappa'_1)$ where $\delta(\kappa_1 - \kappa'_1)$ is the usual Dirac δ -function.

In describing process (1), all the final target states $\{\varphi_{f_2}(x_2)\}$ must be included for both the discrete and the continuum parts of the full spectrum of the hydrogen-like atomic system $(Z_T, e_2)_{f_2}$. The set $\{\varphi_{f_2}(x_2)\}$ is complete as expressed by the closure relation:

$$\sum_{f_2} \varphi_{f_2}^*(x_2) \varphi_{f_2}(x'_2) = \delta(x_2 - x'_2). \quad (29)$$

Here, the sum over f_2 includes the summation over all the bound states $\{nlm\}$ and integration over continuum κ_2 :

$$\sum_{f_2} = \sum_{nlm} + \int d\kappa_2. \quad (30)$$

6. THE T-MATRIX FOR SHORT-RANGE INTERACTIONS

If we are to apply the standard formalism of the formal scattering theory from nuclear physics, the exact transition amplitude in the prior form for process (1) would be:

$$T_{if}^- = \langle \Psi_f^- | H - H_i | \Phi_i \rangle = \langle \Psi_f^- | V_i | \Phi_i \rangle. \quad (31)$$

The state vector Ψ_f^- is the full scattering wave function in the exit channel satisfying the complete Schrödinger equation:

$$H\Psi_f^- = E\Psi_f^-, \quad (32)$$

where E is the total energy which obeys the conservation law:

$$E = \frac{k_i^2}{2\mu_i} + E_i = \frac{k_f^2}{2\mu_i} + E_f. \quad (33)$$

6.1. First Born approximation

Using directly the T -matrix element (31) from nuclear scattering theory, the conventional four-body first Born (B1-4B) approximation [53–79] can be introduced through the replacement of the full wave function by the final unperturbed state $\Psi_f^- \approx \Phi_f$. The B1-4B approximation assumes that e_1 is always slow enough to be under the influence of Z_P alone. This hypothesis is valid if the contribution of the target continuous spectrum in the exit channel is predominantly due to the part lying in the close vicinity of the

ionization threshold. Such an assumption together with neglect of electron exchange, polarization, and distortion of the channel wave functions constitute the B1-4B approximation in which the transition amplitude (31) reads as:

$$T_{if}^{(B1)-} = \langle \Phi_f | H - H_i | \Phi_i \rangle = \langle \Phi_f | V_i | \Phi_i \rangle. \quad (34)$$

The perturbation potential V_f in the exit channel within the B1-4B method is equal to V_i . This also implies the equality between the prior and the post transition amplitude, $T_{if}^{(B1)-} = T_{if}^{(B1)+} \equiv T_{if}^{(B1)}$, with:

$$\begin{aligned} T_{if}^{(B1)} &= \langle \Phi_f | V_i | \Phi_i \rangle \\ &= \iiint d\mathbf{s}_1 d\mathbf{x}_2 d\mathbf{r}_i e^{iq \cdot \mathbf{r}_i} \varphi_{\kappa_1}^{-*}(\mathbf{s}_1) \varphi_{f_2}^*(\mathbf{x}_2) \\ &\quad \times \left[\left(\frac{Z_P Z_T}{R} - \frac{Z_P}{s_2} \right) + \left(\frac{1}{x_{12}} - \frac{Z_T}{x_1} \right) \right] \varphi_{i_1}(\mathbf{s}_1) \varphi_{i_2}(\mathbf{x}_2), \end{aligned} \quad (35)$$

where q is the momentum transfer:

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f. \quad (36)$$

7. THE T-MATRIX FOR LONG-RANGE INTERACTIONS

In nuclear physics, the main nuclear interactions are of short range. This justifies the usage of the unperturbed channels states Φ_i and Φ_f from (26) and (27), respectively, as the product of the internal states of the aggregates and the plane waves for their relative motions. However, such a treatment ceases to be adequate for physics of atomic collisions that involve long-range Coulomb interactions. For example, in the entrance channel of process (1), even in the asymptotic region of infinitely large distance r_i , the scattering aggregates $(Z_P, e_1)_{i_1}$ and $(Z_T, e_2)_{i_2}$ are still found to interact through their Coulomb potential, $V_{\text{aggr}} = (Z_P - 1)(Z_T - 1)/R$. This latter particular form of V_{aggr} is not introduced ad hoc. Rather, it is uniquely determined by the asymptotic behavior of the perturbation V_i according to $V_i \approx V_i^\infty \equiv (Z_P - 1)(Z_T - 1)/R = V_{\text{aggr}}$ at $r_i \rightarrow \infty$. Since, in general, for $Z_P \neq 1$ and $Z_T \neq 1$, the asymptotic form of V_i^∞ for V_i does not vanish, the initial state Φ_i will always be perturbed by the residual potential V_i^∞ to become the more adequate scattering state Φ_i^+ in the entrance channel:

$$\Phi_i^+ = \Phi_i e^{i\nu_i \ln(k_i r_i - \mathbf{k}_i \cdot \mathbf{r}_i)}, \quad (37)$$

where $\nu_i = (Z_P - 1)(Z_T - 1)/v$. Here, the logarithmic phase factor which distorts Φ_i is generated by V_i^∞ , and it represents the asymptotic form of the

corresponding full Coulomb wave function. Due to large values of k_i , the full Coulomb wave for relative motion of two scattering aggregates can always be replaced at all distances by its asymptotic form $\exp[i\nu_i \ln(k_i r_i - \mathbf{k}_i \cdot \mathbf{r}_i)]$ and not only for large $|k_i r_i - \mathbf{k}_i \cdot \mathbf{r}_i|$. The error invoked by such a replacement is of the order of $O(1/\mu_i)$, which has a negligible numerical value which is smaller than or equal to 10^{-4} . Similarly, within the first-order perturbation theory, Φ_f will also be distorted by $V_f^\infty = V_i^\infty$ in the exit channel. This yields the Coulomb-dressed asymptotic state Φ_f^- :

$$\Phi_f^- = \Phi_f e^{-i\nu_f \ln(k_f r_i - \mathbf{k}_f \cdot \mathbf{r}_i)}, \quad (38)$$

where $\nu_f = \nu_i$. However, one is not allowed to change the channel states and simultaneously keep the unaltered perturbation potentials. Quite the contrary, consistency of theory requires that the newly defined channel states $\Phi_{if}^\pm$ can be used only if the old perturbations V_{if} are adjusted accordingly. The rule of thumb is simple: whenever the channel states are modified, the corresponding perturbation potentials must also be altered. This comes from the meaning and definition of general perturbations as the differences between the full and channel Hamiltonians. In other words, if Φ_{if} are changed to $\Phi_{if}^\pm$, the channel Hamiltonians cannot be H_{if} any longer, and they must also undergo a change. The question is how to change H_{if} ?

Just like the modification of Φ_{if} , the change in H_{if} cannot be done in an arbitrary manner either. As a matter of fact, once the asymptotic channel states $\Phi_{if}^\pm$ have been fixed in a chosen way, the old channel Hamiltonians H_{if} can be modified only in one way via $H_{if}^d = H_{if} - V_{if}^\infty$. This automatically gives the new perturbation potentials in the entrance and exit channel via $H - H_i^d = H - H_f^d$ ($H_f = H_i$, $V_f^d = V_i^d$):

$$\begin{aligned} V_i^d &\equiv H - H_i^d = H - H_i - V_i^\infty = V_i - V_i^\infty \\ &= Z_P \left(\frac{1}{R} - \frac{1}{s_2} \right) + Z_T \left(\frac{1}{R} - \frac{1}{x_1} \right) + \left(\frac{1}{x_{12}} - \frac{1}{R} \right) \\ &= Z_P \left(\frac{1}{R} - \frac{1}{s_2} \right) + (Z_T - 1) \left(\frac{1}{R} - \frac{1}{x_1} \right) + \left(\frac{1}{x_{12}} - \frac{1}{x_1} \right). \end{aligned} \quad (39)$$

Such a request modifies the transition amplitude (31) from nuclear physics to the following expression which is adequate for atomic collisions:

$$T_{if}^- = \langle \Psi_f^- | H - H_i^d | \Phi_i^+ \rangle = \langle \Psi_f^- | V_i^d | \Phi_i^+ \rangle. \quad (40)$$

The fivefold cross sections, that are differential in the scattering angle of the projectile as well as in the energy and angles of the emitted electron e_1 , are proportional to $|T_{if}^-|^2$:

$$\frac{d^5 Q_{if}^-}{d\Omega_i d\mathbf{k}_1} = \left(\frac{\mu_i}{2\pi}\right)^2 \frac{k_f}{k_i} |T_{if}^-|^2. \quad (41)$$

Here, $\Omega_i = \{\theta_i, \phi_i\}$ is the solid angle around $\mathbf{k}_i$, where the polar angle $\theta_i \in [0, \pi]$ is the projectile scattering angle $\theta_i = \cos^{-1}(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{k}}_f)$ and $\phi_i \in [0, 2\pi]$ is the corresponding azimuthal angle. The cross sections that are differential only in $\mathbf{k}_1$ are obtained by integrating (41) over Ω_i :

$$\frac{d^3 Q_{if}^-}{d\mathbf{k}_1} = \left(\frac{\mu_i}{2\pi}\right)^2 \frac{k_f}{k_i} \int d\Omega_i |T_{if}^-|^2, \quad (42)$$

where $d\Omega_i = \sin \theta_i d\theta_i d\phi_i$. In a coordinate system of spherical coordinates with polar axis chosen in the projectile direction, quantity $|T_{if}^-|^2$ has no azimuthal dependence and the integral over ϕ_i can be carried out in (42) to yield:

$$\frac{d^3 Q_{if}^-}{d\mathbf{k}_1} = \frac{\mu_i^2 k_f}{2\pi k_i} \int_0^\pi |T_{if}^-|^2 \sin \theta_i d\theta_i. \quad (43)$$

This remaining integration over θ_i can alternatively be carried out over the magnitude of momentum transfer $q = |\mathbf{q}|$ using the relation $q^2 = k_i^2 - 2k_i k_f \cos \theta_i + k_f^2$ from Eq. (36) which gives:

$$\frac{d^3 Q_{if}^-}{d\mathbf{k}_1} = \frac{1}{2\pi v^2} \int_{q_{\min}}^{q_{\max}} dq q |T_{if}^-|^2, \quad (44)$$

where

$$q_{\min} = |k_i - k_f|, \quad q_{\max} = k_i + k_f. \quad (45)$$

Employing (33), we have $k_i^2 - k_f^2 = 2\mu_i \Delta E$, where $\Delta E = E_f - E_i$ so that

$$q_{\min}^2 = \left(\frac{\Delta E}{v}\right)^2 \left[1 + \frac{\Delta E}{\mu_i v^2} + \dots\right], \quad (46)$$

where the term in the square brackets is the Maclaurin series in powers of $(\Delta E)/(\mu_i v^2)$.

7.1. Boundary-corrected first Born approximation

Using the modified T -matrix element (40) from atomic scattering theory, the four-body first Born method with the correct boundary conditions (CB1-4B) can be derived through the replacement of the full wave function

Ψ_f^- by the appropriate asymptotic state Φ_f^- in the exit channel, $\Psi_f^- \approx \Phi_f^-$. This maps (40) into

$$T_{if}^{(\text{CB1})-} = \langle \Phi_f^- | H - H_i^d | \Phi_i^+ \rangle = \langle \Phi_f^- | V_i^d | \Phi_i^+ \rangle. \quad (47)$$

Since $V_f^d = V_i^d$, there is no post-prior discrepancy in the CB1-4B method, so that $T_{if}^{(\text{CB1})+} = T_{if}^{(\text{CB1})-} \equiv T_{if}^{(\text{CB1})}$, where:

$$T_{if}^{(\text{CB1})} = \iiint d\mathbf{s}_1 d\mathbf{x}_2 d\mathbf{r}_i (\mu\nu\rho)^{2i\nu_i} e^{iq \cdot \mathbf{r}_i} \varphi_{\mathbf{k}_1}^{-*}(\mathbf{s}_1) \varphi_{f_2}^*(\mathbf{x}_2) \varphi_{i_1}(\mathbf{s}_1) \varphi_{i_2}(\mathbf{x}_2) \\ \times \left[Z_P \left(\frac{1}{R} - \frac{1}{s_2} \right) + (Z_T - 1) \left(\frac{1}{R} - \frac{1}{x_1} \right) + \left(\frac{1}{x_{12}} - \frac{1}{x_1} \right) \right], \quad (48)$$

where $\mu = M_P M_T / (M_P + M_T)$. As opposed to the B1-4B method, it is by construction that the CB1-4B method satisfies the correct boundary conditions in both the entrance and the exit channels.³ The consequence of this general difference between the two methods for arbitrary nuclear charges Z_P and Z_T can be seen by comparing the transition amplitudes $T_{if}^{(\text{B1})}$ and $T_{if}^{(\text{CB1})}$ from Eqs (35) and (48).

Specifically, the T -matrix elements in the B1-4B and CB1-4B methods differ in the perturbation potentials that cause the transition from the initial to final states in process (1). The difference is in the terms:

$$W^{(\text{B1})}(R) \equiv \frac{Z_P Z_T}{R}, \quad W^{(\text{CB1})}(R) \equiv \frac{Z_P + Z_T - 1}{R}. \quad (49)$$

In the B1-4B method, $W^{(\text{B1})}$ is the internuclear potential $V_{\text{PT}} = Z_P Z_T / R$, which is absent from the perturbation interaction in the CB1-4B method. Potential $W^{(\text{CB1})}$ from Eq. (49) is unrelated to V_{PT} in the general case.⁴ The emergence of potential $W^{(\text{CB1})}$ is due to the asymptotic convergence problem, which requires that the perturbation as a whole must be a short-range interaction. In particular, the remaining part,

$$V_{e_1 - e_2, Z_P - e_2, Z_T - e_1} \equiv \frac{1}{x_{12}} - \frac{Z_P}{s_2} - \frac{Z_T}{x_1}, \quad (50)$$

in the perturbation potential (39) from the CB1-4B method has a long-range asymptote at large interaggregate distances:

$$V_{e_1 - e_2, Z_P - e_2, Z_T - e_1} \approx V_{e_1 - e_2, Z_P - e_2, Z_T - e_1}^\infty(R) \\ = \frac{1 - Z_P - Z_T}{R} \quad (r_i \rightarrow \infty). \quad (51)$$

According to Eq. (49), the rhs of Eq. (51) coincides with $-W^{(\text{CB1})}(R)$. Thus, $-W^{(\text{CB1})}(R)$ is a physical potential, since it represents the asymptotic form of the

³ The correct boundary conditions in the B1-4B method for electron loss are fulfilled fortuitously only in one particular case which is for collisions between two hydrogen atoms.

⁴ Accidentally, $Z_P Z_T / R$ coincides with $(Z_P + Z_T - 1)/R$ only when either $Z_P = 1$ or $Z_T = 1$.

sum of the three genuine interactions $V_{e_1-e_2} = V_{12} = 1/x_{12}$, $V_{Z_P-e_2} = -Z_P/s_2$, and $V_{Z_T-e_1} = -Z_T/x_1$. The reason for having the sign minus multiplying the said sum, which is potential $V_{e_1-e_2, Z_P-e_2, Z_T-e_1}^\infty$ from Eq. (51), is in the solution of the convergence asymptotic problem [110–118] within the CB1-4B method. As we saw, this solution amounts merely to distorting Φ_{if} by the long-range Coulomb phases due to V_{if}^∞ , while establishing the new channel states $\Phi_{if}^\pm$ that, in turn, demand subtraction of V_{if}^∞ from V_{if} :

$$\begin{aligned} V_i - V_i^\infty &\equiv V_i^d \\ &= Z_P \left(\frac{1}{R} - \frac{1}{s_2} \right) + (Z_T - 1) \left(\frac{1}{R} - \frac{1}{x_1} \right) + \left(\frac{1}{x_{12}} - \frac{1}{x_1} \right), \end{aligned} \quad (52)$$

in accordance with the earlier stated perturbation potential (39), and similarly for V_f^d with the outcome $V_f^d = V_i^d$.

Besides differing in the perturbation potentials, the integrands in the transition amplitudes $T_{if}^{(B1)}$ and $T_{if}^{(CB1)}$ from Eqs (35) and (48) also differ in the phase factor $(\mu\nu\rho)^{2i\nu_i}$, which is absent from the former and present in the latter. The term $(\mu\nu\rho)^{2i\nu_i}$ from $T_{if}^{(CB1)}$ is a distortion function, which is the product of the two Coulomb logarithmic phases in Φ_i^+ and Φ_f^{-*} from Eqs (37) and (38). This remaining phase originates from the correct boundary conditions in the general case of the two charged hydrogen-like system. Such a phase describes the Rutherford internuclear scattering, which dominates the electron–nuclei collisions at larger scattering angles. Therefore, the phase $\rho^{2i\nu_i}$ must be retained in fivefold differential cross sections (DCS)⁵ $d^5Q_{if}^{(CB1)}/(d\Omega, d\mathbf{\kappa}_1)$ from Eq. (41) whenever $Z_P \neq 1$ and $Z_T \neq 1$.

The Sommerfeld factors ν_i and ν_f are the same for any Z_P and Z_T , and not just $Z_P = 1$ or $Z_T = 1$. Therefore, regarding $dQ_{if}^{(CB1)}/d\mathbf{\kappa}_1$, even the remaining phase $\rho^{2i\nu_i}$ disappears altogether from the cross sections that are differential only in $\mathbf{\kappa}_1$:

$$\frac{d^3Q_{if}^{(CB1)}}{d\mathbf{\kappa}_1} = \frac{1}{2\pi\nu^2} \int_{q_{\min}}^{q_{\max}} dq q \left| T_{if}^{(CB1)} \right|^2 = \frac{1}{2\pi\nu^2} \int_{q_{\min}}^{q_{\max}} dq q \left| R_{if}^{(CB1)} \right|^2, \quad (53)$$

where

$$\begin{aligned} R_{if}^{(CB1)} &= \iiint d\mathbf{s}_1 d\mathbf{x}_2 d\mathbf{r}_i e^{iq \cdot \mathbf{r}_i} \varphi_{\mathbf{\kappa}_1}^{-*}(s_1) \varphi_{f_2}^*(x_2) \varphi_{i_1}(s_1) \varphi_{i_2}(x_2) \\ &\times \left[Z_P \left(\frac{1}{R} - \frac{1}{s_2} \right) + (Z_T - 1) \left(\frac{1}{R} - \frac{1}{x_1} \right) + \left(\frac{1}{x_{12}} - \frac{1}{x_1} \right) \right]. \end{aligned} \quad (54)$$

⁵ The unimportant phase $(\mu\nu)^{2i\nu_i}$ of unit modulus can be ignored throughout.

Notice that the matrix elements $T_{if}^{(\text{CB1})}$ and $R_{if}^{(\text{CB1})}$ from Eqs (48) and (54), respectively, differ only in that the latter has no phase $(\mu\nu\rho)^{2i\nu_i}$.

For a later purpose, it is convenient to alternatively denote the DCS $d^3Q_{if}^{(\text{CB1})}/d\kappa_1$ by $Q_{i_1,\kappa_1;i_2,f_2}^{(\text{CB1})}$:

$$Q_{i_1,\kappa_1;i_2,f_2}^{(\text{CB1})} \equiv \frac{d^3Q_{if}^{(\text{CB1})}}{d\kappa_1}. \quad (55)$$

The whole system's state-to-state transition $i \rightarrow f$ for processes (2), (4), and (5) will interchangeably be symbolized also as a pair of two subsystems' transitions via

$$i \rightarrow f : \quad (i_1 \rightarrow \kappa_1) \cup (i_2 \rightarrow f_2) \equiv \{i_1 \rightarrow \kappa_1; i_2 \rightarrow f_2\} \\ \equiv \{i_1, \kappa_1; i_2, f_2\}. \quad (56)$$

The last line in Eq. (56) is used in Eq. (55) as the composite subscript in the cross section $Q_{i_1,\kappa_1;i_2,f_2}^{(\text{CB1})}$ and such a transparent notation will be employed throughout. Total cross section, which is denoted by $Q_{i_1,c;i_2,f_2}^{(\text{CB1})}$ (where $c_1 \equiv c$ stands for continuum of electron e_1), is obtained by integrating Eq. (55) over κ_1 :

$$Q_{i_1,c;i_2,f_2}^{(\text{CB1})} = \int d\kappa_1 Q_{i_1,\kappa_1;i_2,f_2}^{(\text{CB1})}, \quad (57)$$

where $d\kappa_1 = \kappa_1^2 d\kappa_1 d\Omega_1$ and $\Omega_1 = (\theta_1, \phi_1)$ is the solid angle around κ_1 with $d\Omega_1 = \sin \theta_1 d\theta_1 d\phi_1$. Regarding the distribution over κ_1 , the main contribution to $Q_{i_1,c;i_2,f_2}^{(\text{CB1})}$ comes from small values of κ_1 . Therefore, the integration limits for the κ_1 -integral can be taken to be 0 and ∞ .

Since f_2 can be associated with the bound and continuous spectrum of the final target states, we have from Eq. (57):

$$Q_{i_1,c;i_2,nlm}^{(\text{CB1})} = \int d\kappa_1 Q_{i_1,\kappa_1;i_2,nlm}^{(\text{CB1})} \quad (58)$$

$$Q_{i_1,c;i_2,\kappa_2}^{(\text{CB1})} = \int d\kappa_1 Q_{i_1,\kappa_1;i_2,\kappa_2}^{(\text{CB1})}. \quad (59)$$

8. DEFINING, EXACT SUM OVER ALL THE TARGET FINAL STATES

In process (1), we are not interested in state-selective cross sections relative to $f_2 = \{nlm, \kappa_2\}$. Therefore, the cross section for electron loss in this process is obtained by performing the sum over f_2 in Eq. (57) and denoting the result as $Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})}$:

$$Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})} = \sum_{f_2} Q_{i_1,c;i_2,f_2}^{(\text{CB1})} = \sum_{f_2} \int d\kappa_1 Q_{i_1,\kappa_1;i_2,f_2}^{(\text{CB1})} \quad (60)$$

where the sum over f_2 is treated as in Eq. (30). In practice, the computation is done separately for the bound and continuum final target states. Thus, the sum over nlm and integration over κ_2 produce the partial results denoted by $Q_{i_1,c;i_2,b}^{(CB1)}$ and $Q_{i_1,c;i_2,c}^{(CB1)}$ respectively:

$$Q_{i_1,c;i_2,b}^{(CB1)} = \sum_{nlm} \int d\kappa_1 Q_{i_1,\kappa_1;i_2,nlm}^{(CB1)} \quad (61)$$

$$Q_{i_1,c;i_2,c}^{(CB1)} = \int d\kappa_1 \int d\kappa_2 Q_{i_1,\kappa_1;i_2,\kappa_2}^{(CB1)} \quad (62)$$

where label b indicates the sum over the whole set of target-bound states $\{nlm\}$. The last subscript $c_2 \equiv c$ in $Q_{i_1,c;i_2,c}^{(CB1)}$ from Eq. (62) designates the whole continuum of electron e_2 . We could have written more pedantically $Q_{i_1,c_1;i_2,c_2}^{(CB1)}$ instead of $Q_{i_1,c;i_2,c}^{(CB1)}$. However, the notation from Eq. (59) which utilizes the same letter c for continuum of both e_1 and e_2 should cause no confusion, since these subscripts appear consecutively in the pairs $\{i_1, c\}$ and $\{i_2, c\}$ indicating the explicit transitions of electrons e_1 and e_2 from the initial to their respective final states, that is, $\{i_1, c_1\} \equiv \{i_1 \rightarrow c\}$ and $\{i_2, c_2\} \equiv \{i_2 \rightarrow c\}$. Note also that the integration range over κ_2 in Eq. (62) can be taken to be $\kappa_2 \in [0, \infty]$ for the same reason mentioned earlier in the case of the integration over κ_1 .

8.1. The mass approximation for heavy particle collisions

For heavy particle collisions, the masses of nuclei are much larger than those of the electron:

$$M_P \gg 1; \quad M_T \gg 1, \quad (63)$$

and therefore, $\mu_i \gg 1$. Thus, all the terms of the order of or smaller than $1/\mu_i$ can safely be ignored throughout the analysis. Physically, neglect of such terms is equivalent to neglect of recoil of nuclei. Such a mass approximation leads to an extremely fast convergence of the series in Eq. (46) for $q_{\min}$. As a matter of fact, a negligible loss of accuracy would be incurred by retaining only the first term in this series yielding:

$$q_{\min} \approx \frac{\Delta E}{v} = \frac{E_{f_2} + E_{\kappa_1} - E_{i_1} - E_{i_2}}{v}, \quad (64)$$

$$q_{\max} \approx 2\mu v.$$

Also due to large μ , we can replace $q_{\max}$ by infinity, especially given that the CB1-4B method belongs to high-energy approximations. Further, the mass approximation (63) implies the useful relationship $\mathbf{r}_i \approx \mathbf{R} = \mathbf{x}_1 - \mathbf{s}_1 = \mathbf{x}_2 - \mathbf{s}_2$. In such a case, all the three integrals in $R_{if}^{(CB1)}$ from Eq. (54) are separable. This permits us to show that the potential $\mathcal{W}^{(CB1)} - Z_P/s_2$ gives exactly zero

contribution on account of orthogonality of the bound and continuum states $\varphi_{i_1}(s_1)$ and $\varphi_{\mathbf{k}_1}^-(s_1)$ in the Z_P field.⁶ Therefore, the matrix element $R_{if}^{(\text{CB1})}$ simplifies as:

$$R_{if}^{(\text{CB1})} = \iiint d\mathbf{s}_1 d\mathbf{x}_2 d\mathbf{R} e^{iq\cdot\mathbf{R}} \varphi_{\mathbf{k}_1}^{-*}(s_1) \varphi_{f_2}^*(\mathbf{x}_2) \times \left(\frac{1}{x_{12}} - \frac{Z_T}{x_1} \right) \varphi_{i_1}(s_1) \varphi_{i_2}(\mathbf{x}_2). \quad (65)$$

Further, it will prove convenient to rewrite this matrix element via:

$$R_{if}^{(\text{CB1})} = \iint d\mathbf{s}_1 d\mathbf{x}_2 e^{iq\cdot\mathbf{R}} \varphi_{\mathbf{k}_1}^{-*}(s_1) \varphi_{f_2}^*(\mathbf{x}_2) K(s_1, \mathbf{x}_2) \varphi_{i_1}(s_1) \varphi_{i_2}(\mathbf{x}_2), \quad (66)$$

where

$$K(s_1, \mathbf{x}_2) = \int d\mathbf{R} e^{iq\cdot\mathbf{R}} \left(\frac{1}{x_{12}} - \frac{Z_T}{x_1} \right). \quad (67)$$

These are the well-known Bethe integrals [121] or their variants with the results:

$$\int d\mathbf{x}_1 \frac{e^{iq\cdot\mathbf{R}}}{x_1} = \frac{4\pi}{q^2} e^{-iq\cdot s_1}, \quad \int d\mathbf{x}_1 \frac{e^{iq\cdot\mathbf{R}}}{|\mathbf{x}_1 - \mathbf{x}_2|} = \frac{4\pi}{q^2} e^{iq\cdot(\mathbf{x}_2 - s_1)}. \quad (68)$$

Therefore, it follows from (67) that:

$$K(s_1, \mathbf{x}_2) = \frac{4\pi}{q^2} e^{-iq\cdot s_1} (e^{-iq\cdot\mathbf{x}_2} - Z_T), \quad (69)$$

and with this result the matrix element (66) becomes:

$$R_{if}^{(\text{CB1})} = \frac{4\pi}{q^2} = \left\{ \int d\mathbf{s}_1 e^{-iq\cdot s_1} \varphi_{\mathbf{k}_1}^{-*}(s_1) \varphi_{i_1}(s_1) \right\} \times \left\{ \int d\mathbf{x}_2 (e^{iq\cdot\mathbf{x}_2} - Z_T) \varphi_{f_2}^*(\mathbf{x}_2) \varphi_{i_2}(\mathbf{x}_2) \right\}. \quad (70)$$

Here, in the second term $-Z_T$, we can use the orthonormality relation,

$$\int d\mathbf{x}_2 \varphi_{f_2}^*(\mathbf{x}_2) \varphi_{i_2}(\mathbf{x}_2) = \delta_{i_2, f_2} \quad (71)$$

⁶Note that in the exact T -matrix element from Eq. (40), potentials $\propto 1/R$ and $\propto 1/s_2$ would not give zero contributions. Their nonzero yield would come from the effect of these potentials on the scattering waves. Of course, this cannot be verified in applications of Eq. (40) due to the unavailability of the exact scattering state Ψ_f^- , but nonzero contributions from the potential $W^{(\text{CB1})} - Z_P/s_2$ can be obtained within four-body Born distorted wave (BDW-4B) method [119,120] which can be readily extended to electron loss.

to arrive at:

$$R_{if}^{(\text{CB1})} \equiv R_{i_1, \kappa_1; i_2, f_2}^{(\text{CB1})} = \frac{4\pi}{q^2} J_{i_1, \kappa_1} \{I_{i_2, f_2} - Z_T \delta_{i_2, f_2}\}, \quad (72)$$

where

$$I_{i_2, f_2} = \int d\mathbf{x}_2 e^{iq \cdot \mathbf{x}_2} \varphi_{f_2}^*(\mathbf{x}_2) \varphi_{i_2}(\mathbf{x}_2), \quad (73)$$

$$J_{i_1, \kappa_1} = \int d\mathbf{s}_1 e^{-iq \cdot \mathbf{s}_1} \varphi_{\kappa_1}^{-*}(\mathbf{s}_1) \varphi_{i_1}(\mathbf{s}_1). \quad (74)$$

Quantities I_{i_2, f_2} and J_{i_1, κ_1} are recognized as the bound-bound and bound-free atomic form factors, the results of which are available in the literature via their analytical expressions for any set $\{i_1, i_2, f_2\}$ associated with hydrogen-like wave functions [122–127]. In particular, for $f_2 = nlm$ in Eq. (72) only the term $f_2 = i_2$ survives via $\delta_{i_2, f_2} = \delta_{i_2, i_2} = 1$. Likewise for f_2 in the continuous spectrum, it follows $\delta_{i_2, f_2} = \delta_{i_2, \kappa_2} = 0$. It is clear from the above derivation that the great simplicity of the main result (72) in the CB1-4B method is a direct consequence of isolating the integration over R in Eq. (67) and using subsequently the Bethe integrals from Eq. (68). However, the possibility of using the Bethe integrals will be absent from second-order distorted wave methods due to presence of an electronic Coulomb wave which depends on coordinate $\mathbf{x}_1$ or $\mathbf{s}_2$ [2,3]. This distorting function would prevent obtaining an analytical result for the matrix element with the interelectronic potential $1/x_{12}$, and moreover, the contribution from $\Delta V_{P2} \equiv 1/R - 1/s_2$ will not be zero any longer. Nevertheless, no significant error would be invoked with omission of ΔV_{P2} , as was the case with transfer-excitation [4–8] and electron detachment [128,129]. Of course, no such omission can be made with the dynamic interelectron correlation $1/x_{12}$ which must be kept throughout. In Refs [3–8], where the TE process (9) has been treated by means of the four-body continuum distorted wave (CDW-4B) method, the repulsion term $1/x_{12}$ was represented by its three-dimensional Fourier integral in order to be able to perform the remaining matrix elements analytically via the Nordsieck integral [130]. This procedure yields a three-fold increase of the dimension of the final numerical quadrature for the cross sections.

Inserting Eq. (72) into Eq. (53) and using the notation from Eq. (55), the cross section which is differential in momentum κ_1 of the ejected electron e_1 becomes:

$$Q_{i_1, \kappa_1; i_2, f_2}^{(\text{CB1})} = \frac{8\pi}{v^2} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, f_2} - Z_T \delta_{i_2, f_2}|^2. \quad (75)$$

From here, the corresponding cross sections for the final bound and continuum target states are:

$$Q_{i_1, \kappa_1; i_2, nlm}^{(CB1)} = \frac{8\pi}{v^2} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, nlm} - Z_T \delta_{i_2, nlm}|^2, \quad (76)$$

$$Q_{i_1, \kappa_1; i_2, \kappa_2}^{(CB1)} = \frac{8\pi}{v^2} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, \kappa_2}|^2. \quad (77)$$

The total cross section $Q_{i_1, c; i_2, f_2}^{(CB1)}$ is obtained through integration of $Q_{i_1, \kappa_1; i_2, f_2}^{(CB1)}$ by means of Eq. (57) so that:

$$Q_{i_1, c; i_2, f_2}^{(CB1)} = \frac{8\pi}{v^2} \int d\kappa_1 \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, f_2} - Z_T \delta_{i_2, f_2}|^2. \quad (78)$$

This could also be written more explicitly highlighting both the discrete and the continuous part of the whole spectrum $\{f_2\}$ as:

$$Q_{i_1, c; i_2, nlm}^{(CB1)} = \frac{8\pi}{v^2} \int d\kappa_1 \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, nlm} - Z_T \delta_{i_2, nlm}|^2, \quad (79)$$

$$Q_{i_1, c; i_2, \kappa_2}^{(CB1)} = \frac{8\pi}{v^2} \int d\kappa_1 \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, \kappa_2}|^2. \quad (80)$$

9. PRACTICAL, EXACT SUM OVER DOMINANT TARGET TRUE FINAL STATES

In process (1), the exact sum over all the final states f_2 of the target (bound and free) is required as in Eq. (60). This is achieved by inserting Eq. (78) into Eq. (60) leading to:

$$Q_{i_1, c; i_2, \Sigma}^{(CB1)} = \frac{8\pi}{v^2} \int d\kappa_1 \sum_{f_2} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \kappa_1}|^2 |I_{i_2, f_2} - Z_T \delta_{i_2, f_2}|^2. \quad (81)$$

In computations, the sum Σ_{f_2} is performed using its definition (30), that is, by splitting Σ_{f_2} into two separate parts Σ_{nlm} and $\int d\kappa_2$ as in Eqs. (61) and (62). Explicitly, Eq. (81) becomes:

$$Q_{i_1,c;i_2,b}^{(\text{CB1})} = \frac{8\pi}{v^2} \int d\mathbf{\kappa}_1 \sum_{nlm} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1,\mathbf{\kappa}_1}|^2 |I_{i_2,nlm} - Z_T \delta_{i_2,nlm}|^2, \quad (82)$$

$$Q_{i_1,c;i_2,c}^{(\text{CB1})} = \frac{8\pi}{v^2} \int d\mathbf{\kappa}_1 \int d\mathbf{\kappa}_2 \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1,\mathbf{\kappa}_1}|^2 |I_{i_2,\mathbf{\kappa}_2}|^2. \quad (83)$$

In practice, only a small fraction $\{f'_2\}$ of the otherwise infinite set $\{f_2\}$ can be taken into account, and this is symbolized by $\Sigma_{f'_2}$:

$$\sum_{f_2} = \sum_{f'_2} + \sum_{f_2^\perp}; \quad \{f'_2\} \subset \{f_2\}; \quad \{f_2^\perp\} = \{f_2\} - \{f'_2\}, \quad (84)$$

where the sets $\{f'_2\}$ and $\{f_2^\perp\}$ are complementary with no common elements. This leads to the identity:

$$Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})} \equiv Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})} + Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})} \quad (85)$$

where

$$Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})} = Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})} - Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})} \quad (86)$$

with

$$Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})} = \sum_{f'_2} Q_{i_1,c;i_2,f'_2}^{(\text{CB1})} \quad (87)$$

$$Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})} = \sum_{f_2^\perp} Q_{i_1,c;i_2,f_2^\perp}^{(\text{CB1})} \quad (88)$$

or, explicitly,

$$Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})} = \frac{8\pi}{v^2} \int d\mathbf{\kappa}_1 \sum_{f'_2} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1,\mathbf{\kappa}_1}|^2 |I_{i_2,f'_2} - Z_T \delta_{i_2,f'_2}|^2, \quad (89)$$

$$Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})} = \frac{8\pi}{v^2} \int d\mathbf{\kappa}_1 \sum_{f_2^\perp} \int_{q_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1,\mathbf{\kappa}_1}|^2 |I_{i_2,f_2^\perp} - Z_T \delta_{i_2,f_2^\perp}|^2. \quad (90)$$

Hence, in the exact CB1-4B method, one basically chooses a finite set of dominant true final states $\{f'_2\} \subset \{f_2\}$ to compute $Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})}$ using Eq. (89) and

subsequently neglects the remainder $Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})}$ from Eq. (90). This leads to the approximation $Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})}$ of $Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})}$ from Eq. (85):

$$Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})} \approx Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})} \quad (91)$$

which amounts to the assumption:

$$Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})} \approx 0. \quad (92)$$

Importantly, while carrying out separately the sum over nlm and integration over κ_2 , it is not possible to exchange these two operations with the subsequent integral over q , since $q_{\min}$ depends on the energy E_{f_2} via Eq. (64). Nevertheless, for discrete states $\{nlm\}$, the binding energy $E_{f_2} = E_n$ is a function of the principal quantum number n alone. In such a case, $q_{\min}$ does not depend on $\{lm\}$, and this permits the exchange of Σ_{lm} and $\int dq$ with the advantage of exploiting the sum rule for degenerate states $\{lm\}$. This latter sum rule would yield a simple algebraic expression for $\Sigma_{lm} |I_{i_2,nlm}|^2$ as has first been obtained by May [131] for $i_2=1s$ and elaborated further by Cheshire and Kyle [132,133]. In the present computations within the exact CB1-4B method, we used only the sum rule for magnetic quantum numbers m , and this gives the state-to-state cross sections $Q_{i_1,\kappa_1;i_2,nl}^{(\text{CB1})}$ for any quantum numbers $\{nl\}$. Of course, regarding the continuum states of $e_2(\kappa_2)$, the integration over κ_2 in Eq. (83) cannot be exchanged either with the integral over q , since $q_{\min}$ depends on $E_{f_2} = E_{\kappa_2} = \kappa_2^2/2$.

10. ACCELERATION OF CONVERGENCE FOR FINAL STATES

As mentioned, if one is not interested in state-to-state transitions, process (1) should be investigated. To this end, the explicit exact computations in the CB1-4B method via Eq. (91) could be lengthy, since many states $\{f_2'\}$ might contribute significantly until convergence is reached. Convergence over the final states $\{f_2'\}$ is needed to justify omission of the neglected subset $\{f_2^\perp\} = \{f_2\} - \{f_2'\}$ via Eq. (92). Therefore, it is natural to see how to enhance the convergence rate of the summation over $\{f_2'\}$. We presently propose to achieve this goal via a direct improvement of the usual approximation (91) by supplementing $Q_{i_1,c;i_2,\Sigma'}^{(\text{CB1})}$ with an estimate of the previously neglected term $Q_{i_1,c;i_2,\Sigma^\perp}^{(\text{CB1})}$. This would speed up computation if the added correction could significantly reduce the original size of the set $\{f_2'\}$. Assuming that this indeed will occur, the proposed procedure is hereafter called the accelerated four-body first Born method with correct boundary conditions (ACB1-4B).

The sought estimate will be introduced as the closure bound $\bar{Q}_{i_1, c; i_2, \Sigma^\perp}^{(\text{CB1})}$ which is computed from the same expression as $Q_{i_1, c; i_2, \Sigma^\perp}^{(\text{CB1})}$ except that $q_{\min}$ is replaced by $\bar{q}_{\min}$:

$$q_{\min} \approx \bar{q}_{\min}; \quad \bar{q}_{\min} = \frac{\Delta \bar{E}}{v} = \frac{\bar{E} + E_{\kappa_1} - E_{i_1} - E_{i_2}}{v}, \quad (93)$$

where $\bar{E}$ is an average energy to be judiciously chosen. Explicitly, this closure bound is found to be:

$$\begin{aligned} \bar{Q}_{i_1, c; i_2, \Sigma^\perp}^{(\text{CB1})} &= \overline{[Q_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})}]} = \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} \\ &\equiv \Delta Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})}. \end{aligned} \quad (94)$$

Therefore, the cross section for process (1) in the ACB1-4B method is:

$$Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} = Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} + \Delta Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} \quad (95)$$

where

$$\Delta Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} = \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} \quad (96)$$

with

$$Q_{i_1, c; i_2, \Sigma}^{(\text{CB1})} = \sum_{f_2} \bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})} \quad (97)$$

$$\bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} = \sum_{f_2'} \bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})}. \quad (98)$$

The first term $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ in the correction Eq. (96) represents the closure approximation (CA) to the CB1-4B method for the whole set $\{f_2\}$ of bound and continuum states included using Eq. (97) together with the subsequently and explicitly exploited closure relation Eq. (29). The second term $\bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})}$ in Eq. (96) uses Eqs. (93) and (98) in computation of cross sections separately for each state f_2' so that closure relation Eq. (29) is not used here.

Care should be exercised about the bar sign above cross sections. Confusion will not arise if the bar sign is placed on Q provided that this cross section is specified, especially by the last subscript. For example, in $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ the last subscript is Σ which means that all the target states $\{f_2\}$ are approximately included. Hence, the bar sign in $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ is used to draw

attention to the fact that the closure relation is already implemented as a follow-up of the replacement of the exact minimal momentum transfer $q_{\min}$ by its approximation $\bar{q}_{\min}$. In other words, $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ strictly represents the cross section of the CA for the transition $(i_1 \rightarrow c) \cup (i_2 \rightarrow \Sigma)$ in process (1) where Σ includes the entire target spectrum (discrete and continuous). On the other hand, in individual cross section $\bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})}$ the last subscript f_2 indicates that this is a cross section for the state-to-state transition $(i_1 \rightarrow c) \cup (i_2 \rightarrow f_2)$ for a fixed f_2 with the usage of $\bar{q}_{\min}$ in lieu of $q_{\min}$. As such, $\bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})}$ is the cross section describing processes (2), (4), and (5) approximately by using $q_{\min} \approx \bar{q}_{\min}$ with an arbitrary, but fixed $\varphi_{f_2}(\mathbf{x}_2)$ for either bound or continuous states. Stated differently, $\bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})}$ does not use the closure relation, and hence, it is not a cross section of the CA. Rather, the bar sign in $\bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})}$ indicates that $q_{\min} \approx \bar{q}_{\min}$ is the only feature which makes this approximate cross section differ from its exact counterpart $Q_{i_1, c; i_2, f_2}^{(\text{CB1})}$. In short, $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ is the estimate of the CA, whereas $\bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})}$ is not, despite the bar sign over both quantities. This means that the acronym CA can be used only for a cross section which employs the closure relation Eq. (29) together with Eq. (93), as occurs exclusively in $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$. The CA itself will be elaborated in Section 11.

Another equivalent way of writing Eq. (95) is through the separate contributions from the discrete and continuous target spectrum:

$$Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} \approx Q_{i_1, c; i_2, b'+c}^{(\text{CB1})} + \Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})} \quad (99)$$

where

$$\Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})} \approx \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, b'+c}^{(\text{CB1})} \quad (100)$$

and

$$Q_{i_1, c; i_2, b'+c}^{(\text{CB1})} \approx Q_{i_1, c; i_2, b'}^{(\text{CB1})} + Q_{i_1, c; i_2, c}^{(\text{CB1})} \quad (101)$$

$$\bar{Q}_{i_1, c; i_2, b'+c}^{(\text{CB1})} = \bar{Q}_{i_1, c; i_2, b'}^{(\text{CB1})} + \bar{Q}_{i_1, c; i_2, c}^{(\text{CB1})} \quad (102)$$

$$\bar{Q}_{i_1, c; i_2, b'}^{(\text{CB1})} = \sum_{n'l'm'} \bar{Q}_{i_1, c; i_2, n'l'm'}^{(\text{CB1})} ; \quad 1 \leq n' \leq M', \quad M' < \infty. \quad (103)$$

Here, the label b' symbolizes that all the states from the segment $\{n'l'm'\}$ are included, where $\{n'l'm'\} \subset \{nlm\}$.

For any chosen average energy $\bar{E}$, the estimate $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ of the CA for the exact counterpart $Q_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ includes the approximations $\bar{Q}_{i_1, c; i_2, b'}^{(\text{CB1})}$ and $\bar{Q}_{i_1, c; i_2, c}^{(\text{CB1})}$ to the corresponding exact cross sections $Q_{i_1, c; i_2, b'}^{(\text{CB1})}$ and $Q_{i_1, c; i_2, b'}^{(\text{CB1})}$, respectively. Therefore, Eq. (100) can formally be rewritten as:

$$\begin{aligned} \Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})} &= \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, b'+c}^{(\text{CB1})} \\ &= \left\{ \bar{Q}_{i_1, c; i_2, b'+c}^{(\text{CB1})} + \sum_{\forall f_2 \neq \{b', c\}} \bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})} \right\} - \bar{Q}_{i_1, c; i_2, b'+c}^{(\text{CB1})} \\ &= \sum_{\forall f_2 \neq \{b', c\}} \bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})}. \end{aligned}$$

This signifies that Eq. (100) has no errors for the target final states $\{b', c\}$, since these states are not present in the ignored remainder, which formally reads as:

$$\begin{aligned} \Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})} &= \sum_{\forall f_2 \neq \{b', c\}} \bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})} \\ &= \sum_{n''=n'+1}^{\infty} \sum_{l'', m''} \bar{Q}_{i_1, c; i_2, n'' l'' m''}^{(\text{CB1})}. \end{aligned} \quad (104)$$

Therefore, $\Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})}$ effectively contains only the approximate bound states of the target above the n' th level. The sole purpose of this formal derivation is to illuminate the information provided by the correction $\Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})}$. The actual computation of $\Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})}$ is not carried out using Eq. (104), but rather by employing the defining relationship (100). The approximate cross section (99) from the ACB1-4B method will be in satisfactory agreement with the corresponding exact result of the CB1-4B method provided that the corrections of the orders higher than $\Delta Q_{i_1, c; i_2, b'+c}^{(\text{CB1})}$ are negligible, and this would occur for:

$$\Delta Q_{i_1, c; i_2, M'_1 l' m'+c}^{(\text{CB1})} \approx 0; \quad M'_1 = M' + 1, \quad (105)$$

where, by reference to Eq. (103), $M' = n'_{\max}$. In other words, if the contributions from the corrections for the final target bound states above the n' th level could be neglected, we will have:

$$Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} \approx Q_{i_1, c; i_2, \Sigma}^{(\text{CB1})}. \quad (106)$$

Thus, when applying the ACB1-4B method, we first include explicitly several dominant states exactly using only a small set $\{f'_2\}$ of size M' . This step is identical to the usual exact computations by means of the CB1-4B method from Eq. (91), convergence of which, however, necessitates a much larger set $\{f'_2\}$ of size N' with $N' \gg M'$. Second, the remainder $Q_{i_1, c; i_2, \Sigma^\perp}^{(\text{CB1})}$ from Eq. (85) is included approximately in the ACB1-4B method through Eqs. (95) and (96), rather than being totally neglected, as done in the CB1-4B method via Eq. (92).

The ACB1-4B method would be computationally superior over the CB1-4B method if indeed $M' \ll N'$, which means that only a small number of corrections $\Delta Q_{i_1, c; i_2, b'}^{(\text{CB1})}$ to $Q_{i_1, c; i_2, b'}^{(\text{CB1})}$ would suffice. Yet, albeit small, the number M' of the accounted exact bound states should still assure that the main physics are included through the selected dominant contributions. The question is which states are the most important?

It is well known that double ionization is the most probable event when a high-energy nucleus strikes a helium-like target. This leads us to the expectation that at high energies, double ionization should also dominate over all the other one- and two-electron processes in collisions between two hydrogen-like atomic systems. As to discrete target final states, the general Oppenheimer n^{-3} rule [134] implies that the low-lying energy levels should dominate in the spectrum $\{\varphi_{nlm}(x_2)\}$. Therefore, the set $\{f'_2\}$ of the exact target final states should contain the entire continuous spectrum and also certain low-lying bound states $\{n'l'm'\}$ as already indicated in Eq. (99). Obviously, the most profitable choice would be to take the minimal value $M' = 1$, which accounts exactly only for the target final true ground state $b' = f'_2 = 1s$ (besides the already included exact continuum). This would yield the main working formula of what is projected to be the optimal variant of the ACB1-4B method as a reduction of Eq. (99) via:

$$Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} \approx Q_{i_1, c; i_2, 1s+c}^{(\text{CB1})} + \Delta Q_{i_1, c; i_2, 1s+c}^{(\text{CB1})} \quad (107)$$

where

$$\Delta Q_{i_1, c; i_2, 1s+c}^{(\text{CB1})} \approx \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - \left\{ \bar{Q}_{i_1, c; i_2, 1s}^{(\text{CB1})} + \bar{Q}_{i_1, c; i_2, c}^{(\text{CB1})} \right\}. \quad (108)$$

The approximation (107) will be adequate if the corrections of the order higher than $\Delta Q_{i_1, c; i_2, 1s+c}^{(\text{CB1})}$ could be neglected.

Since Eq. (107) includes exactly the whole continuum and the ground state, it is obviously advantageous to choose $\bar{E}$ to coincide with the exact energy $E_2 = -Z_T^2/8$. In such a case, the main working formula (107) of the ACB1-4B method would be improved due to inclusion of the exact contribution from the set $\{1s, 2s, 2p, \kappa_1\}$. This occurs because for $\bar{E} = E_2$, the level

$n = 2$ of the final target state is also included exactly by way of $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ from the rhs of Eq. (108). Therefore, in view of the evident relation $\Delta Q_{i_1, c; i_2, 2l'm'}^{(\text{CB1})} \equiv 0$ for $\bar{E} = E_2$, it follows that the ACB1-4B method from Eq. (107) will be adequate in the sense of closely agreeing with the CB1-4B method via Eq. (106) provided that:

$$\Delta Q_{i_1, c; i_2, 3l'm'+c}^{(\text{CB1})} \approx 0, \quad \bar{E} = E_2 = -\frac{Z_T^2}{8}. \quad (109)$$

Computationally, the correction $\Delta Q_{i_1, c; i_2, 1s+c}^{(\text{CB1})}$ from Eq. (107) does not invoke any considerable effort, since both $\bar{Q}_{i_1, c; i_2, 1s}^{(\text{CB1})}$ and $\bar{Q}_{i_1, c; i_2, c}^{(\text{CB1})}$ can be obtained in the same way as their respective counterparts $Q_{i_1, c; i_2, 1s}^{(\text{CB1})}$ and $Q_{i_1, c; i_2, c}^{(\text{CB1})}$ through replacement of $q_{\min}$ by $\bar{q}_{\min}$. Validity of Eq. (107) rests on the assumption that higher order corrections $n > 2$ are negligible as stated by Eq. (109). By showing that the sole expression Eq. (107) could suffice in practice, one would demonstrate a significant efficiency gain in the ACB1-4B method relative to the CB1-4B method. Explicit computations are needed to assess whether the variant Eq. (107) of the ACB1-4B method could be both accurate and fast, that is, optimal in comparison with the exact CB1-4B method. This is the subject of Section 13.

11. CLOSURE APPROXIMATION

The CA is explicitly present in the ACB1-4B method through the term $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ in the correction $\Delta Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})}$ from Eq. (95). Therefore, to complete the computation in the ACB1-4B method, the cross sections $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ of the CA are necessary. Aside from this, the CA is interesting in its own right and, as such, it deserves to be analyzed separately, as we shall do in this section.

Whenever state-to-state transitions are not of interest, as in process Eq. (1), the efficiency of computations would be significantly enhanced by carrying out simultaneously and at once the sum over both the discrete and continuous parts of the target spectrum considered as a whole. This could be readily accomplished using the closure relation (29). However, computations without an additional approximation, such as summation over the composite label f_2 , are impossible due to the dependence of $q_{\min}$ on the energy E_{f_2} . Nevertheless, it is still important to investigate the usefulness of the CA which consists of replacing the exact energy E_{f_2} in $q_{\min}$ from (64) by a certain average energy $\bar{E}$ as in $\bar{q}_{\min}$ from Eq. (93) and subsequently using the closure relation (29).

In physics, the bar sign over a quantity is usually employed to indicate a certain average value of that quantity. In the present context, $\bar{E}$ can but does not necessarily need to present an average energy of all the true energies E_{f_2} of $(Z_T, e_2)_{f_2}$. Quite the contrary, $\bar{E}$ might be any fixed energy which could be totally unrelated to $(Z_T, e_2)_{f_2}$. Of course, $\bar{E}$ could coincide with any given exact energy $E_{f_{2,0}}$ of the system $(Z_T, e_2)_{f_2}$, where $f_{2,0}$ is one chosen value from the whole spectrum f_2 , such that $E_{f_{2,0}}$ can be either negative or positive for bound or continuum states, respectively.⁷ The CB1-4B method is well suited for implementation of the CA because of the availability of the corresponding exact results within the same theory.

To proceed, we pick up a fixed average energy $\bar{E}$ which can be any negative, zero, or positive number. The replacement $E_{f_2} \approx \bar{E}$ leads to the approximation (93) for the minimal value of the momentum transfer. Utilizing Eqs. (54), (55), and (93) with $\bar{q}_{\min}$ instead of $q_{\min}$, the estimate $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ within the CA is obtained for the associated exact $Q_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ in the CB1-4B method via:

$$\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} = \sum_{f_2} \bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})} \quad (110)$$

as in Eq. (97) where

$$\bar{Q}_{i_1, c; i_2, f_2}^{(\text{CB1})} = \frac{1}{2\pi v^2} \int d\mathbf{\kappa}_1 \int_{\bar{q}_{\min}}^{2\mu v} dq q \left| R_{i_1, \mathbf{\kappa}_1; i_2, f_2}^{(\text{CB1})} \right|^2. \quad (111)$$

Upon insertion of cross section (111) into (110), the sum over f_2 and the integral over q can now exchange their order of applications, since $\bar{q}_{\min}$ does not depend on f_2 :

$$\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} = \frac{1}{2\pi v^2} \int d\mathbf{\kappa}_1 \int_{\bar{q}_{\min}}^{2\mu v} dq q S_{i_1, \mathbf{\kappa}_1; i_2, \Sigma}^{(\text{CB1})} \quad (112)$$

where

$$S_{i_1, \mathbf{\kappa}_1; i_2, \Sigma}^{(\text{CB1})} = \sum_{f_2} \left| R_{i_1, \mathbf{\kappa}_1; i_2, f_2}^{(\text{CB1})} \right|^2. \quad (113)$$

⁷ In two different contexts, the closure relation inserted after the replacement of exact energies by their average counterparts has first been used by Unsöld [135] and subsequently applied by Massey and Mohr [136] as well as by many other authors (see, e.g., Ref. [137]).

Substituting the matrix element $R_{i_1, k_1; i_2, f_2}^{(\text{CB1})}$ from Eq. (65) into Eq. (113), we first exploit the closure relation (29) to arrive at:

$$\begin{aligned}
 S_{i_1, \mathbf{k}_1; i_2, \Sigma}^{(\text{CB1})} &= \iiint \mathrm{d}\mathbf{s}_1 \mathrm{d}\mathbf{x}_2 \mathrm{d}\mathbf{R} e^{i\mathbf{q} \cdot \mathbf{R}} \varphi_{\mathbf{k}_1}^{-*}(\mathbf{s}_1) \left(\frac{1}{x_{12}} - \frac{Z_T}{x_1} \right) \varphi_{i_1}(\mathbf{s}_1) \varphi_{i_2}(\mathbf{x}_2) \\
 &\times \left\{ \iiint \mathrm{d}\mathbf{s}'_1 \mathrm{d}\mathbf{x}'_2 \mathrm{d}\mathbf{R}' e^{i\mathbf{q} \cdot \mathbf{R}'} \varphi_{\mathbf{k}_1}^{-}(\mathbf{s}'_1) \left(\frac{1}{|\mathbf{x}'_1 - \mathbf{x}'_2|} - \frac{Z_T}{x'_1} \right) \varphi_{i_1}^*(\mathbf{s}'_1) \varphi_{i_2}^*(\mathbf{x}'_2) \right\} \\
 &\times \delta(\mathbf{x}_2 - \mathbf{x}'_2) \\
 &= \iiint \mathrm{d}\mathbf{s}_1 \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 e^{i\mathbf{q} \cdot (\mathbf{x}_1 - \mathbf{s}_1)} \varphi_{\mathbf{k}_1}^{-*}(\mathbf{s}_1) \left(\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} - \frac{Z_T}{x_1} \right) \varphi_{i_1}(\mathbf{s}_1) \varphi_{i_2}(\mathbf{x}_2) \\
 &\times \left\{ \iint \mathrm{d}\mathbf{x}'_1 \mathrm{d}\mathbf{s}'_1 e^{-i\mathbf{q} \cdot (\mathbf{x}'_1 - \mathbf{s}'_1)} \varphi_{\mathbf{k}_1}^{-}(\mathbf{s}'_1) \left(\frac{1}{|\mathbf{x}'_1 - \mathbf{x}_2|} - \frac{Z_T}{x'_1} \right) \varphi_{i_1}^*(\mathbf{s}'_1) \varphi_{i_2}^*(\mathbf{x}_2) \right\}.
 \end{aligned} \tag{114}$$

In the two last lines from Eq. (114), the Jacobian of the transformation from the integration volume $\mathrm{d}\mathbf{s}_1 \mathrm{d}\mathbf{x}_2 \mathrm{d}\mathbf{R}$ to $\mathrm{d}\mathbf{s}_1 \mathrm{d}\mathbf{x}_2 \mathrm{d}\mathbf{x}_1$ is equal to unity. Further, integrations over $\mathbf{x}_1$ and $\mathbf{x}'_1$ can be carried out by means of the Bethe integrals from Eq. (68) so that:

$$\begin{aligned}
 S_{i_1, \mathbf{k}_1; i_2, \Sigma}^{(\text{CB1})} &= \frac{4\pi}{q^2} \iint \mathrm{d}\mathbf{s}_1 \mathrm{d}\mathbf{x}_2 e^{-i\mathbf{q} \cdot \mathbf{s}_1} \varphi_{\mathbf{k}_1}^{-*}(\mathbf{s}_1) (e^{i\mathbf{q} \cdot \mathbf{x}_2} - Z_T) \varphi_{i_1}(\mathbf{s}_1) \varphi_{i_2}(\mathbf{x}_2) \\
 &\times \left\{ \frac{4\pi}{q^2} \iint \mathrm{d}\mathbf{s}'_1 e^{i\mathbf{q} \cdot \mathbf{s}'_1} \varphi_{\mathbf{k}_1}^{-}(\mathbf{s}'_1) (e^{-i\mathbf{q} \cdot \mathbf{x}_2} - Z_T) \varphi_{i_1}^*(\mathbf{s}'_1) \varphi_{i_2}^*(\mathbf{x}_2) \right\} \\
 &= \frac{16\pi^2}{q^4} \left| \int \mathrm{d}\mathbf{s}_1 e^{-i\mathbf{q} \cdot \mathbf{s}_1} \varphi_{\mathbf{k}_1}^{-*}(\mathbf{s}_1) \varphi_{i_1}(\mathbf{s}_1) \right|^2 \\
 &\times \int \mathrm{d}\mathbf{x}_2 \varphi_{i_2}^*(\mathbf{x}_2) \varphi_{i_2}(\mathbf{x}_2) (Z_T - e^{i\mathbf{q} \cdot \mathbf{x}_2} - e^{-i\mathbf{q} \cdot \mathbf{x}_2} + Z_T) \\
 &= \frac{32\pi^2}{q^4} \left| \int \mathrm{d}\mathbf{s}_1 e^{-i\mathbf{q} \cdot \mathbf{s}_1} \varphi_{\mathbf{k}_1}^{-*}(\mathbf{s}_1) \varphi_{i_1}(\mathbf{s}_1) \right|^2 \\
 &\times \left\{ Z_T - \text{Re} \int \mathrm{d}\mathbf{x}_2 e^{i\mathbf{q} \cdot \mathbf{x}_2} \varphi_{i_2}^*(\mathbf{x}_2) \varphi_{i_2}(\mathbf{x}_2) \right\},
 \end{aligned} \tag{115}$$

where the symbol $\text{Re}(z)$ denotes the real part of the complex number z . This result can be rewritten in terms of the form factors from Eqs. (73) and (74) as:

$$S_{i_1, \mathbf{k}_1; i_2, \Sigma}^{(\text{CB1})} = \frac{32\pi^2}{q^4} |J_{i_1, \mathbf{k}_1}|^2 \{Z_T - \text{Re}(I_{i_2, i_2})\}. \tag{116}$$

Inserting the result (116) into (112), it follows:

$$\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} = \frac{16\pi}{v^2} \int d\mathbf{\kappa}_1 \int_{\bar{q}_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \mathbf{\kappa}_1}|^2 \{Z_T - \text{Re}(I_{i_2, i_2})\}. \quad (117)$$

Using the property $\varphi_{i_2}(-\mathbf{x}_2) = \varphi_{n_2 l_2 m_2}(-\mathbf{x}_2) = (-1)^{l_2} \varphi_{n_2 l_2 m_2}(\mathbf{x}_2) = (-1)^{l_2} \varphi_{i_2}(\mathbf{x}_2)$, we have:

$$\begin{aligned} I_{i_2, i_2}^* &= \int d\mathbf{x}_2 e^{iq \cdot \mathbf{x}_2} \varphi_{i_2}(\mathbf{x}_2) \varphi_{i_2}^*(\mathbf{x}_2) \\ &= \int d\mathbf{x}_2 e^{-iq \cdot \mathbf{x}_2} \varphi_{i_2}(-\mathbf{x}_2) \varphi_{i_2}^*(-\mathbf{x}_2) \\ &= (-1)^{2l_2} \int d\mathbf{x}_2 e^{-iq \cdot \mathbf{x}_2} \varphi_{i_2}(\mathbf{x}_2) \varphi_{i_2}^*(\mathbf{x}_2) = I_{i_2, i_2}^* \end{aligned}$$

so that

$$I_{i_2, i_2}^* = I_{i_2, i_2} = \int d\mathbf{x}_2 e^{-iq \cdot \mathbf{x}_2} |\varphi_{i_2}(\mathbf{x}_2)|^2, \quad \text{Re}(I_{i_2, i_2}) = I_{i_2, i_2}. \quad (118)$$

Thus, the integral I_{i_2, i_2} is always real for any state i_2 and, therefore, the cross section (117) of the CA can acquire its final form as:

$$\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} = \frac{16\pi}{v^2} \int d\mathbf{\kappa}_1 \int_{\bar{q}_{\min}}^{2\mu v} \frac{dq}{q^3} |J_{i_1, \mathbf{\kappa}_1}|^2 (Z_T - I_{i_2, i_2}). \quad (119)$$

This is a manageable formula due to the simplicity of the remaining bound-bound (I_{i_2, i_2}) and bound-free ($J_{i_1, \mathbf{\kappa}_1}$) form factors that possess their easily obtainable, analytical expressions [122–127].

In general, an advantage of the CA is that it includes the whole final target spectrum at once. However, a disadvantage is that the cross section (119) in the CA depends on a free parameter $\bar{E}$, which is an average energy used in $\bar{q}_{\min}$ instead of the exact energy E_{f_2} from $q_{\min}$. As mentioned, the arbitrary parameter $\bar{E}$ can be chosen to coincide with any fixed exact binding energy E_{n_0} of the target (Z_T, e_2) $_{nlm}$ for a selected principal quantum number $n = n_0$ in the interval $n_0 \in [1, \infty]$. The special value $n_0 = \infty$ for the highest Rydberg state can also be selected for $\bar{E}$ in which case the average energy becomes the ionization threshold $\bar{E} = E_{n_0} = E_{\infty} = 0$. Also any positive energy from the unbound, continuum spectrum can be selected for the average energy $\bar{E}$, as discussed.

In any case, for an arbitrarily chosen $\bar{E}$, one ends up by using $\bar{q}_{\min}$ from Eq. (93) in place of the exact $q_{\min}$, which is given by Eq. (64). Since $\bar{E}$ is arbitrary, the pertinent question is how serious this arbitrariness could be?

To answer this question only qualitatively, in the first instance, it is sufficient to observe that the main contribution to the integral over q comes from the close neighborhood of the lower limit $\bar{q}_{\min}$ or $q_{\min}$ in both the cross sections with or without the CA, respectively. Also when $f_2 = \{nlm\}$, the lowest energy levels provide the dominant contributions in the discrete part of the target spectrum. For any chosen $\bar{E}$, the difference between $q_{\min}$ and $\bar{q}_{\min}$ is given by:

$$\Delta q_{\min} \equiv q_{\min} - \bar{q}_{\min} = \frac{E_{f_2} - \bar{E}}{v}. \quad (120)$$

If we choose $\bar{E} = E_{n_0}$ where E_{n_0} is any fixed exact energy $E_{n_0} = E_{f_{2,0}} \equiv -Z_T^2/(2n_0^2)$, we will have $q_{\min} = (E_n + \kappa_1^2 + |E_i|)/v$ and $\bar{q}_{\min} = (E_{n_0} + \kappa_1^2 + |E_i|)/v$. In this case, Eq. (120) becomes:

$$\Delta q_{\min} = \frac{E_n - E_{n_0}}{v} = \frac{Z_T^2}{2v} \left(\frac{1}{n_0^2} - \frac{1}{n^2} \right). \quad (121)$$

In both the general and particular cases of $\bar{E}$ from Eqs. (120) and (121), respectively, we see that $\Delta q_{\min}$ increases when v is diminished. Hence, the replacement of $q_{\min}$ by $\bar{q}_{\min}$ will affect most appreciably the cross sections at lower and intermediate impact energies. In other words, the CA is expected to be primarily a high-energy approximation. Moreover, it is also clear from Eq. (120) that the approximation $q_{\min} \approx \bar{q}_{\min}$ will influence most noticeably the lowest bound states that contribute dominantly in the discrete part of the spectrum. As the values of n are augmented, $\Delta q_{\min}$ from Eq. (121) becomes progressively smaller.

Still staying with the said choice $\bar{E} = E_{n_0} = -Z_T^2/(2n_0^2)$, it follows that for the energies below E_{n_0} ($n < n_0$), we will have $\Delta q_{\min} < 0$ so that $q_{\min} < \bar{q}_{\min}$ and $\bar{Q}_{i_1,c;i_2,nlm}^{(CB1)} < Q_{i_1,c;i_2,nlm}^{(CB1)}$. Thus, in such a case, the contribution to the cross section (119) in the CA from all the discrete states $\{nlm\}$ of binding energy below $\bar{E} = E_{n_0}$ will be underestimated. Simultaneously, for all the energy levels above $\bar{E} = E_{n_0}$ ($n > n_0$), we have $\Delta q_{\min} > 0$ so that $q_{\min} > \bar{q}_{\min}$ and, therefore, $\bar{Q}_{i_1,c;i_2,nlm}^{(CB1)} > Q_{i_1,c;i_2,nlm}^{(CB1)}$. This implies overestimation of the true cross section by the CA. Moreover, the whole exact continuous spectrum in the CA will also be overestimated, since $\Delta q_{\min} = (\kappa_2^2 + |E_{n_0}|) > 0$ implying $q_{\min} > \bar{q}_{\min}$ for any E_{n_0} so that $\bar{Q}_{i_1,c;i_2,c}^{(CB1)} > Q_{i_1,c;i_2,c}^{(CB1)}$. All told, we have

$$\begin{aligned} \bar{Q}_{i_1,c;i_2,nlm}^{(CB1)} &< Q_{i_1,c;i_2,nlm}^{(CB1)}; & \bar{q}_{\min} &> q_{\min}, & n < n_0 \\ \bar{Q}_{i_1,c;i_2,nlm}^{(CB1)} &> Q_{i_1,c;i_2,nlm}^{(CB1)}; & \bar{q}_{\min} &< q_{\min}, & n > n_0 \\ \bar{Q}_{i_1,c;i_2,c}^{(CB1)} &> Q_{i_1,c;i_2,c}^{(CB1)}; & \bar{q}_{\min} &< q_{\min}. \end{aligned} \quad (122)$$

In other words, underestimation or overestimation of the exact cross section $Q_{i_1,c;i_2,f_2}^{(\text{CB1})}$ by the corresponding estimate $\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})}$ occurs for $\Delta\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})} > 0$ and $\Delta\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})} < 0$, respectively, where:

$$\Delta\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})} \equiv Q_{i_1,c;i_2,f_2}^{(\text{CB1})} - \bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})}, \quad (123)$$

or, explicitly,

$$\Delta\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})} = \frac{8\pi}{v^2} \int d\kappa_1 \int_{\bar{q}_{\min}}^{q_{\min}} \frac{dq}{q^3} |I_{i_1,\kappa_1}|^2 |I_{i_2,f_2} - Z_T \delta_{i_2,f_2}|^2. \quad (124)$$

Note that ΔQ from Eq. (96) and $\bar{\Delta Q}$ from Eq. (114) are two different quantities. Of course, for the particular choice $\bar{E} = E_{n_0}$ where E_{n_0} is one element from the set of the exact target binding energies $\{E_n\}$, the true state with $n = n_0$ is included exactly in $\bar{Q}_{i_1,c;i_2,n_0}^{(\text{CB1})}$ in which case:

$$\Delta\bar{Q}_{i_1,c;i_2,n_0}^{(\text{CB1})} = 0, \quad \bar{E} = E_{n_0} = -\frac{Z_T^2}{2n_0^2}. \quad (125)$$

Since the integrands in the exact and approximate q -integral over the interval $[q_{\min}, 2\mu v]$ and $[\bar{q}_{\min}, 2\mu v]$ in $Q_{i_1,c;i_2,f_2}^{(\text{CB1})}$ and $\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})}$, respectively, are both positive functions, the sign of $\Delta\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})}$ is determined exclusively by the sign of $\Delta q_{\min}$ via $\text{sgn}\{\Delta\bar{Q}_{i_1,c;i_2,f_2}^{(\text{CB1})}\} = -\text{sgn}\{\Delta q_{\min}\}$ where $\text{sgn}(x) = |x|/x$.

For example, if $\bar{E} = E_2 = -Z_T^2/8$, only the yield from the ground state ($n=1=1s$) with energy $E_1 = -Z_T^2/2$ will be underestimated by the CA, which simultaneously would overestimate the contribution due to all the excited final target states with $n > 2$, as well as the total yield from the whole continuum $\{\kappa_2\}$. This would specify the relationships in Eq. (122) as:

$$\begin{aligned} \bar{Q}_{i_1,c;i_2,nlm}^{(\text{CB1})} &< Q_{i_1,c;i_2,nlm}^{(\text{CB1})}; & \bar{q}_{\min} &> q_{\min}, & n < 2 \\ \bar{Q}_{i_1,c;i_2,nlm}^{(\text{CB1})} &> Q_{i_1,c;i_2,nlm}^{(\text{CB1})}; & \bar{q}_{\min} &< q_{\min}, & n > 2 \\ \bar{Q}_{i_1,c;i_2,c}^{(\text{CB1})} &> Q_{i_1,c;i_2,c}^{(\text{CB1})}; & \bar{q}_{\min} &< q_{\min}. \end{aligned} \quad (126)$$

The level $n=2$ with the exact $2s$ and $2p$ states is accounted for exactly in $\bar{Q}_{i_1,c;i_2,nlm}^{(\text{CB1})}$ so that $\Delta\bar{Q}_{i_1,c;i_2,2lm}^{(\text{CB1})} \equiv 0$ for $\bar{E} = E_1 = -Z_T^2/8$. Veracity of these qualitatively established relationships will be assessed quantitatively in the Section 13 using a number of illustrations.

12. CORRECTED CLOSURE APPROXIMATION

Given the anticipated inadequacy of the CA at lower and intermediate impact energies, the key question is to see whether there could be a way to systematically improve this procedure in order to make it a practical and useful theoretical tool within the CB1-4B method or the like.

It turns out that this question has precisely the same answer as the related question in Section 10: how can convergence of the CB1-4B method be accelerated with respect to the increasing number of final target states?

This comes about from a mere rearrangement of the defining expression (95) for the cross section in the ACB1-4B method:

$$\begin{aligned} Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} &= Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} + \left\{ \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} \right\} \\ &= \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} + \left\{ Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} \right\}, \end{aligned}$$

so that

$$Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} = \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} + \Delta \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} \quad (127)$$

where

$$\Delta \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} = Q_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})}. \quad (128)$$

We can also write Eq. (128) in terms of the state-to-state difference term from Eq. (123) via:

$$\Delta \bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})} = \sum_{f_2'} \Delta \bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})} \quad (129)$$

where $\Delta \bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})}$ is of the form (123) except for using f_2' instead of f_2 :

$$\Delta \bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})} = Q_{i_1, c; i_2, f_2'}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})} \quad (130)$$

or, explicitly, by way of Eq. (124):

$$\Delta \bar{Q}_{i_1, c; i_2, f_2'}^{(\text{CB1})} = \frac{8\pi}{v^2} \int d\mathbf{\kappa}_1 \int_{\bar{q}_{\min}}^{q_{\min}} \frac{dq}{q^3} |J_{i_1, \mathbf{\kappa}_1}|^2 |I_{i_2, f_2'} - Z_T \delta_{i_2, f_2'}|^2. \quad (131)$$

In both Eqs. (128) and (129), barred cross sections employ $\bar{q}_{\min}$ but since they do not invoke the closure relation (29) they are not from the CA, as per our previous, related remark.

As seen, only a re-shuffling of the terms in the passage from Eqs. (95) to (127) resulted in rewriting the same general result $Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})}$ in an alternative form with a different emphasis. This time, the equivalent form (127) singles out the CA ansatz $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ which is then automatically accompanied by the correcting term $\Delta\bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{CB1})}$ from (128). The correction in Eq. (128) is of a localized character in the sense of being dependent only on a small set $\{f'_2\} \subset \{f_2\}$. This local feature of the correction from Eq. (128) is more transparent in Eq. (129) by way of which Eq. (127) becomes:

$$Q_{i_1, c; i_2, \Sigma'}^{(\text{ACB1})} = \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} + \sum_{f'_2} \Delta\bar{Q}_{i_1, c; i_2, f'_2}^{(\text{CB1})}. \quad (132)$$

Thus, the cross section in the ACB1-4B method can equivalently be expressed as the sum of two terms. The first term is $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ the CA to the CB1-4B method. The second term $\sum_{f'_2} \Delta\bar{Q}_{i_1, c; i_2, f'_2}^{(\text{CB1})}$ represents the sum of all the individual corrections for each exact state f'_2 which one intends to explicitly include.⁸ As such, this different aspect of the ACB1-4B method has the meaning of the corrected closure approximation (CCA).

Suppose that the average energy $\bar{E}$ is chosen to coincide with a fixed exact energy $E_{f'_{2,0}}$ from the subset $\{E_{f'_2}\}$ of the final target energies $\{E_{f_2}\}$. In such a case, the particular exact state vector $\varphi_{f'_{2,0}}(\mathbf{x}_2)$ would be included fully in the closure result $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ through the term $\bar{Q}_{i_1, c; i_2, f'_{2,0}}^{(\text{CB1})}$. Hence, the corresponding correction $\Delta\bar{Q}_{i_1, c; i_2, f'_{2,0}}^{(\text{CB1})}$ should be unnecessary. Indeed, for $\bar{E} = E_{f'_{2,0}}$, we have $\bar{q}_{\min} = q_{\min}$ which leads to $\bar{Q}_{i_1, c; i_2, f'_{2,0}}^{(\text{CB1})} = Q_{i_1, c; i_2, f'_{2,0}}^{(\text{CB1})}$ and, therefore, $\Delta\bar{Q}_{i_1, c; i_2, f'_{2,0}}^{(\text{CB1})} = 0$.

In the spirit of the simplest version (107) of the ACB1-4B method, we can also retain only two corrections in Eq. (132), one for the ground state $f'_2 = 1s$ and the other for continuum $f'_2 = c$. This gives:

$$Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})} = \bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})} + \Delta\bar{Q}_{i_1, c; i_2, 1s+c}^{(\text{CB1})} \quad (133)$$

where

$$\Delta\bar{Q}_{i_1, c; i_2, 1s+c}^{(\text{CB1})} = \Delta\bar{Q}_{i_1, c; i_2, 1s}^{(\text{CB1})} + \Delta\bar{Q}_{i_1, c; i_2, c}^{(\text{CB1})} \quad (134)$$

$$\Delta\bar{Q}_{i_1, c; i_2, 1s}^{(\text{CB1})} = Q_{i_1, c; i_2, 1s}^{(\text{CB1})} - \bar{Q}_{i_1, c; i_2, 1s}^{(\text{CB1})} \quad (135)$$

⁸ Contributions of the selected exact states f'_2 emerge explicitly through $Q_{i_1, c; i_2, f'_2}^{(\text{CB1})}$ contained in $\Delta\bar{Q}_{i_1, c; i_2, f'_2}^{(\text{CB1})}$ which simultaneously cancels $\bar{Q}_{i_1, c; i_2, f'_2}^{(\text{CB1})}$ in $\bar{Q}_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ while obtaining $\bar{Q}_{i_1, c; i_2, \Sigma'}^{(\text{ACB1})}$ by means Eq. (127).

$$\Delta\bar{Q}_{i_1,c;i_2,1c}^{(\text{CB1})} = Q_{i_1,c;i_2,c}^{(\text{CB1})} - \bar{Q}_{i_1,c;i_2,c}^{(\text{CB1})}. \quad (136)$$

The CCA from Eq. (133) will be as accurate as the CB1-4B method itself provided that the sum of all the corrections of the order higher than $\Delta\bar{Q}_{i_1,c;i_2,1s+c}^{(\text{CB1})}$ give a negligible contribution.

In Eq. (133), the CA estimate $\bar{Q}_{i_1,c;i_2,\Sigma}^{(\text{CB1})}$ includes approximately the ground state and the whole continuum of the target via $\Delta\bar{Q}_{i_1,c;i_2,1s+c}^{(\text{CB1})}$ from Eq. (134). This approximate contribution is afterwards cancelled in the CCA by the corresponding part from the correction $\Delta\bar{Q}_{i_1,c;i_2,1s+c}^{(\text{CB1})}$ as is clear from Eqs. (133), (135), and (136). Stated differently, by computing merely a single correction $\Delta\bar{Q}_{i_1,c;i_2,c}^{(\text{CB1})}$ to the CA estimate $\bar{Q}_{i_1,c;i_2,\Sigma}^{(\text{CB1})}$ it is clear that the CCA removes all the errors from the replacement of $q_{\min}$ by $\bar{q}_{\min}$ in the continuum part of the target spectrum. And this is likewise the case for the target ground state.

Importantly, the CCA includes the target exact ground state and continuum for any value of the average energy $\bar{E}$. Thus, nothing would be gained by choosing $\bar{E} > 0$, since the target continuum does not need any correction. Therefore, an average energy $\bar{E} < 0$ is recommended, in general. In particular, a negative $\bar{E}$ should coincide with one of the exact binding energies $E_n = -Z_T^2/(2n^2)$ of the target discrete spectrum. Such a choice $\bar{E} = E_{n_0}$ where E_{n_0} is a fixed binding target energy from the exact set $\{E_n\}$, would automatically include the exact cross section $Q_{i_1,c;i_2,n_0}^{(\text{CB1})}$ in $\bar{Q}_{i_1,c;i_2,\Sigma}^{(\text{CB1})}$ with the added value $\Delta\bar{Q}_{i_1,c;i_2,n_0}^{(\text{CB1})} = 0$. Here, specification of quantum numbers l and m is omitted as inessential. Of course, we should not choose $n_0 = 1$, since the ground state $\bar{E} = E_1 = -Z_T^2/2$ is already included exactly in Eq. (133) so that $\Delta\bar{Q}_{i_1,c;i_2,1s}^{(\text{CB1})} = 0$.

Note that $\Delta q_{\min}$ from Eq. (121) is the length of the integration interval in the correction term $\Delta\bar{Q}_{i_1,c;i_2,f_2'}^{(\text{CB1})}$ from Eq. (131). For the mentioned choice $\bar{E} = E_{n_0}$ the quantity $\Delta q_{\min}$ declines rapidly with n as $1/n^2$. Therefore, with increasing n , the correction term $\Delta\bar{Q}_{i_1,c;i_2,f_2'}^{(\text{CB1})}$ will quickly become negligible because of shrinkage of the integration range $\Delta q_{\min} = q_{\min} - \bar{q}_{\min}$ in Eq. (131). This points to the possibility for good convergence features of the CCA.

In applying the CCA within the CB1-4B method, one would be interested in obtaining a reliable upper bound to the otherwise unavailable exact cross section $Q_{i_1,c;i_2,\Sigma}^{(\text{CB1})}$. It is here where a significant efficiency gain can be achieved by a judicious choice of $\bar{E}$ which we already said should preferably be one of the exact target binding energies $\{E_n\}$, say $E_{n_0} \in \{E_n\}$. In such a case, the corrections $\Delta\bar{Q}_{1s,c;1s,nlm}^{(\text{CB1})}$ will be positive and negative for $E_n < E_{n_0}$ and $E_n > E_{n_0}$ respectively. Thus, the cross section $Q_{i_1,c;i_2,\Sigma}^{(\text{ACB1})}$ within the CCA will

represent an upper bound to the corresponding exact result $Q_{i_1, c; i_2, \Sigma}^{(\text{CB1})}$ by retaining only $\Delta \bar{Q}_{1s, c; 1s, nlm}^{(\text{CB1})}$ below the n_0 th level ($n \leq n_0 - 1$).

For instance, by choosing $n_0 = 2$, that is, setting $\bar{E} = E_2 = -Z_T^2/8$, the cross section $Q_{i_1, c; i_2, \Sigma}^{(\text{ACB1})}$ from Eq. (133) would represent the sought upper bound to the exact result $Q_{1s, c; 1s, \Sigma}^{(\text{CB1})}$. Theoretically, it is appealing to obtain an upper bound to the exact cross section by improving the CA result merely through two corrections (one for the whole continuum and the other for the ground state) as in Eq. (133). Nevertheless, this does not say anything about the accuracy of such an upper bound. Explicit computations are needed to address this critical issue and this is the subject of Section 13.

We re-emphasize that the ACB1 method is identical to the CCA, and they both rely on the CB1-4B method. The ACB1-4B method initially computes exact cross sections for a few true target states that are afterwards corrected to compensate for neglect of the remaining part of the whole spectrum. The CCA initially evaluates the CA which is then subsequently corrected to a posteriori include a number of exact target states. The sum of the cross sections that are singled out in these two procedures and their corresponding corrections is the same. In other words, the mentioned two summands are different, but their sums give the same cross section. The interest in forming such two different summands is in seeing how the cross section which is singled out converges by adding the associated corrections. By so doing, we can verify that the convergence rate of the CB1 method is improved by the ACB1 method in which cross sections from the CB1 method are factored out. On the other hand, the CCA cannot accelerate convergence of its factored part, which is the CA, as the closure approximation already includes the entire target spectrum. Since the CA takes into account the whole target spectrum approximately, the severity of the invoked approximation can be mitigated by the appropriate corrections, and this is what the CCA is set to accomplish. In computations, it is sufficient to use only one of the two procedures, for example, in their variants (107) or (133), since they both lead to the same result. It is not until the two subsequent and different comparisons with the CA and CB1 method are made that the purposes of the introduction of the CCA and ACB1 method could fully be appreciated and differentiated. Overall, although at first glance it might have seemed superfluous to split a given expression for a cross section into a pair of two different parts, the above outlines of the two splittings have their well-designed purpose which will be illustrated in Section 13.

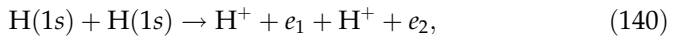
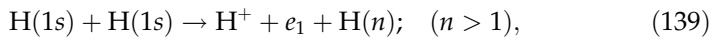
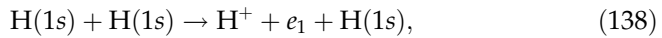
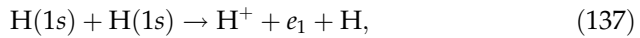
13. COMPARISON BETWEEN THEORIES AND EXPERIMENTS

Here we shall illustrate one- and two-electron transitions (target excitation $i_2 \rightarrow f_2$ with $f_2 \neq i_2$ and ionization $i_2 \rightarrow c$) that can accompany projectile

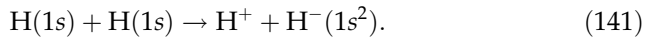
ionization (electron loss $i_1 \rightarrow c$) as the primary collision via processes (4) and (5). Of course, the simplest process (2) of electron loss in which the target is left as intact ($f_2 = i_2$) will also be investigated to assess the relative contributions of both single and double transitions. To compare the theory with experiments (that are not state-selective), process (1) will be analyzed, as well. Finally, the capture channel via process (3) will also be examined for production of the projectile's nuclei.

The first natural example to study is the process of electron loss in collisions between two hydrogen atoms, one as a projectile $H(n_1 l_1 m_1)$ and the other as a target $H(n_2 l_2 m_2)$ for which the experimental data are available. In this Section, we shall limit the analysis to collisions involving two hydrogen atoms in their initial ground states ($i_1 = 1s$, $i_2 = 1s$) in the entrance channel, since mainly these states are also present in the corresponding measurements. Fractions of excited hydrogen atoms $H(n_1 l_1)$ in the projectile beams from measurements are usually estimated to be small (within a few percent). Note, however, that even if the initial beam was carefully prepared with a totally negligible fraction of the projectile excited states $H(n_1 l_1)$, during the course of measurement this beam could nevertheless possess a sizeable fraction of such excited states. Projectile excited atoms $H(n_1 l_1)$ can be formed by electron capture in the $H^+ - H(1s)$ encounter once protons H^+ become available from the primary process, which is electron loss $H(1s) + H(1s) \rightarrow H^+ + e_1 + H$.

In the forthcoming illustrations, we shall consider the following channels of the electron loss process:



and the corresponding electron capture process:



The bare symbol H without any specification in process (137) indicates that the atomic hydrogen target is left in an arbitrary postcollisional state in the exit channel. Recall that for process (139), the part of the label f_2 for the final target bound state denotes the triple of the principal, angular, and magnetic quantum numbers $\{nlm\}$ as in (18). Although we used the CB1-4B method to compute the cross sections $Q_{1s,c;1s,nl}$ for the final target states with the specific values $\{nl\}$, where the sum over all the corresponding magnetic quantum numbers m is carried out, these results for formation of $H(nl)$

will not be given in this work, since there are no corresponding state-selective experimental data available in the literature. Instead, we shall presently be concerned with the cross sections $Q_{1s,c;1s,n}$ for formation of $H(n)$ in the exit channel of process (139), with the understanding that the two sums over $\{lm\}$ have been carried out via:

$$Q_{1s,c;1s,n} = \sum_{l=0}^{n-1} \sum_{m=-1}^{+1} Q_{1s,c;1s,nlm}. \quad (142)$$

Further, the sum over n will also be carried out from unity up to a certain fixed finite positive integer N which secures convergence. The resulting cross sections for formation of $\Sigma_{n=1}^N H(n) \equiv H(\Sigma_1^N)$ will be denoted by $Q_{1s,c;1s,\Sigma_1^N}$:

$$Q_{1s,c;1s,\Sigma_1^N} = \sum_{n=1}^N Q_{1s,c;1s,n}. \quad (143)$$

Since we already set $i_1 = 1s$ as well as $i_2 = 1s$ and, moreover, we integrate over κ_1 for the projectile's ejected electron, it will be convenient to simplify the notation as follows:

$$\begin{aligned} Q_n &= Q_{1s,c;1s,n} \\ Q_c &= Q_{1s,c;1s,c} \\ Q_{\Sigma_1^N} &= Q_{1s,c;1s,\Sigma_1^N} \\ Q_{\Sigma} &\approx Q_{c+\Sigma_1^N} = Q_{1s,c;1s,c} + Q_{1s,c;1s,\Sigma_1^N}. \end{aligned} \quad (144)$$

Likewise, the corresponding notation for the CA is:

$$\begin{aligned} \bar{Q}_n &= \bar{Q}_{1s,c;1s,n} \\ \bar{Q}_c &= \bar{Q}_{1s,c;1s,c} \\ \bar{Q}_{\Sigma} &\equiv \bar{Q}_{c+\Sigma_1^{\infty}} = \bar{Q}_{1s,c;1s,\Sigma} \end{aligned} \quad (145)$$

where symbol Σ in $\bar{Q}_{1s,c;1s,\Sigma}$ is from Eq. (30). We shall also analyze the possibility for stepwise improvements of the CB1-4B method regarding enhancement of the convergence rate as a function of the included exact states of the target in the exit channel by using the ACB1-4B method:

ACB1 :

$$\begin{aligned} Q_1 + \Delta Q_1; \quad \Delta Q_1 &= \bar{Q}_{\Sigma} - \bar{Q}_1 \\ Q_c + \Delta Q_c; \quad \Delta Q_c &= \bar{Q}_{\Sigma} - \bar{Q}_c \\ Q_1 + Q_c + \Delta Q_{1+c}; \quad \Delta Q_{1+c} &= \bar{Q}_{\Sigma} - (\bar{Q}_1 + \bar{Q}_c). \end{aligned} \quad (146)$$

Further, a mere re-shuffling of these partial cross sections from the ACB1-4B method gives an opportunity to seek an improvement of the CA

by means of the CCA:

CCA :

$$\begin{aligned}\bar{Q}_{\Sigma} + \Delta\bar{Q}_1; \quad \Delta\bar{Q}_1 &= Q_1 - \bar{Q}_1 \\ \bar{Q}_{\Sigma} + \Delta\bar{Q}_c; \quad \Delta\bar{Q}_c &= Q_c - \bar{Q}_c \\ \bar{Q}_{\Sigma} + \Delta\bar{Q}_{1+c}; \quad \Delta\bar{Q}_{1+c} &= \Delta\bar{Q}_1 + \Delta\bar{Q}_c.\end{aligned}\tag{147}$$

As stated earlier, either Eq. (146) or Eq. (147) needs to be used in explicit computations since both procedures yield the same result for the CCA and ACB1 method. Nevertheless, the same result obtained from Eq. (146) or Eq. (147) can simultaneously serve two different purposes if compared with CB1 and CA, respectively. In the case of the comparison between the ACB1 and CB1 methods, we will verify whether the former accelerates the latter (i.e., whether the ACB1 method with only a handful of exact states obtains the same result as the CB1 method for nearly all the target states). Likewise, when comparing the CCA and CA, we will check whether the former bridges the gap between the latter approximation and the fully converged CB1-4B method. In these two comparisons, the CB1-4B method is the reference theory within which both the CCA and ACB1-4B are introduced. Therefore, the ultimate goal of the CCA and ACB1-4B method is to achieve agreement with the CB1-4B method which includes exactly all target states (or, in practical terms, those dominant states for which convergence has been reached).

In all the cross sections from Eqs. (144)–(147), the subscripts relate exclusively to the final state of the target electron e_2 . Specifically, in the present computations, we have varied N from 1 to 6. Regarding process (140) with double ionization, we shall introduce the symbol $H(c)$ to denote the continuum of the final target states, $H(c) \equiv H^+ + e_2 \equiv H^+ + e$ (hereafter there is no need to distinguish the electrons by their subscripts). Finally, to refer to process (137) in which the target H is left in any state (where summation over all discrete and continuum states of the target in the exit channel should be performed), the appropriate symbol is $H \equiv H(c + \Sigma_1^N)$. In principle, we should have $N = \infty$, but in practice, of course, a finite N is selected for which the sum in Eq. (143) has converged to a sufficient accuracy. Our illustrations will show that it is largely sufficient to set $N = 6$. This justifies that the exact cross sections Q_{Σ} for process (137), with the target left in any state, can be approximated by:

$$Q_{\Sigma} \approx Q_{c+\Sigma_1^6} = Q_c + \sum_{n=1}^6 Q_n.\tag{148}$$

In addition to cross sections from the exact CB1-4B method illustrated in Figures 6.1–6.8, we shall also show the corresponding results from the ACB1-4B method (Figures 6.9–6.11), as well as those due to the CA (Figure 6.12), and

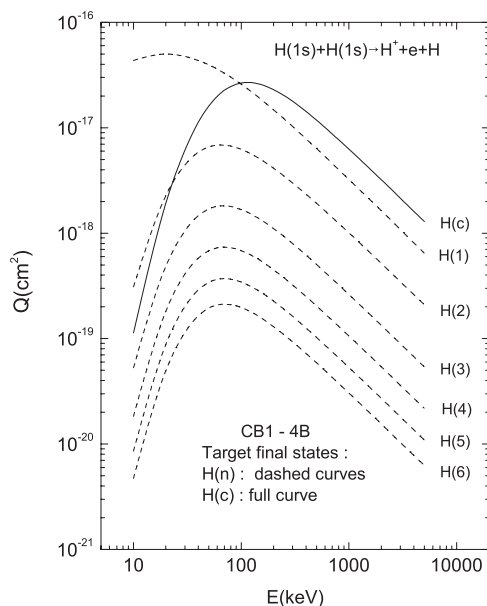
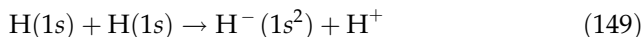


Figure 6.1 Cross sections Q as a function of the impact energy E for electron loss processes (138)–(140). Theory (exact CB1-4B method): (i) dashed curves, cross sections Q_n for target bound states $H(n)$ with $n = 1$ (target unaltered) and $2 \leq n \leq 6$ (target excitation), where the sum over the $\{lm\}$ degeneracies is carried out according to Eq. (142). (ii) Full curve, cross sections Q_c for all target continuum states $H(c)$ (target ionization).

the CCA (Figures 6.15–6.17). Moreover, Figure 6.13 illustrates the difference between Q_1 and $\bar{Q}_1$. Likewise, Figure 6.14 shows the discrepancy between Q_c and $\bar{Q}_c$. The CA, CCA, and ACB1-4B methods are all introduced and implemented within the CB1-4B method, as stated.

At lower energies, the capture process becomes important. Therefore, it is important to include this channel, as well, in the computations when comparing theory with those experimental data that contain the yield from electron capture via process (141). In this latter process, only formation of $H^-(1s^2)$ is included in the computations. This is because the ground state $1s^2$ is the only bound state which exists for this two-electron hydrogen ion [138]. Note that processes (141) and:



have the same cross sections [3].

13.1. Testing the CB1-4B method

Cross sections Q_1 for the target unaffected by collision, as well as $Q_{n>1}$ for target excitation to the selected states, and target ionization Q_c are all

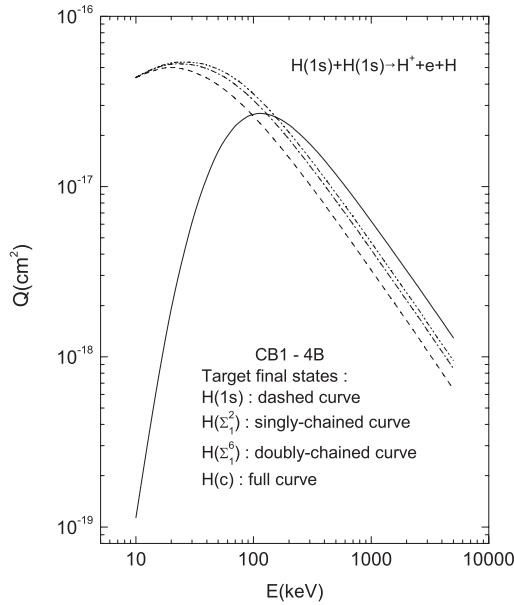


Figure 6.2 Cross sections Q as a function of the impact energy E for electron loss processes (138)–(140). Theory (exact CB1-4B method): (i) dashed curve, cross sections Q_1 for $H(1s) \equiv H(1)$. (ii) Singly chained curve, cross sections $Q_{\Sigma_1^2}$ for the sum of states $H(1)$ and $H(2)$ as denoted by $H(\Sigma_1^2)$. (iii) Doubly chained curve, cross sections $Q_{\Sigma_1^6}$ for the sum of states $H(1), \dots, H(6)$, as symbolized by $H(\Sigma_1^6)$. (iv) Full curve, cross sections Q_c for target ionization $H(c)$ as per Eq. (140).

illustrated in Figure 6.1. Recall that the quantities Q_1 , $Q_{n>1}$, and Q_c describe formation of $H(1)$, $H_{n>1}$, and $H(c)$ in processes (138), (139), and (140), respectively. Dashed curves in Figure 6.1 are for discrete transitions alone and they represent $Q_{n \geq 1}$. The full curve is associated with Q_c for target ionization. The key physical difference between Q_1 and $Q_{n>1}$ is that the former and the latter describe the single- and double-electron transitions, respectively. At all energies, Figure 6.1 shows a distinct dominance of Q_1 over $Q_{n>1}$ ($2 \leq n \leq 6$). A broad maximum in Q_1 is seen precisely at 25 keV, as expected from the resonance criterion for the Massey peak (matching of the velocity of the projectile and target electron)⁹. The peaks in $Q_{n>1}$ are relatively narrower and they are shifted to around 75 keV relative to Q_1 . All the peaks in $Q_{n>1}$ are regularly superimposed on top of each other, and the

⁹ A proton impact energy of 24.98 keV and the ionization potential of 13.6 eV for $H(1s)$ have approximately the same velocity which is equal to the classical Bohr velocity of electron orbiting around proton in the ground state of the atomic hydrogen.

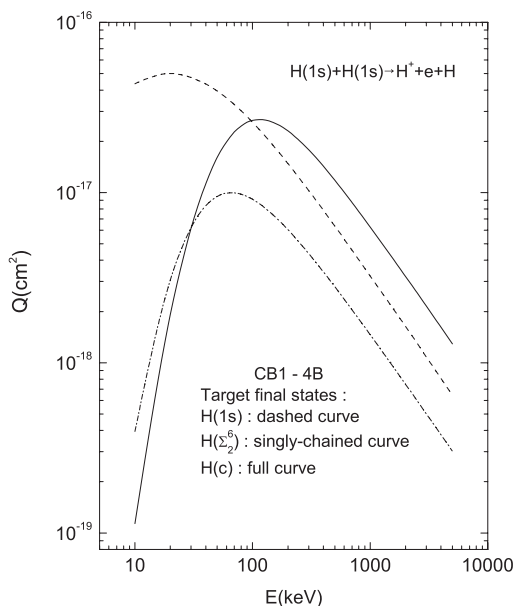


Figure 6.3 Cross sections Q as a function of the impact energy E for electron loss processes (138)–(140). Theory (exact CB1-4B method): (i) dashed curve, cross sections Q_1 for $H(1s) \equiv H(1)$. (ii) Singly chained curve, cross sections $Q_{\Sigma_2^6}$ for the sum of states $H(2), \dots, H(6)$, as symbolized by $H(\Sigma_2^6)$. (iii) Full curve, cross sections Q_c for target ionization $H(c)$ as per Eq. (140).

related dashed curves are mutually parallel at high energies, in accordance with the Oppenheimer n^{-3} scaling law [134]. This latter law for any ion–atom collision is generally valid only at high energies. The cross sections $Q_{n>1}$ rise steeply with the increasing impact energy E prior to the Massey maxima. The difference between Q_1 and $Q_{n>1}$ is largest at lower energies, $E < 100$ keV. Thus, regarding the discrete target states alone in processes (138) and (139) for $n=1$ and $n>1$, respectively, single transitions (projectile ionization and target unaltered) are more important than the double ones (simultaneous projectile ionization and target excitation) at all impact energies.

As to its shape, the full curve Q_c in Figure 6.1 for target ionization in process (140) exhibits a similar pattern as the dashed curves $Q_{n>1}$, except for a steeper rise on the left wing of the Massey peak. The peak in Q_c occurs at a larger energy around $E \approx 100$ keV. Above this maximum, the full and all the dashed curves are parallel to each other. However, regarding the magnitudes of Q_c they are seen in Figure 6.1 to dominate over $Q_{n \geq 1}$ above 125 keV. Even below 100 keV, only Q_1 and partially Q_2 at impact energies $10 \leq E \leq 20$ keV are larger than Q_c . Therefore, at high energies, the most important contribution to electron loss process (137) comes from the double

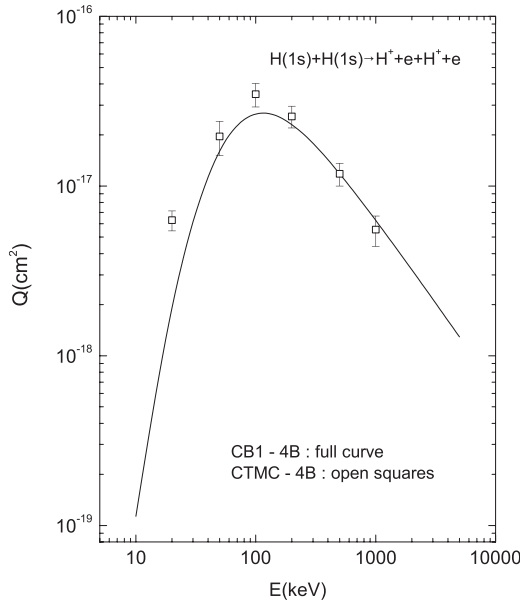


Figure 6.4 Cross sections Q_c for the LI channel via target ionization $H(c)$ as a function of the impact energy E for electron loss process (140). Theory: (i) full curve (exact CB1-4B method) and (ii) open squares (CTMC-4B method [139]). The error bars on the open squares show the statistical uncertainties (standard deviations) estimated in the CTMC-4B method.

transition involving the simultaneous ionization of both the projectile and the target in collisions between two hydrogen atoms, that is, in process (140). This coheres with a similar occurrence that double ionization of two-electron atoms or ions by nuclei dominates over all other channels at high energies.

Figure 6.2 illustrates convergence of $Q_{\Sigma_1^N}$ for formation of $H(\Sigma_1^N)$ with N varying in the interval $1 \leq N \leq 6$. To avoid clutter, explicitly shown are only the three sets of the results for $N=1$, $N=2$, and $N=6$ as the dashed, singly, and doubly chained curves, respectively. The most noticeable increase in the sum $Q_{\Sigma_1^6}$ is observed by adding Q_2 to Q_1 to obtain $Q_{\Sigma_1^2}$, as seen from the dashed and singly chained curve. A further addition of the strip $Q_{3 \leq n \leq 6}$ yields the fully converged results $Q_{\Sigma_1^6}$ given by the doubly chained curve. As we saw in Figure 6.1, cross sections Q_1 and $Q_{n>1}$ peak at different energies (25 and 75 keV, respectively). Therefore, their sum $Q_1 + Q_{\Sigma_2^6}$ which gives the converged cross sections $Q_{\Sigma_1^6}$ should, in principle, have two peaks, one for single- and the other for double-transitions due to Q_1 and $Q_{n>1}$, respectively. However, because of the discussed dominance of Q_1 over $Q_{n>1}$, the second peak stemming from $Q_{n>1}$ is masked and, as such, it does not show up in the composite quantities $Q_{\Sigma_1^N}$ for any $N > 1$, as seen in Figure 6.2. Also shown in Figure 6.2 is Q_c for target ionization (full curve). This is done to compare the

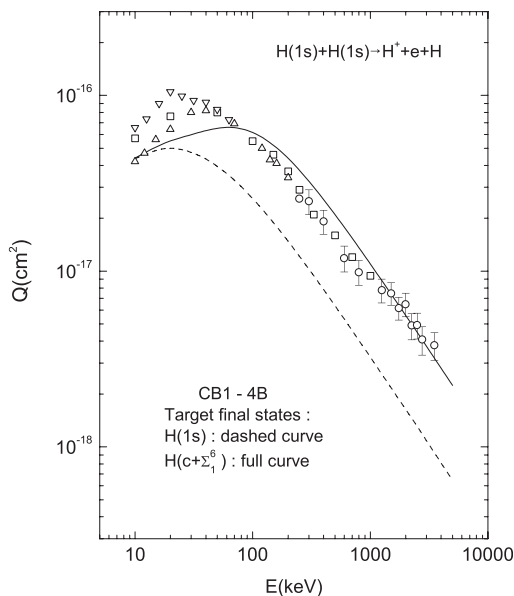


Figure 6.5 Cross sections Q as a function of the impact energy E for electron loss processes (137) and (138). Theory (exact CB1-4B method): (i) dashed curve, cross section Q_1 for target $H(1s)$ unaffected by collision. (ii) Full curve, cross sections $Q_{c+\Sigma_1^6}$ for all target states $H(c + \Sigma_1^6)$. Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

two separate contributions, one from the whole discrete spectrum, as accurately approximated by the converged cross sections $Q_{\Sigma_1^6}$, and the other from the full continuum spectrum described exactly by Q_c . Remarkably, Q_c dominates over $Q_{\Sigma_1^6}$ above 200 keV. This relationship will not be visibly altered by adding the ignored discrete part $Q_{n \geq 7}$, since a steady convergence has already been reached by $Q_{\Sigma_1^6}$. The pattern is reversed below 100 keV, where Q_1 and, hence, $Q_{\Sigma_1^6}$ are seen in Figure 6.2 to be much larger than Q_c .

The cross sections for formation of $H(1)$, $H(\Sigma_2^6)$, and $H(c)$ is further illuminated in Figure 6.3 through the dashed, singly chained, and full curve. In this figure, we explicitly exhibit the relative contributions from the sum of all the excited states $H(\Sigma_2^6)$ (where full convergence in $Q_{\Sigma_2^\infty}$ is achieved with $Q_{\Sigma_2^N}$ for $N=6$) compared to the corresponding yields from $H(1s)$ when the target remains unaltered by collision and from $H(c)$ for ionization. It is seen from Figure 6.3 that at low impact energies, double-electron transitions (LE and LI) are negligible relative to single-electron transition (projectile ionization with the target unchanged). The situation is dramatically changed at high energies at which Q_c for LI becomes dominant and $Q_{\Sigma_2^6}$ for LE also gives a sizeable contribution relative to Q_1 for $H(1s)$.

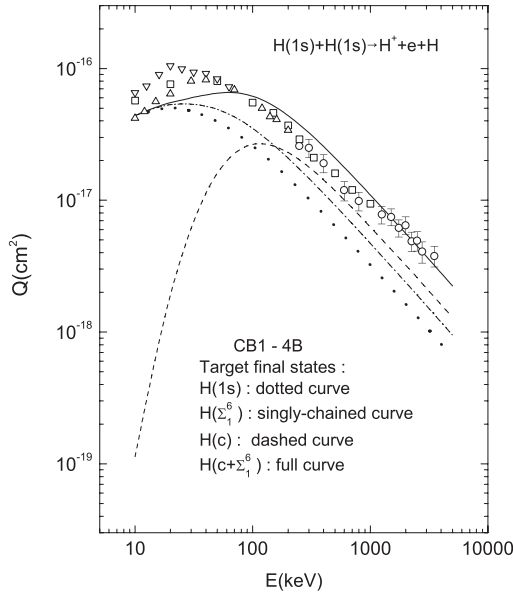


Figure 6.6 Total cross sections Q as a function of the impact energy E for electron loss processes (137)–(140). Theory (exact CB1-4B method): (i) dotted curve, cross section Q_1 for target H(1s) unaffected by collision. (ii) Singly chained curve, cross sections $Q_{\Sigma_1^6}$ for all target bound states H(Σ_1^6). (iii) Dashed curve, cross sections Q_c for H(c). (iv) Full curve, cross sections $Q_{c+\Sigma_1^6}$ for all target states H(c + Σ_1^6). Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

Figure 6.4 deals only with simultaneous electron loss and ionization, that is, the LI process (140). In this figure, a comparison is made between cross sections Q_c computed by means of the exact CB1-4B method and the corresponding results reported by Becker and MacKellar [139] using the four-body classical trajectory Monte Carlo (CTMC-4B) method.¹⁰ Good agreement is found especially regarding the shape of cross sections Q_c with a peak at nearly the same impact energy in both methods. The magnitudes of Q_c predicted by the CB1-4B and CTMC-4B methods are also quite similar, particularly above 100 keV where high-energy methods are expected to be most adequate. In the CTMC-4B method, the Newton equations are solved numerically to generate a large number of trajectories. The appropriate initial conditions are imposed through stochastic samplings over a microcanonical ensemble for the hydrogen target H(1s) in the entrance channel and for a representative set of impact parameter bins of a width which is much smaller than the Bohr radius. In order to attain the needed statistical significance, care

¹⁰For another related subsequent application of the CTMC-4B method, see Ref. [140].

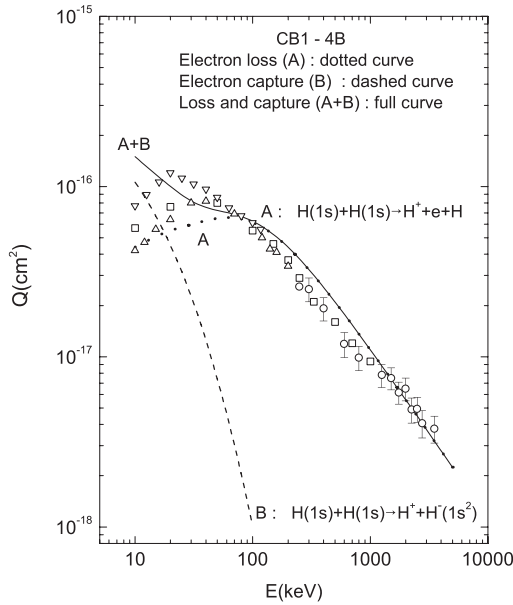


Figure 6.7 Cross sections Q as a function of the impact energy E for processes of electron loss [137] and electron capture [141]. Theory (exact CB1-4B method): (i) dotted curve A, cross sections $Q_{c+\Sigma_1^6}$ for electron loss including all target states $H(c + \Sigma_1^6)$. (ii) Dashed curve B, cross sections for electron capture via formation of the only existing bound state $H^-(1s^2)$. (iii) Full curve $(A + B)$, the sum of cross sections for electron loss and electron capture. Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (with electron capture), and $\circ$ [28].

ought to be exercised in these simulations to secure that all the trajectories were followed for a sufficiently long period of time to reach the asymptotic region of scattering for the final state in the exit channel. The statistical standard deviations estimated in Ref. [139] are shown in Figure 6.4 as error bars on the cross sections from the CTMC-4B method. It is seen that only at 20 and 100 keV these estimated uncertainties of the CTMC-4B method do not overlap with the full curve from the CB1-4B method.

Comparison between theory and experiment is presented in Figure 6.5. Both cross sections Q_1 and $Q_{c+\Sigma_1^6}$ from the CB1-4B method are shown in order to assess the relevance of single- and double-electron transitions for predicting the available experimental data. As mentioned, cross sections Q_1 describe the single-electron transition (projectile ionization) with the target left in the same state as prepared initially, according to process (138). Above 30 keV, an account of this channel alone is seen in Figure 6.5 to be completely unable to reproduce the experimental data that are largely underestimated by Q_1 from the CB1-4B method (dashed curve). On the other hand, cross sections $Q_{c+\Sigma_1^6}$ from the CB1-4B method include the two other major channels that are absent

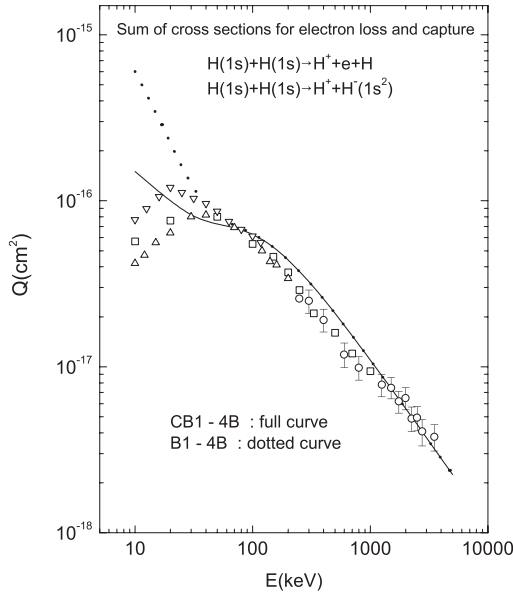


Figure 6.8 Summed cross sections Q as a function of the impact energy E for two processes: electron loss (137) and electron capture (141). Theory (electron loss + capture): (i) full curve (exact CB1-4B method) and (ii) dotted curve (exact B1-4B method). For electron capture, both methods employ the wave function of Hylleraas [146] for the ground state of $H^{-}(1s^2)$. Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (with electron capture), and $\circ$ [28].

from Q_1 , and these are Q_n for target excitation to all the final states $H(n)$ with $2 \leq n \leq 6$ and Q_c for target ionization, $H(c)$. The ensuing result $Q_{c+\Sigma_1^6}$ depicted as the full curve is observed in Figure 6.5 to lead to a remarkable improvement over Q_1 relative to the corresponding measured cross sections. Specifically, cross sections $Q_{c+\Sigma_1^6}$ from the CB1-4B method and the experimental data are in satisfactory agreement at impact energies above 50 keV. A broad maximum in $Q_{c+\Sigma_1^6}$ occurs at 100 keV and it is primarily due to double ionization, as discussed. The associated peak in the experimental data is around 25 keV and these measured cross sections are underestimated by the CB1-4B method. It should be noted that the corresponding cross sections in the CTMC-4B method [139] for the single- and double-electron transitions in electron loss in process (137) largely overestimate all the experimental data from Figure 6.5 (not shown). This is surprising in view of the good agreement found in Figure 6.4 between cross sections Q_c in the CB1-4B and CTMC-4B methods for double ionization in the constituent process (140). This indicates that the cross sections $Q_{n \neq 1}$ in the CTMC-4B method [139] for the final discrete target states have not been simulated with sufficient accuracy.

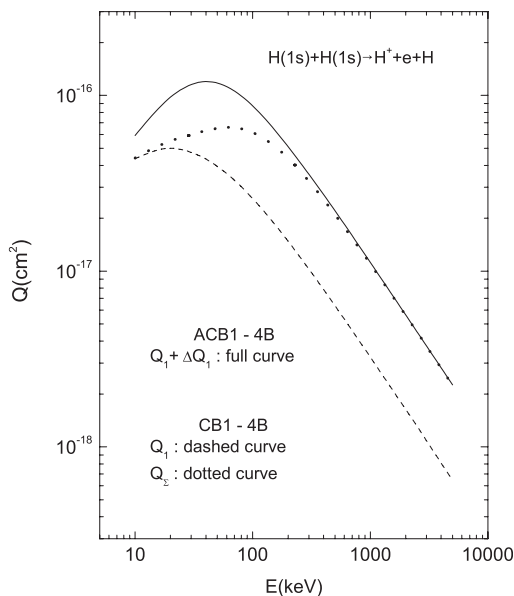


Figure 6.9 Cross sections Q as a function of the impact energy E for electron loss processes (137) and (138). Theory (exact CB1-4B method): dashed curve (cross sections Q_1 for $H(1)$) and dotted curve (cross sections $Q_{c+\Sigma_1^6}$ for $H(c + \Sigma_1^6)$). Theory (ACB1-4B method): full curve (cross sections $Q_1 + \Delta Q_1$ with the correction for the ground state).

Figure 6.6 details the individual components of the composite cross sections $Q_{c+\Sigma_1^6}$ from the CB1-4B method in relation to the experimental data. It is seen that the inclusion of all the converged bound states of the target by addition of the cross sections Q_n to generate $Q_{\Sigma_1^6}$ (singly chained curve) is still totally insufficient to approach the experimental data above 30 keV. On the other hand, above 200 keV, the cross sections Q_c alone (dashed curve) for double ionization in process (140) are closer to the experimental data than $Q_{\Sigma_1^6}$. Around 30 keV, a broad maximum in $Q_{\Sigma_1^6}$ which is inherited from Q_1 (dotted curve), and the narrower peak in Q_c at 100 keV produce merely one rather than two maxima in the composite, full curve for $Q_{c+\Sigma_1^6}$. The addition of $Q_{\Sigma_1^6}$ and Q_c completely masks the peaks due to Q_n . Nevertheless, the peaks from Q_n are indirectly felt in the total process via broadening of the peak due to Q_c . Another consequence of summing $Q_{\Sigma_1^6}$ and Q_c is shifting the position of the peak in Q_c from 100 to 80 keV.

Figure 6.7 illustrates the description by the CB1-4B method of the relative role of the two major pathways to electron loss, one through projectile ionization (137) and the other through electron capture (141). Both pathways liberate protons from the incident hydrogen atoms, $H(1s)$. Recall that the cross sections for processes (149) and (141) describing capture by projectile

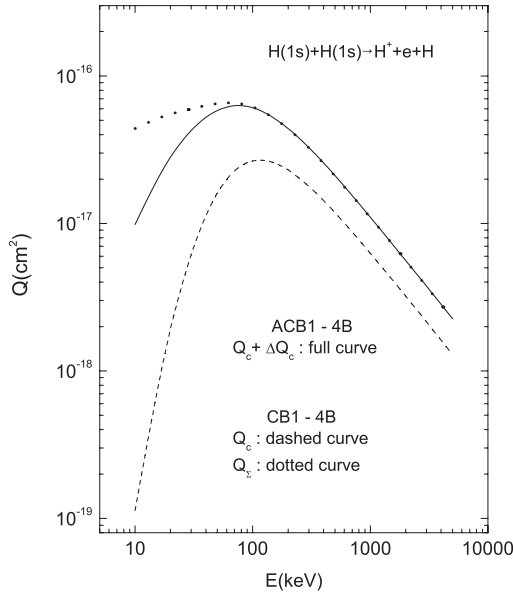


Figure 6.10 Cross sections Q as a function of the impact energy E for electron loss processes (137) and (140). Theory (exact CB1-4B method): dashed curve (cross sections Q_c for H(c)) and dotted curve (cross sections $Q_{c+\Sigma_1^6}$ for H(c + Σ_1^6)). Theory (ACB1-4B method): full curve (cross sections $Q_c + \Delta Q_c$ with the correction for the continuum state).

$H(n_1 l_1)$ and target $H(n_2 l_2)$, respectively, are the same for $n_1 l_1 = 1s = n_2 l_2$. Therefore, although capture by the target is of relevance here, the cross sections for capture by the projectile could be used as well. Dashed curve B in Figure 6.7 represents the cross section for electron capture from projectile $H(1s)$ by target $H(1s)$ via process (141) where the negative hydrogen ion $H^-(1s^2)$ is created on $Z_T = 1$, while the proton H^+ with $Z_P = 1$ from the incident particle is set free. As is also known from a previous related study [141], these capture cross sections decrease rapidly with the impact energy. Only below 100 keV, capture is seen in Figure 6.7 to be appreciable relative to the projectile ionization (dotted curve A). The sum of the capture and loss cross sections is represented by the full curve $A + B$. Above 100 keV, the curve $A + B$ (loss + capture) is indistinguishable from the curve A (projectile ionization alone). A sizeable contribution from electron capture below 100 keV makes the full curve $A + B$ come noticeably closer to the experimental data from Ref. [16] that also include capture. This agreement extends to 15 keV, below which the full curve begins to depart from the experimental data. This is because the structureless capture cross sections in the CB1-4B method wash out the peak in $Q_{c+\Sigma_1^6}$ from projectile ionization.

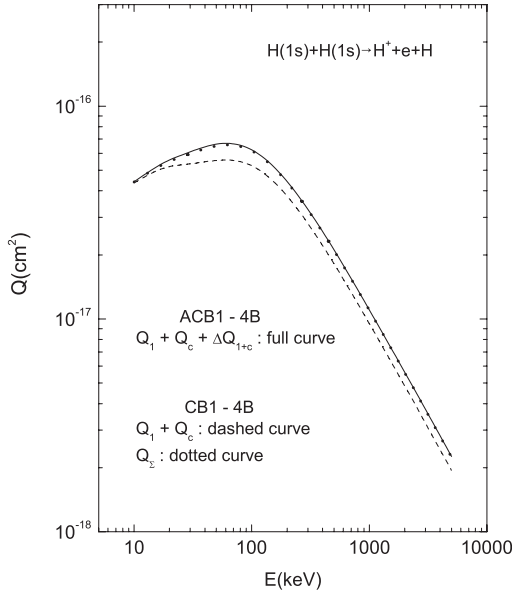


Figure 6.11 Cross sections Q as a function of the impact energy E for electron loss processes (137), (138), and (140). Theory (exact CB1-4B method): dashed curve (cross sections $Q_1 + Q_c$ for $H(l + c)$) and dotted curve (cross sections $Q_{c+\Sigma_1^6}$ for $H(c + \Sigma_1^6)$). Theory (ACB1-4B method): full curve (cross sections $Q_1 + Q_c + \Delta Q_{1+c}$ with the corrections for the ground and continuum states).

Cross sections for the sum of electron loss and capture are shown again in Figure 6.8, where the corresponding results from the B1-4B method are also displayed for comparison. Here, the B1-4B method is identical to the four-body first-order Jackson-Schiff (JS1-4B) approximation (which contains an unphysical nonzero contribution to total cross sections stemming from the internuclear interaction). Considering only electron capture process (141), it has been shown [141] that below 100 keV, the B1-4B method [142,143] was outperformed by the CB1-4B method (see also [2,3]). The B1-4B method does not satisfy the correct boundary condition in the exit channel of capture process (141), since it uses the plane wave to describe the relative motion of two charged particles H^+ and H^- . This is in contrast to the CB1-4B method, which always fulfils the correct boundary conditions in both channels for arbitrary values of nuclear charges Z_P and Z_T in Eq. (3), including the values $Z_P = 1$ and $Z_T = 1$ from Eq. (141). In particular, the relative motion of H^+ and H^- in the exit channel of process (141) is described in the CB1-4B method by the appropriate full Coulomb wave, or equivalently, its eikonal phase. The CB1-4B method also uses a similar Coulomb wave or its equally good asymptotic form with fully screened nuclear charges $Z_P - 1$ and $Z_T - 1$

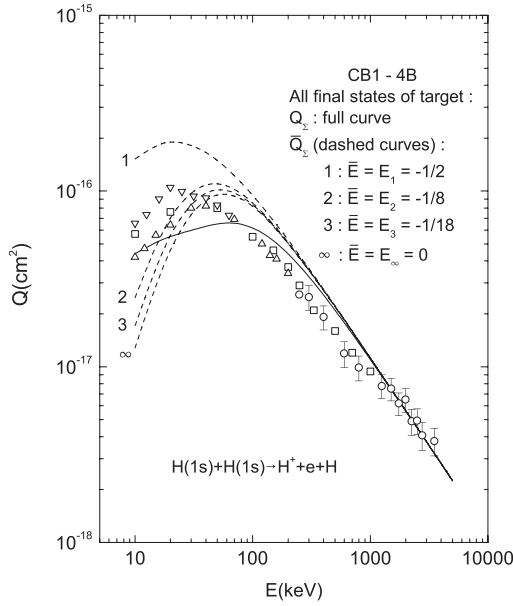


Figure 6.12 Cross sections Q as a function of the impact energy E for process (137). Theory (CB1-4B method with and without the CA): dashed curves, $\bar{Q}_\Sigma$ for $H(c + \Sigma_1^\infty)$ with $\bar{E}$ set to coincide with one exact energy at a time, $E_n = -1/(2n^2)$ ($n = 1, 2, 3$ and ∞) (the values of n are written next to the dashed curves). Full curve, cross sections $Q_{c+\Sigma_1^6}$ for $H(c + \Sigma_1^6)$. Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

in the entrance channel for relative motion of aggregates $(Z_P, e_1)_{i_1}$ and $(Z_T, e_2)_{i_2}$ in process (3). Overall, in the product of the two logarithmic Coulomb phase factors for these two relative motions in the entrance and exit channels, one such phase remains in the total cross sections for both general and particular capture processes (3) and (141), respectively. This remaining phase and the appropriately modified perturbative interactions (that do not contain the internuclear potential) constitute the important difference between the CB1-4B and B1-4B model for electron capture (3) or:

$$(Z_P, e_1)_{i_1} + (Z_T, e_2)_{i_2} \rightarrow (Z_P; e_1, e_2)_f + Z_T, \quad (150)$$

as well as Eqs. (141) or (149). Therefore, a difference is expected to exist between the B1-4B and the CB1-4B method, when electron capture cross sections are added to those for electron loss. This is indeed observed in Figure 6.8 below 70 keV where the B1-4B approximation is seen to largely overestimate the CB1-4B method. For example, the ratio of the cross sections in the B1-4B and CB1-4B method at 10 keV exceeds a factor of 3. Below 30 keV, the cross sections in the B1-4B method overestimate the experimental data.

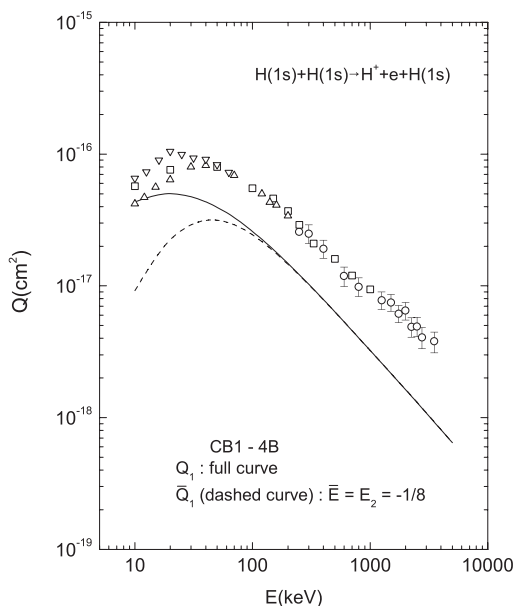


Figure 6.13 Cross sections Q as a function of the impact energy E for process (138) with the target left unaffected by collision as $H(1s)$. Theory (CB1-4B method with the exact and average energy): dashed curve (cross sections $\bar{Q}_1$ with average energy $\bar{E} = E_2 = -1/8$) and full curve (cross sections Q_1 with exact energy $E = E_1 = -1/2$). Experimental data for all target states in process (137): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

Above 80 keV, the B1-4B and the CB1-4B methods give practically the same cross sections for the sum of electron loss and capture. This is due to dominance of electron loss over capture at higher energies. Recall that the B1-4B and CB1-4B methods yield the same cross sections for electron loss (to which the internuclear potential does not contribute due to orthogonality between the initial and the final states, as discussed). It should be pointed out that neither of these two methods are expected to be adequate below 50 keV or so, since these are first-order high-energy approximations. Possibly, a more adequate description and, hence, better quantitative agreement with experimental data especially around the Massey peak could be obtained by using some of the second-order distorted wave methods. For example, it would be advantageous to employ the modified Coulomb-Born (MCB-4B) method for electron loss judging on the remarkable success of this theory for electron detachment process $H^+ + H(1s^2) \rightarrow H^+ + H + e$ [2,3,128,129]. The MCB-4B method for electron capture should peak in the vicinity of the Massey maximum, as this is typical for methods that employ electronic Coulomb eikonal phase as a distortion of the unperturbed initial state in the entrance channel (see Refs [128,129] and [144]). As such, it is

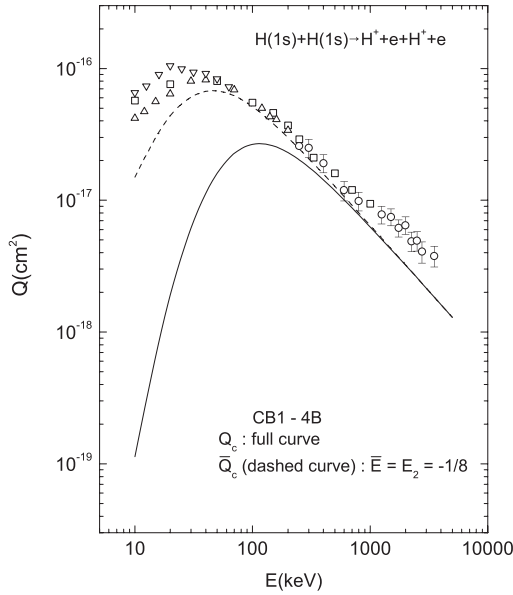


Figure 6.14 Cross sections Q as a function of the impact energy E for process (140) with the target ionized after collision as symbolized by H(c). Theory (CB1-4B method with the exact and average energy): dashed curve (cross sections $\bar{Q}_c$ with average energy $\bar{E} = E_2 = -1/8$) and full curve (cross sections Q_c with exact energies $E_{\kappa_2} = \kappa_2^2/2$ in the numerical quadrature over continuum states of H(c)). Experimental data for all target states in process (137): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

anticipated that the MCB-4B method for the sum of cross sections for electron loss and capture should exhibit the Massey peak in a close vicinity of experimentally observed maximum in McClure's [16] measurement. A very important application of the MCB-4B method would also be to study electron loss from fast $\text{He}^+(1s)$ ions passing through atomic hydrogen $\text{H}(1s)$. In this collision, the B1-4B method from computations of Boyd et al. [61] as well as Bell and Kingston [76] has been found to fail by largely overestimating the experimental data of Shah et al. [19] as well as of Hvelplund and Andersen [28] at high energies. Also important would be an application of the CDW-4B method to electron loss processes by extending the corresponding theory of Belkić [145] for ionization of target by bare nuclei. The CDW-4B method is a more complete theory than the MCB-4B approximation, since the former employs the full Coulomb wave for the continuum intermediate state of the active electron in the entrance channel, whereas the latter uses merely the corresponding asymptotic logarithmic phase factor.

It should be re-emphasized that the experimental data of McClure [16] shown in Figures 6.7 and 6.8 include capture, as opposed to Figures 6.5 and 6.6.

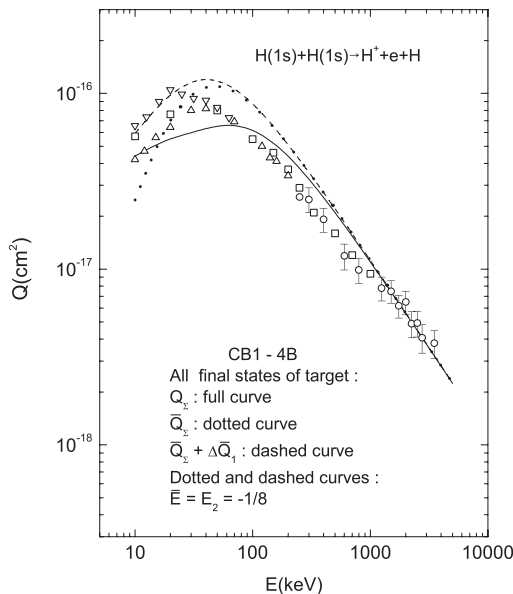


Figure 6.15 Total cross sections Q as a function of the impact energy E for process (137). Theory (CB1-4B method with and without the CA or CCA): dotted curve (cross sections Q_{Σ} in the CA for $H(c + \Sigma_1^{\infty})$ with $\bar{E} = E_2 = -1/8$), dashed curve (cross sections $\bar{Q}_{\Sigma} + \Delta\bar{Q}_1$ in the CCA for $H(c + \Sigma_1^{\infty})$ with $\bar{E} = E_2 = -1/8$ and the correction $\Delta\bar{Q}_1$ for the ground state), and full curve (exact cross sections $Q_{c+\Sigma_1^6}$ for $H(c + \Sigma_1^6)$). Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

Capture cross sections have been measured separately by McClure [16], and in Figures 6.5 and 6.6 such data were subtracted from the corresponding measured total loss cross sections (loss plus capture) to extract cross sections for pure projectile ionization. These latter experimental data from Ref. [16] without their capture contribution will also be shown in Figures 6.12–6.17 that deal exclusively with electron loss conceived as projectile ionization, that is, by ignoring altogether the channel of electron capture.

13.2. Testing the ACB1-4B method

Figures 6.9–6.11 compare the loss cross sections for certain target final states using the ACB1-4B and CB1-4B methods. The usefulness of the cross sections from the ACB1-4B method, prior to convergence with respect to the included target final states, needs to be assessed only through comparisons with the converged results $Q_{c+\Sigma_1^6}$ from the CB1-4B method. The cross sections $Q_{c+\Sigma_1^6}$ from the CB1-4B method are already known from Figures 6.5 to 6.7 to be in good agreement with experimental data above 50 keV. For this reason, it is

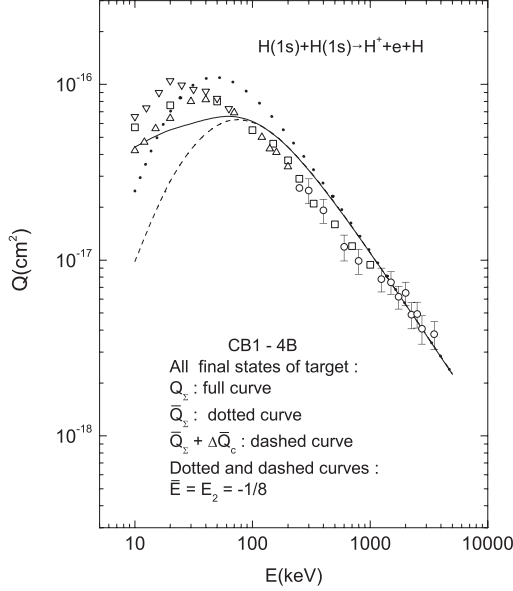


Figure 6.16 Total cross sections Q as a function of the impact energy E for process (137). Theory (CB1-4B method with and without the CA or CCA): dotted curve (cross sections Q_{Σ} in the CA for $H(c + \Sigma_1^{\infty})$ with $\bar{E} = E_2 = -1/8$), dashed curve (cross sections $\bar{Q}_{\Sigma} + \Delta\bar{Q}_c$ for $H(c + \Sigma_1^{\infty})$ in the CCA with $\bar{E} = E_2 = -1/8$ and the correction $\Delta\bar{Q}_c$ for the continuum state), and full curve (exact cross sections $Q_{c+\Sigma_1^6}$ for $H(c + \Sigma_1^6)$). Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

not necessary to include also experimental data to validate the ACB1-4B method per se, since the result $Q_{c+\Sigma_1^6}$ from the CB1-4B method would suffice for this purpose. We recall that the key difference between the CB1-4B and the ACB1-4B methods is that the former/latter excludes/includes the term $\Delta Q_{\Sigma'}$ which represents the truncation error given as the closure bound to the neglected part $Q_{\Sigma^{\perp}}$ of the exact cross section Q_{Σ} for the complete spectrum Σ where $\Sigma^{\perp} = \Sigma - \Sigma'$. In particular, the analysis from Section 9 suggests that the exact results from the CB1-4B method should be used for explicit testing of the simplest variant (107) of the ACB1-4B method with the average energy $\bar{E}$ coinciding with the exact energy of the second level of the target, $\bar{E} = E_2 = -Z_T^2/8$. The results of such testings are displayed in Figures 6.9–6.11. From the whole sum $\Sigma' \subset \Sigma$, the proposed variant (107) or (146) of the ACB1-4B method includes only the sum $Q_1 + Q_c$ of the two leading exact cross sections for the true ground and continuum states, respectively, as well as the correction ΔQ_{1+c} . The latter correction defined by $\Delta Q_{1+c} = \bar{Q}_{\Sigma} - (\bar{Q}_1 + \bar{Q}_c)$ represents a closure bound of the remainder $Q_{\Sigma^{\perp}}$ via $\Delta Q_{\Sigma'} \approx Q_{\Sigma^{\perp}}$. Quantity $\bar{Q}_{\Sigma}$ appearing in ΔQ_{1+c} is the cross section from

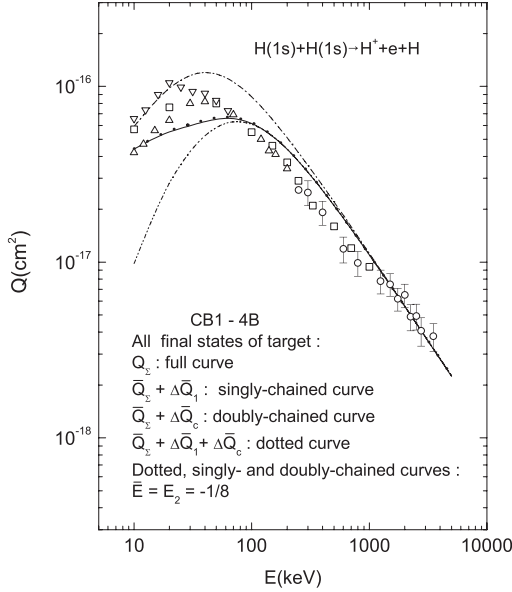


Figure 6.17 Total cross sections Q as a function of the impact energy E for process (137). Theory (CB1-4B method with and without the CCA): singly chained curve (cross sections $\bar{Q}_\Sigma + \Delta\bar{Q}_1$ in the CCA for $H(c + \Sigma_1^\infty)$ with $\bar{E} = E_2 = -1/8$ and the ground-state correction ΔQ_1), doubly chained curve (cross sections $\bar{Q}_\Sigma + \Delta\bar{Q}_c$ in the CCA for $H(c + \Sigma_1^\infty)$ with $\bar{E} = E_2 = -1/8$ and the continuum-state correction $\Delta\bar{Q}_c$), dotted curve (cross sections $\bar{Q}_\Sigma + \Delta\bar{Q}_1 + \Delta\bar{Q}_c$ in the CCA for $H(c + \Sigma_1^\infty)$ with $\bar{E} = E_2 = -1/8$ and the corrections $\Delta Q_{1+c} \equiv \Delta Q_1 + \Delta Q_c$ for the ground and continuum states), and full curve (exact cross sections $Q_{c+\Sigma_1^6}$ for $H(c + \Sigma_1^\infty)$). Experimental data (all target states): Δ [11], $\square$ [13], ∇ [16] (without electron capture), and $\circ$ [28].

the CA. With the choice $\bar{E} = E_2$, the term $\bar{Q}_\Sigma$ in the correction ΔQ_{1+c} guarantees that the ACB1-4B method includes the contribution of the exact target $2s$ and $2p$ states. For comparison, the corresponding result from the CB1-4B method is $Q_1 + Q_c$ which does not include any estimate of the neglected remainder $Q_{\Sigma^\perp}$. In other words, setting the estimate of the truncation error to zero in this case via $\Delta Q_{1+c} = 0$ would make the ACB1-4B and CB1-4B methods coincide with each other.

Prior to the main test of the proposed working formula $Q_1 + Q_c + \Delta Q_{1+c}$ of the ACB1-4B method from Eq. (146), it is also instructive to compare the exact converged cross sections $Q_{c+\Sigma_1^6}$ with the partial estimates $Q_1 + \Delta Q_1$ and $Q_c + \Delta Q_c$ that are all listed in Eq. (146). This is important in order to assess the relative role of the two separate corrections ΔQ_1 and ΔQ_c . The outcomes of testings of cross sections $Q_1 + \Delta Q_1$ and $Q_c + \Delta Q_c$ are shown in Figures 6.9 and 6.10, respectively. Figure 6.9 compares the predictions Q_1 and $Q_1 + \Delta Q_1$ in the CB1-4B and ACB1-4B methods, respectively, alongside

the reference data $Q_{\Sigma} \approx Q_{c+\Sigma_1^6}$. Recall that cross section Q_1 describes a single-electron transition for electron loss process (138) in which the target is left unaffected by collision. As already known from Figure 6.5, it is seen again in Figure 6.9 that Q_1 (dashed curve) considerably underestimates $Q_{c+\Sigma_1^6}$ (dotted curve) at all impact energies above 30 keV. At the same time, this figure shows that above 200 keV, the corresponding cross section $Q_1 + \Delta Q_1$ (full curve) from the ACB1-4B method significantly improves agreement with the reference data $Q_{c+\Sigma_1^6}$. In particular, the full and dotted curve are in excellent accord above 500 keV where the dashed curve is too low by a factor larger than 3 relative the exact result $Q_{c+\Sigma_1^6}$.

The reason for the superiority of $Q_1 + \Delta Q_1$ over Q_1 is that the former has two additional contributions both stemming from the CA part $\bar{Q}_{\Sigma}$ in ΔQ_1 . These supplements to Q_1 are the inclusion of the exact second manifold $\{\varphi_{2lm}(x_2)\}$ secured by the choice of the average energy $\bar{E} = E_{E_2}$, and the approximation $\bar{Q}_c$ to the true continuum Q_c . The term ΔQ_1 cancels the approximate cross section $\bar{Q}_1$ which is implicitly present in $\bar{Q}_{\Sigma}$. Further, $\bar{Q}_{\Sigma}$ also possesses an approximate contribution of the target excited states with $n \geq 3$. As anticipated in Section 11, for $\bar{E} = E_{E_2}$, both the contributions $\bar{Q}_{n \geq 3}$ and $\bar{Q}_c$ to $\bar{Q}_{\Sigma}$ should overestimate the corresponding true contributions of $Q_{n \geq 3}$ and Q_c to Q_{Σ} . This is confirmed in Figure 6.9, since the full curve for $Q_1 + \Delta Q_1$ is seen to be always above the dotted curve for $Q_{\Sigma} \approx Q_{c+\Sigma_1^6}$. The full curve is an upper bound to the exact cross section $Q_{c+\Sigma_1^{\infty}}$. Notice that in Figure 6.9, overestimation of $Q_{c+\Sigma_1^6}$ by $Q_1 + \Delta Q_1$ is most noticeable at lower impact energies below 150 keV. This is expected from Eq. (120) which shows that the error introduced by using $\bar{E}$ instead of the exact target energies $\{E_{f_2}\}$ should increase as the impact velocity v is diminished.

In Figure 6.10, comparison is made between Q_c and $Q_c + \Delta Q_c$ from the CB1-4B and ACB1-4B methods together with the converged cross sections $Q_{c+\Sigma_1^6}$ of the former theory. Cross section Q_c describes a double-electron transition for electron loss process (140) in which both the projectile and the target are ionized. As previously encountered in Figure 6.6, it is seen again in Figure 6.10 that Q_c (dashed curve) considerably underestimates $Q_{c+\Sigma_1^6}$ (dotted curve), especially at low energies. For example, at 10 keV, Q_c is about 23.5 times smaller than $Q_{c+\Sigma_1^6}$. Simultaneously, the same figure indicates that the corresponding cross section $Q_c + \Delta Q_c$ (full curve) from the ACB1-4B method dramatically improves agreement with the exact result $Q_{\Sigma} \approx Q_{c+\Sigma_1^6}$. For example, above 95 keV, the discrepancy between the full and the dotted curve is completely negligible. At 10 keV, $Q_c + \Delta Q_c$ is only about 3.5 times smaller than $Q_{c+\Sigma_1^6}$ compared to $Q_{c+\Sigma_1^6}/Q_c \approx 23.5$. This proves that the gap between the converged cross sections in the exact CB1-4B method and its approximation given by the ACB1-4B method is bridged more adequately by ΔQ_c than ΔQ_1 . The full curve represents a lower bound to the exact cross section $Q_{\Sigma} \approx Q_{c+\Sigma_1^{\infty}}$.

The CA estimate $\bar{Q}_\Sigma$ for Q_Σ implicitly contains the approximate continuum $\bar{Q}_c$ via $\bar{Q}_\Sigma = \Sigma_n \bar{Q}_n + \bar{Q}_c$ which is cancelled by $\Delta Q_c = \bar{Q}_\Sigma - \bar{Q}_c = \Sigma_n \bar{Q}_n$ so that $Q_c + \Delta Q_c = Q_c + \Sigma_n \bar{Q}_n$. This shows that the full curve from [Figure 6.10](#) due to $Q_c + \Delta Q_c$ from the ACB1-4B method describes effectively the sum of positive quantities Q_c and $\Sigma_n \bar{Q}_n$. Hence, this latter sum leads to larger cross sections than Q_c itself, and this results in improved agreement with $Q_{c+\Sigma_1^6}$. As mentioned earlier, the derived expression $\Delta Q_c = \Sigma_n \bar{Q}_n$ is not used for the computation of ΔQ_c but mainly to exhibit here the actual and explicit content of ΔQ_c . Correction ΔQ_c itself is computed from the defining formula $\Delta Q_c = \bar{Q}_\Sigma - \bar{Q}_c$. The supplementary term ΔQ_c contains the exact contribution from the second level, since $\bar{Q}_2 = Q_2$ for $\bar{E} = E_2$. All other individual cross sections $\bar{Q}_1$ and $\bar{Q}_{n \geq 3}$ from $\Sigma_n \bar{Q}_n$ underestimate and overestimate the corresponding exact results Q_1 and $Q_{n \geq 3}$, respectively.

Returning to [Figure 6.1](#), we see that Q_1 is much larger than $Q_{n > 1}$ below 100 keV. This means that the most noticeable errors in ΔQ_c will come from $\bar{Q}_1$ which is not corrected in $Q_c + \Delta Q_c$. As such, the discrepancy between the full and the dotted curve in [Figure 6.10](#) is mainly due to underestimation of Q_1 by $\bar{Q}_1$ in ΔQ_c from $Q_c + \Delta Q_c$. The most remarkable conclusion from [Figure 6.10](#) is that Q_c together with merely a single correction ΔQ_c suffices to have practically the exact result $Q_{c+\Sigma_1^6}$ at impact energies $E \geq 100$ keV, which covers most of the whole region of applicability of the CB1-4B method.

[Figure 6.11](#) shows a comparison between $Q_1 + Q_c$ and $Q_1 + Q_c + \Delta Q_{1+c}$ from the CB1-4B and ACB1-4B methods alongside the corresponding exact cross sections $Q_{c+\Sigma_1^6}$. Cross sections $Q_1 + Q_c$ describe the two pathways (138) and (140) of the compound process (137). They correspond to the situations when the target is unaffected by collision and ionized, respectively. The pertinent question to ask here within the CB1-4B method is how much could only the two-pathway processes (138) and (140) be capable of describing collision (137) as a whole (which is our ultimate goal)? If the answer is in the affirmative, the cross sections $Q_{n \geq 2}$ could be ignored. However, the answer to this question is in the negative, since already [Figures 6.2 and 6.6](#) show that the contribution from $Q_{n \geq 2}$ to $Q_{c+\Sigma_1^6}$ is significant throughout and, as such, cannot be neglected. The same situation is also replicated in [Figure 6.11](#) where the sum $Q_1 + Q_c$ (dashed curve) significantly underestimates the reference cross section $Q_{c+\Sigma_1^6}$ (dotted curve) at impact energies $E \geq 20$ keV. However, the mentioned question when raised within the ACB1-4B method for the corresponding corrected sum $Q_1 + Q_c + \Delta Q_{1+c}$ (full curve) is answered in the affirmative. This time, cross sections $Q_1 + Q_c + \Delta Q_{1+c}$ and $Q_{c+\Sigma_1^6}$ are seen in [Figure 6.11](#) to be in a nearly perfect agreement at all impact energies under consideration $10 \leq E \leq 5000$ keV. This came as the result of an almost exact compensation of the overestimation and underestimation effects associated with the full curves from [Figures 6.9 and 6.10](#) leading to the very important achievement of the ACB1-4B method via the conclusion $Q_1 + Q_c + \Delta Q_{1+c} \approx Q_{c+\Sigma_1^6}$. This is the proof that the ACB1-4B method indeed

significantly accelerates convergence of the CB1-4B method as a function of the increased number of the final target states.

In relation to the exact cross sections $Q_1 + Q_c$ for $H(1s + c)$ from Figure 6.11, let us revisit the summands Q_1 and Q_c shown in Figure 6.1. Cross sections Q_1 and Q_c for $H(1)$ and $H(c)$ peak at 25 and 100 keV, respectively. Therefore, one would expect two peaks in the sum $Q_1 + Q_c$. However, this is not the case, as seen via the dashed curve for $Q_1 + Q_c$ in Figure 6.11. Here, as discussed earlier, only one peak appears clearly around 100 keV due to Q_c whereas the other maximum from Q_1 is masked. Nevertheless, the presence of the peak in Q_1 is still felt in $Q_1 + Q_c$ via a bump at impact energies $10 \leq E \leq 30$ keV, as can distinctly be seen in Figure 6.11. It is possible that for some other colliding particles, the two clear maximae would emerge in cross sections $Q_1 + Q_c$. The remnant of the peak in Q_1 is hardly noticeable in $Q_{c+\Sigma_1^6}$ (only a very slight change of curvature of the full line in Figure 6.11 is barely perceivable).

13.3. Testing the CCA method

Finally, through Figures 6.12–6.17, we analyze the cross sections obtained in the CA and CCA method by carrying out approximate computations within the CB1-4B method. The supplementary approximations consist first of using a set of fixed average energies $\bar{E}$ instead of the corresponding exact target energies E_{f_2} . Recall that f_2 is a common label jointly referring to energies of bound and continuum states of the target electron e_2 , such that $E_n = -Z_T^2/(2n^2) = -1/(2n^2)$ and $E_{\kappa_2} = \kappa_2^2/2$, respectively. The replacement of E_{f_2} by $\bar{E}$ enables the subsequent straightforward application of the closure relation (29) for the target states giving certain estimates for the joint contributions from the whole discrete and continuous parts of the target spectrum in the final state. By the nature of the closure relation (29), the estimate $\bar{Q}_\Sigma$ from the CA is an approximation to the corresponding exact cross sections $Q_{c+\Sigma_1^\infty}$. As we saw through the analysis of Figures 6.1–6.7, the exact result $Q_\Sigma \equiv Q_{c+\Sigma_1^\infty}$ within the CB1-4B method is practically attained with $Q_{c+\Sigma_1^6}$ and, therefore, $Q_\Sigma \equiv Q_{c+\Sigma_1^\infty} \approx Q_{c+\Sigma_1^6}$. Generally, any closure estimate $\bar{Q}_\Sigma$ represents only a rough approximation to the corresponding exact cross section Q_Σ in the CB1-4B method. Therefore, the approximate results for $\bar{Q}_\Sigma$ need to be refined. This can be achieved if certain corrections are introduced to amend the closure estimate $\bar{Q}_\Sigma$. To proceed, we add to $\bar{Q}_\Sigma$ two separate corrections $\Delta\bar{Q}_n = Q_n - \bar{Q}_n$ and $\Delta\bar{Q}_c = Q_c - \bar{Q}_c$ for the discrete and continuous target spectrum, yielding the CCA. Such a procedure can, in principle, produce the exact result Q_Σ by summing over all the corrections $\Delta\bar{Q}_n$. However, in practice, the key question to address is how many of the discrete target states need to be corrected via $\Delta\bar{Q}_n (n = 1, 2, \dots)$ in order to make the whole procedure useful in exhaustive applications? This can only be answered by performing the computation using a selected method with

and without the CCA. We shall proceed precisely in this way within the CB1-4B method.

Figure 6.12 shows four different estimates $\bar{Q}_\Sigma$ (dashed curves) computed in the CA within the CB1-4B method for four average energies $\bar{E} = E_n$ ($n = 1, 2, 3$, and ∞). The first, second, and third choices $\bar{E} = E_1 = -1/2$, $\bar{E} = E_2 = -1/8$, and $\bar{E} = E_3 = -1/18$ correspond to setting the average energy to coincide with the first, second, and third exact energy level of the final discrete spectrum of $H(n)$, respectively. The fourth average energy $\bar{E} = E_\infty$ is associated with choosing $n = \infty$ in $\bar{E} = E_n = -1/(2n^2)$ giving zero energy $\bar{E} = E_\infty = 0$, which signifies the target ionization threshold. The largest gap among the results between the two adjacent average energies $\bar{E}$ is seen in Figure 6.12 to be between $\bar{Q}_\Sigma$ for $\bar{E} = E_1 = -1/2$ (curve 1) and $\bar{E} = E_2 = -1/8$ (curve 2). Otherwise the three curves denoted by 2, 3, and ∞ for $\bar{Q}_\Sigma$ with $\bar{E}$ equal to E_2 , E_3 , and E_∞ , respectively, are seen as being clustered tightly together. Interestingly, this constellation is formally reminiscent, in a qualitative shape-wise manner, to the pattern seen in Figure 6.1 for the exact cross sections Q_n ($n = 1, 2, 3$) where, however, different curves are spaced farther apart than those from Figure 6.12 for $\bar{Q}_\Sigma$ with $\bar{E} = E_n$ ($n = 1, 2, 3$). This is expected, since with $\bar{E} = E_1 = -1/2$, the cross section Q_Σ includes (i) exactly only the ground state and (ii) overestimates all the excited states and continuum. Hence, for $\bar{E} = E_1$, the features (i) and (ii) imply that $\bar{Q}_\Sigma$ should have (a) a shape similar to the related exact cross section Q_1 and (b) the magnitudes larger than the associated exact values $Q_{c+\Sigma_1^6}$. Feature (a) holds true, as seen from the curves labeled by H(1) and 1 in Figures 6.1 and 6.12, respectively. Similarly, property (b) also takes place, as evidenced by the result $\bar{Q}_\Sigma$ of the CA given by the dashed curve 1 and the full curve, which represents the converged cross sections $Q_{c+\Sigma_1^6}$ from the exact CB1-4B method (see Figure 6.12). Similar relationships can also be observed for cross section $\bar{Q}_\Sigma$ computed with other choices for $\bar{E}$. Another noteworthy point from Figure 6.12 is that irrespective of the choice for the average energy $\bar{E}$, all the ensuing cross sections $\bar{Q}_\Sigma$ from the CA differ only a little above 200 keV. More importantly, it is also seen in this figure that the values of $\bar{Q}_\Sigma$ agree well with the theoretical reference data $Q_{c+\Sigma_1^6}$ only above 500 keV. Obviously, this lowest impact energy E for the validity of the CA is way too large to make the closure approximation itself a practical and useful procedure. This conclusion also raises a question: can the CA be salvaged by amending it with certain easily obtainable corrections?

The remaining Figures 6.13–6.17 deal precisely with certain amendments to the CA. As shown in Section 12, the way to introduce the sought corrections to the CA with systematic improvements reveals itself clearly by exposing the nature of the approximation invoked prior to the usage of the closure relation (29). To illustrate the corrections to the CA, we shall

present only the results for $\bar{E} = E_2 = -1/8$, as a practical variant of the CCA. Any other choice could also yield similar results although admittedly with a bit more computations. In the closure cross section $\bar{Q}_\Sigma$ with $\bar{E} = E_2 = -1/8$, the level $n=2$ is taken into account exactly and, thus, no correction is needed for this excited state. All the other states are either underestimated or overestimated, and this calls for the corresponding corrections. Thus using the average energy $\bar{E} = E_2 = -1/8$ to compute the loss cross section $\bar{Q}_1$ for process (138) for $i_2 = 1s$ (target unaffected by collision), it follows that $\bar{Q}_1 < Q_1$, since $|\bar{E}| < |E_1|$, as discussed in Section 11.

The relationship $\bar{Q}_1 < Q_1$ is confirmed by Figure 6.13, where $\bar{Q}_1$ and Q_1 are shown by the dashed and full curve, respectively. The largest underestimation of Q_1 by $\bar{Q}_1$ is within a factor of 4, and it occurs at lower energies. Otherwise, the two curves are close to each other above 100 keV. While Q_1 has a broad maximum at 25 keV, as noted earlier regarding Figure 6.1, the more pronounced peak in $\bar{Q}_1$ is shifted to a higher energy of about 40 keV. The maximum of cross sections (78) for electron loss is generated by the atomic form factors I_{i_1, κ_1} and J_{i_1, f_2} from Eqs. (73) and (74). For example, the bound-bound form factor $J_{i_1, mlm}$ is comprised of powers of rational functions of the form $1/(q^2 + E_n^2)$. This latter rational function is a symmetric (Lorentzian) distribution of width $|E_n|$. Therefore, the said inequality $|\bar{E}| = |E_2| < |E_1|$ implies that the peak in $\bar{Q}_1$ will be narrower than in Q_1 , as is indeed seen to be the case in Figure 6.13.

In an analogous manner, regarding the continuous part of the target spectrum associated with process (140), we compute both the exact cross section Q_c and $\bar{Q}_c$ with the exact free energy $E_{\kappa_2} = \kappa_2^2/2$ and the average binding energy $\bar{E} = E_2 = -1/8$, respectively. For double ionization in process (140), according to the discussion in Section 11, we expect to have $\bar{Q}_c > Q_c$. This expectation is indeed confirmed in Figure 6.14, where $\bar{Q}_c$ and Q_c are depicted by the dashed and full curve, respectively. However, as opposed to the preceding case with $\bar{Q}_1$ from Figure 6.13, it is seen in Figure 6.14 that the errors in $\bar{Q}_c$ are very large, attaining even two orders of magnitude below the Massey peak. Moreover, $\bar{Q}_c$ tends to Q_c only above 500 keV (to be compared to 100 keV in the case of $\bar{Q}_1$ and Q_1 from Figure 6.13). Thus, the target continuum states are much more sensitive to the replacement of the exact energies by the average values than the corresponding discrete spectrum. By implication, correcting the error for the target continuum will be critical for the sought improvement of the CA. One obvious reason for a more pronounced sensitivity of $\bar{Q}_c$ relative to $\bar{Q}_1$ vis-à-vis $\bar{E}$ is a sharp dissimilarity between the exact positive energy $E_{\kappa_2} = \kappa_2^2/2 > 0$ and the negative average energy $\bar{E} = E_2 = -1/8 < 0$. By contrast, for any discrete states, at least the sign of all the exact binding energies $E_n < 0$ is the same as the average energy $\bar{E} = E_2 < 0$. Note that the experimental data are not used in

Figures 6.13 and 6.14 to make quantitative comparisons with theory, since the latter is incomplete due to the inclusion of only the ground state and continuum. Rather, these experimental data are shown to merely indicate the directionality of the departure of both pairs of the computed cross sections $\{Q_1, \bar{Q}_1\}$ and $\{Q_c, \bar{Q}_c\}$ from the measured results that themselves contain the contribution from all the target states.

The availability of Q_1 and $\bar{Q}_1$ makes it possible to exactly correct the estimate $\bar{Q}_\Sigma$ from the CA for the error in the $n=1$ state introduced by using the average energy $\bar{E}=E_2$ rather than the exact value E_1 . As discussed, this correction, which is given by $\Delta\bar{Q}_1 \equiv Q_1 - \bar{Q}_1$, will be positive at any impact energy (see the difference between the full and dashed curves in Figure 6.13). According to (147), the CA corrected for the ground state is defined by $\bar{Q}_\Sigma + \Delta\bar{Q}_1$, and this represents the first iteration in the CCA, which is shown by the dashed curve in Figure 6.15. The correction $\Delta\bar{Q}_1 > 0$ is seen to further enlarge the cross section $\bar{Q}_\Sigma$ (dotted curve) from the CA. In other words, rather than converging to the reference cross sections $Q_{c+\Sigma_1^6}$ (full curve), the CCA with the ground-state correction alone ($\bar{Q}_\Sigma + \Delta\bar{Q}_1$) is seen in Figure 6.15 to depart even further from the corresponding exact result $Q_{c+\Sigma_1^6}$ than the CA estimate $\bar{Q}_\Sigma$.

Since Q_c and $\bar{Q}_c$ are also available, it is possible to correct exactly the result $\bar{Q}_\Sigma$ from the CA for the error in continuum states invoked by employing the average energy $\bar{E}=E_2$ instead of the exact energy E_{κ_2} . Such a correction, which is introduced by $\Delta\bar{Q}_c \equiv Q_c - \bar{Q}_c$ will be negative at all impact energies, as implied by the difference between the full and dashed curves in Figure 6.14. As per Eq. (147), the CA corrected for the target continuum is given by $\bar{Q}_\Sigma + \Delta\bar{Q}_c$ and this defines the second iteration in the CCA, which is displayed as the dashed curve in Figure 6.16. The correction $\Delta\bar{Q}_c$ is seen to improve remarkably the cross section $\bar{Q}_\Sigma$ (dotted curve) from the CA. This is seen through a near coincidence (above 100 keV) of the full curve for the exact cross section $Q_{c+\Sigma_1^6}$ in Figure 6.16 and the CCA with the correction for the continuum states alone, $\bar{Q}_\Sigma + \Delta\bar{Q}_c$. This is a significant gain relative to the corresponding results $\bar{Q}_\Sigma + \Delta\bar{Q}_1$ that are acceptable only above 500 keV (Figure 6.15). Such a circumstance coheres with the earlier anticipation from Figure 6.14 about the possibly most important role of the correction $\Delta\bar{Q}_c$. It should be recalled that the sole term $\Delta\bar{Q}_c$ is capable of correcting for the entire continuum. In other words, the cross sections $\bar{Q}_\Sigma + \Delta\bar{Q}_c$ include exactly the whole target continuum and the level $n=2$ of the corresponding discrete spectrum for $\bar{E}=E_2$. By comparison, the cross sections $\bar{Q}_\Sigma + \Delta\bar{Q}_1$ take into account exactly only the target discrete states with $n=1$ and $n=2$.

In principle, the whole target discrete spectrum can also be corrected by computing the further corrections $\Delta\bar{Q}_n \equiv Q_n - \bar{Q}_n$ ($n \geq 3$). Nevertheless, the usefulness of the CCA in practice rests ultimately on the possibility of using

only the minimal number of the simplest corrections (optimally one per each part of the spectrum, $\Delta\bar{Q}_1$ and $\Delta\bar{Q}_c$ for discrete and continuum states, respectively). The CCA devised in this way is defined by Eq. (147) as $\bar{Q}_\Sigma + \Delta\bar{Q}_1 + \Delta\bar{Q}_c$ and it is given by the dotted curve in Figure 6.17. These results should be compared with the full curve, which represents the exact cross sections $Q_{c+\Sigma_1^6}$ in the CB1-4B method. The dotted and full curves are found in Figure 6.17 to be in a nearly perfect agreement at all impact energies. This success of the CCA is easily understood by reference to the results $\bar{Q}_\Sigma + \Delta\bar{Q}_1$ (singly chained curve) and $\bar{Q}_\Sigma + \Delta\bar{Q}_c$ (doubly chained curve). The former and the latter cross sections overestimate and underestimate, respectively, the exact results $Q_{c+\Sigma_1^6}$. However, such overestimation and underestimation are compensatory so that the combined correction $\Delta\bar{Q}_1 + \Delta\bar{Q}_c$ to the cross section $\bar{Q}_\Sigma$ of the CA brings the result $\bar{Q}_\Sigma + \Delta\bar{Q}_1 + \Delta\bar{Q}_c$ of the CCA into near coincidence with the associated exact data $Q_{c+\Sigma_1^6}$. This establishes the desired practical usefulness of the corrected closure approximation, that is, the CCA, which arrives basically at the exact results within the CB1-4B method for electron loss process (137) with hardly any effort through simple computations of cross sections $\bar{Q}_\Sigma + \Delta\bar{Q}_1 + \Delta\bar{Q}_c$ by means of the expounded and straightforward procedure.

Before closing this section, we recall our earlier remark that the ACB1-4B method and the CCA, in fact, represent the same theory. This is evidenced by the fact that their main working formulae (146) and (147) differ merely in a formal rearrangement of the contributing cross sections. Having one theory with two distinct aspects is rationalized by the need to emphasize simultaneous achievement of two different goals by the same computational procedure: (i) acceleration of the CB1-4B method by way of the ACB1-4B method (see the full curve in Figure 6.11) and (ii) a systematic correction of the CA by the CCA (see the dotted curve in Figure 6.17). As per theory and by reference to Eqs. (146) and (147), it is observed that these two latter curves are identical to each other. It should also be pointed out that convergence of the CCA with respect to the principal quantum number n of $H(n)$ is much faster than in the case of the corresponding direct summation of the exact cross sections Q_n from the CB1-4B method.

14. CONCLUSION

High-energy collisions of heavy positively charged ions with atoms involving emission of electrons from one or both colliding particles are critically important in many applications across various research fields. In addition to basic sciences such as atomic spectroscopy/collision physics and chemical physics, these include several branches of applied physics, for example, heavy ion fusion research, ion beam lifetime in accelerators, collisional and/or radiative processes in the Earth's upper atmosphere, transport of ions in

matter/tissue, and heavy ion radiotherapy. The available experimental and theoretical atomic data bases for ionization of cross sections at intermediate and high impact energies can be considered as quite satisfactory in the sense of being accurate and nearly complete for fully stripped projectiles (bare multiply charged nuclei) impinging on simply or complex atoms/ions. This is in sharp contrast to partially stripped projectiles, carrying one or more electrons (clothed or dressed ions), for which the corresponding cross sections are fragmented and scarce. In such cases, researchers in the mentioned branches of applied physics customarily resort to some empirical formulae with ad hoc functions for cross sections that have no relation whatsoever to any of multifaceted physical mechanisms associated with one- or multiple-electron collisional transitions. To these important applications, even the existing quantum-mechanical first-order Born-type perturbation methods seem to be an obstacle for usage in exhaustive computations and instead various phenomenological formulae are most frequently employed. This unnecessary practice occurs not only for collisions between many-electron atomic systems as projectiles and targets but also for considerably simpler scatterings of two hydrogen-like atoms or ions.

We revisited this problem of energetic ionizing collisions involving dressed ions as projectiles with atomic targets. For the purpose of illustration, electron loss in scattering of two hydrogen-like atomic systems is considered primarily due to the availability of the exact results within a chosen method for theoretical descriptions. However, the presented methodology is general and can be extended in a standard way to more complex colliding particles. Specifically, in an attempt to offer an appealing alternative to the said phenomenological type of modeling, we set the goal to establish a fast, simple, and accurate working formula for differential as well as total cross sections by using exclusively quantum-mechanical scattering amplitudes for bound-bound and bound-free transitions of one and/or both electrons.

For the cases that are most needed in applications in which the target is left in an experimentally undetected postcollisional state, the theory must perform complete summations over the entire discrete and continuous spectrum. The exact computation is usually time-consuming and tedious within most of the existing quantum-mechanical methods. To mitigate this difficulty, the closure relation was previously used to approximately encompass all the target states at once. Many implementations of the closure approximations were proposed in the past with various degree of shortcomings. The common drawback of most of the previous studies is the lack of systematics in using the still unexplored possibilities offered by the closure relation. As a rule, the direct or uncorrected closure approximation fails to agree with the exact cross sections in any given method, except at sufficiently high energies.

The present study illuminates a novel aspect of the closure relation amended by the appropriate corrections in the role of a powerful

convergence accelerator with respect to the number of the included post-collisional target states. For example, the first Born approximation requires a considerable set of the final states to reach the required convergence of the cross sections. As opposed to such an obstacle, the accelerated version of this latter method, provided by the corrected closure relation, yields precisely the same cross sections at all energies with merely two postcollisional target states, for example, the ground state and continuum. Hence the accelerated Born approximation for versatile applications in basic and applied research fields. The same strategy of the accelerated or corrected closure relation can also be used in any other chosen method and especially in the modified Coulomb Born theory for a more adequate description that agrees with experimental data at all the values of impact energies ranging from the threshold via the resonant Massey peak to the Bethe asymptotic region.

These achievements are not limited to only the computational side of studying electron loss collisions. Accounting for the whole spectra (discrete and continuous) of four free particles in the exit channel is an absolute necessity because of the dominance of double- over single-electron transitions. In particular, simultaneous ionization of the projectile and the target is the leading mechanism yielding the dominant contribution to stripping reactions. On the other hand, at lower energies as well as in the region near the resonance via the Massey peak, single-electron transition dominates with the emission of the projectile electron, whereas the target retains the same final state in which it was prepared initially. Both physical mechanisms are properly included in the accelerated Born approximation as well as the corrected closure approximation and yet the overall computational effort is dramatically reduced. This is the virtue of the highlighted accurate, efficient, and simple working formulae of cross sections for electron loss phenomena for multifaceted applications.

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