Journal of Mathematical Chemistry, Vol. 39, Nos. 3/4, May 2006 (© 2006)
DOI: 10.1007/s10910-005-9012-6

Can chemistry be derived from quantum mechanics? Chemical dynamics and structure

O. Tapia

Department of Physical Chemistry, Uppsala University, Box 579, 75123 Uppsala, Sweden
E-mail: orlando.tapia@fki.uu.se

Received 15 October 2004 / Published online: 19 January 2006

Following an early suggestion by Dirac, contemporary quantum mechanics (QM) and measurement theory are used to stepwise construct a conceptual framework to chemistry. In QM arbitrary physical quantum states are represented by linear superpositions. Base sets and quantum states are clearly distinguished; the latter are sets of ordered complex numbers. The generator of time evolution $\mathcal{H}$ is shown to have besides the molecular hamiltonian $H = H_C + K_N$, the electron–phonon and spin–orbit operators. H is shown diagonal in a product base set formed with generalized electronic diabatic (GED) and nuclear wave functions; the latter represented in a plane wave base set and unique inertial frame; these functions form the GEDM base set. Chemical species are assigned to particular GED base functions and a chemical quantum state is given as a linear superposition in the GEDM base set. Thus, given a fixed number of electrons and nuclei, the GEDM base set includes all electronuclear quantum states from clusters, supermolecule, molecular aggregates, asymptotic states, and ionized states (continuum electron states) to all plasma states. Experimentally measurable quantum states are given by linear superpositions. A chemical process is sensed by amplitude changes involving different electronic states in the linear superposition; vibration states intervene in excitation–relaxation processes; a time evolution of a global quantum 1-system is the feature. If sufficient time is allowed to an isolated system, with a given total energy E, unitary time evolution with $\mathcal{H}$ (but not H) ensures that the system will evolve from the initial state to get amplitudes different from zero for all energy conserving final states. Response towards external dynamic couplings, e.g. electromagnetic fields, is given by changes of amplitudes and expressed in correlation functions. For a quantum state, the amplitude at a given base function reflects the *possibility* for the system submitted to excitation sources to respond with its spectral signatures; if the experiment is done, and the amplitude is different from zero, then, there will be a response. Algorithms permitting to relate Hilbert space to real space events are discussed. A chemical compound (analyte) is identified to (i) a fixed electronic quantum state; (ii) linear nuclear base states superpositions; (iii) zero amplitude for all other electronic base states. To get this implies either the action of a chemist introducing constraints to bottle the analyte or an accidental change of external (to the box) conditions producing spontaneous separations.

KEY WORDS: chemical dynamics, conic intersections, generalized electronic diabatic base states, Hilbert space, linear superposition states, molecular structure, Quantum mechanics

0. Introduction

Quantum mechanics (QM), thus far, has been applied in chemistry leading to operational and successful research fields covering many aspects of chemical phenomena and material science [1]. Chemical concepts and foundational ideas, however, have only been wrapped without actually been derived from fundamental quantum mechanics. Interestingly, Dirac referring to QM wrote long ago (1929): "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known..." [2]. This statement suggests a prospect to fully derive chemistry starting from QM. Such a program would help getting a deeper understanding of phenomena that contemporary technology is generating and obtain a fresh view of chemical processes.

For, in spite of Dirac's cogent remark, chemical processes are described in a rather mechanical (classical) way; the introduction of concepts rooted in classical physics and chemistry produces a blurred picture. The blend of computational quantum chemistry permits accurate and sophisticated electronic calculations giving to molecules the status of objects with well defined "equilibrium geometry" parameters as the chemical structure theory requires [3, 4]. But QM is about quantum states and the principle of linear superposition in abstract Hilbert space [5–7]. For a sound criticism (see [8, chapter 5]).

A simple connection between Hilbert space and real space description in chemistry is not evident at all. In theoretical chemistry this results in a perplexing situation, for, on the one hand, chemical paradigms are introduced via numerical algorithms and, on the other hand, QM is contorted into real 3-D space in a way hiding its connections to abstract Hilbert space. The coefficients (amplitudes) of a linear superposition, when translated, without further ado, into population concepts wipe out entanglements that are essential to understand quantum mechanical time evolution. As a result, the core of rigorous QM fades away and numerical algorithms take the place of the theory. This is not an optimal situation.

If we stick to Dirac's stance, chemical phenomena are varieties of quantum ones. For this to be true one must be able to find pathways helping to derive chemistry from QM, the whole of it in its conceptual structure, and show that the chemical description of molecules and processes in real space are phenomenal appearances somehow rooted in Hilbert space. Once all the material elements are given, i.e. number of electrons and nuclei, QM describes a single system with infinite number of quantum states on particular base sets. This is the crux of the new approach. One gets the equivalent of chemical change in a single quantum mechanical system. To accomplish such a program, a new quantum measurement approach is required (see [9]).

Section 1 presents quantum mechanical grounds to fix the language and introduce to a chemical audience some aspects of a more advanced QM; the references, for some cases, are given with great detail to help the reader in finding the adequate material. For physicist and theoretical chemist, the paper can be read from section 2; there is only one point to remind: The total hamiltonian operator $\mathcal{H}$ is the one achieving time evolution proper. Section 2 connects abstract QM to molecular QM. Separability and molecular species are defined at the physical level first. Quantum evolution is examined with some detail. In section 2 the generalized electronic scheme is used to diagonalize the Coulomb hamiltonian H_C. In section 3 chemical species and laboratory chemistry are defined. A discussion section closes the paper.

1. Basic quantum mechanics

Abstract quantum states are symbolized in Dirac's notation as $|\Psi\rangle$; they belong to a linear vector space over the field of complex numbers. A fixed set of base vector is introduced to represent general quantum states as linear superpositions; any change of quantum state is monitored by amplitude variation of the linear superposition. Quantum states are experimentally measurable or manipulate in view to integrate them via their particular response in more complex systems.

Inertial frames provide a link between classical and quantum worlds. Special relativity space–time is implied even if the non-relativistic QM limit is taken for discussion [10]. Invariances reflect homogeneity of space–time; coordinates transform under origin translation and rotations in well-defined manner. Active or passive approaches to symmetry are used [11]. Any symmetry transformation is represented on the Hilbert space of physical states by an operator that is either linear and unitary or antilinear and antiunitary ([12, 13]; cf. [14, chapter 3] and/or [15, chapter 1]). Of key interest for a relativistic approach is the case of massive particle states. Then, it is always possible to find an inertial frame where the classical momentum is zero; in this rest frame the eigenvalues of the F^2 (the total angular momentum) are just the values of the total intrinsic angular momentum, e.g. $s(s+1)$. This means that massive systems can be classified according to their mass and spin; for molecular systems, charge is added. For non-relativistic QM limit, one can treat space and spin in separate manner in so far base function search is concerned.

1.1. General aspects

The real space vector $\mathbf{x}$ is related to base state (BS) $|\mathbf{x}\rangle$ in a rigged Hilbert space [14]; the BS is invariant to origin displacements of the inertial frame given by the operator $\mathcal{T}_\mathbf{a}$, i.e. $\mathcal{T}_\mathbf{a}|\mathbf{x}\rangle = |\mathbf{x}+\mathbf{a}\rangle$. Using $\mathbf{k}$, the reciprocal space vector, $\mathcal{T}_\mathbf{a} = \exp(-i\,\mathbf{k}\cdot\mathbf{a})$; the effect is to remind of the new origin measured from the non-displaced frame.

The projection of an abstract quantum state $|\Psi\rangle$ onto the configuration space reads as usual:

$$|\Psi\rangle = \int d\mathbf{x}|\mathbf{x}\rangle\langle\mathbf{x}|\Psi\rangle, \tag{1}$$

$\langle\mathbf{x}|\Psi\rangle \equiv \Psi(\mathbf{x})$ is the wave function. Thus, $d\mathbf{x}\langle\mathbf{x}|\Psi\rangle$ contains the data about the abstract quantum state. Like in image reconstruction techniques, the largest the domain where we record the wave function, the better reconstruction of the quantum state will be achieved. Anyway, $\langle\mathbf{x}|\Psi\rangle$ is a mathematical function with a domain covering all the configuration space $\mathbf{x}$ referred to an I-frame; this latter is in real space.

Notation: electronic and nuclear configuration coordinates are designated with the vectors $\mathbf{q}$ and $\mathbf{Q}$; $\mathbf{x} = (\mathbf{q}, \mathbf{Q}) : \Psi(\mathbf{x}) = \Psi(\mathbf{q}, \mathbf{Q})$. The wave function is the projection in configuration space of a particular abstract quantum state, nothing more. An abstract quantum state approach is preferred to the particle model; the concept of object is henceforward demoted. At this level, the concept of mechanical molecular structure is absent; a QM correlate to molecular structure will be found later on.

Time evolution in Hilbert space is carried out by the unitary operator $U(t, t_0)$. The generator of the unitary transformation is the total hamiltonian $\mathcal{H}$. Henceforward, $h/2\pi = \hbar = 1$; h is Planck's constant. The operator $U(t, t_0)$ fulfils the differential equation: $-\mathrm{i}\partial U(t, t_0)/\partial t = \mathcal{H}U(t, t_0)$ [11]. A quantum state $|t_0\rangle$, i.e. state prepared at a given time t_0, is propagated in time as usual: $U(t, t_0)|t_0\rangle = |t\rangle$. The time-dependent Schrödinger equation (2) relates hamiltonian and quantum states in a unique manner.

$$-\mathrm{i}\partial\langle\mathbf{q}, \mathbf{Q}|\psi, \mathrm{t}\rangle/\partial t = \mathcal{H}(\mathbf{q}, \mathbf{Q})\langle\mathbf{q}, \mathbf{Q}|\psi, \mathrm{t}\rangle. \tag{2}$$

The linear superposition principle requires of a complete base set to project any arbitrary quantum state. Assume the $\{\langle\mathbf{q}, \mathbf{Q}|\Lambda_j\rangle \equiv \Lambda_j(\mathbf{q}, \mathbf{Q})\}$, is a complete orthonormal set. At this point, we simply assume that these functions serve as a basis that can be used to examine time evolution. Because $\mathcal{H}(\mathbf{q}, \mathbf{Q})$ is not diagonal in this base set, proper time evolution is ensured.

Consider an arbitrary quantum state, prepared at the laboratory and represented by $|\Omega\rangle$. This state, projected in the configuration space, with the help of a unit operator: $1 = \Sigma_j|\Lambda_j(\mathbf{q}, \mathbf{Q})\rangle\langle\Lambda_j(\mathbf{q}, \mathbf{Q})|$, is the wave function $\Omega(\mathbf{q}, \mathbf{Q})$ expanded in the base set $\{\Lambda_j(\mathbf{q}, \mathbf{Q})\}$ that, for the sake of argument, is taken to be the molecular eigen states of the system. The infinite set of complex amplitudes, $\{\mathrm{C}_j(\Omega) = \langle\Lambda_j(\mathbf{q}, \mathbf{Q})|\Omega\rangle\}$ represent the quantum state Ω:

$$\Omega(\mathbf{q}, \mathbf{Q}) = \Sigma_j C_j(\Omega)\Lambda_j(\mathbf{q}, \mathbf{Q}) = (C_0(\Omega)\cdots C_m(\Omega)\cdots) \cdot [\Lambda_0(\mathbf{q}, \mathbf{Q})\cdots\Lambda_m(\mathbf{q}, \mathbf{Q})\cdots]. \tag{3}$$

The row vector $(C_0(\Omega)\cdots C_m(\Omega)\cdots)$ characterizes a particular quantum state with reference to the fixed base set (column vector) $[\Lambda_0(\mathbf{q}, \mathbf{Q})\cdots\Lambda_m(\mathbf{q}, \mathbf{Q})\cdots]$. Note that the unrestricted set of row-vectors contains all states that are experimentally measurable and initial state preparations that can possibly be imagined for a system represented with hamiltonian $\mathcal{H}$.

The infinite set of row vectors $C_0 \cdots C_j \cdots)$ form a linear vector space over the complex field $\alpha : \alpha C_0 \cdots C_j \cdots) = (\alpha C_0 \cdots \alpha C_j \cdots)$ and the sum of two vectors is given as $(C_0 \cdots C_j \cdots) \oplus (C'_0 \cdots C'_j \cdots) = (C_0 + C'_0 \cdots C_j + C'_j \ldots)$ belong to the linear vector space of row vectors. The set is obviously linearly dependent. In particular cases, one can extract linearly independent subsets that may help describing physical situations; a subclass of such sets represent coherent states. Vectors representing physical states are normalized to unity; in general, they are not characterized by quantum numbers.

1.2. *Quantum evolution in molecular physics*

In molecular physics, the material system is defined by invariant composition parameters. They are finite in number: n-leptons and m-hadrons (e.g. mu-mesonic molecules [16]); or, more specifically, n-electrons and m-nuclei; dimensions of $\mathbf{q}$ and $\mathbf{Q}$ are $3n$ and $3m$, respectively. The electric charge of both electrons and nuclei is universally defined; charge conservation characterizes non-relativistic molecular physics. However, Z (atomic number) is not sufficient to characterize the nuclear BS; neither the mass nor the spin is uniquely related to Z. This accidental nature of nuclear BS put them in a particular theoretical status. In general, electron-state wave functions transform under the permutation group by changing sign under odd permutations [17]. Nuclear wave function symmetries must be considered in a case-by-case basis. The total mass of the system $M = nm_e + \Sigma_{k=1,m} M_k$; m_e is electron mass; in atomic units, speed of light $c = 1$; $m_e = 1$. Each nucleus is characterized by charge Z_k, mass M_k and spin I_k.

To construct a molecular state theory, the total hamiltonian separates into two terms: $\mathcal{H} = \mathcal{H}_0 + V$; this help further connection to the standard molecular hamiltonian. The operator $\mathcal{H}_0$ is assumed to be time independent and fulfil the Schrödinger equation:

$$\mathcal{H}_0(\mathbf{q}, \mathbf{Q})\langle \mathbf{q}, \mathbf{Q}|\Phi\rangle = E\langle \mathbf{q}, \mathbf{Q}|\Phi\rangle. \tag{4}$$

For a hamiltonian $\mathcal{H}_0(\mathbf{q}, \mathbf{Q})$ self-adjoint and bounded below, equation (4) may provide a complete set of eigen functions (or BSs) [18], $\{\langle \mathbf{q}, \mathbf{Q}|\Psi_j\rangle \equiv \Psi_j(\mathbf{q}, \mathbf{Q})\}$, that are related to the set of eigenvalues $\{E_j\}$. This new set of BS replaces the arbitrary one, $\{\Lambda_j(\mathbf{q}, \mathbf{Q})\}$; they are related by a unitary transformation.

Time evolution is studied now in the interaction picture; V becomes a time-dependent operator; $V(t) = \exp(\mathrm{i}\mathcal{H}_0 t)V \exp(-\mathrm{i}\mathcal{H}_0 t)$. Defining $U(t, t_0) = U^{(0)}U'$ with $U^{(0)} = \exp(-\mathrm{i}\mathcal{H}_0 t)$ and $\mathrm{i}\mathrm{d}U'/\mathrm{d}t = V(t)U'$; all time evolution is controlled by the operator $V(t)$. The base functions are those related to $\mathcal{H}_0$, and only the amplitudes will be changed under the effect of U'. The normalization $U^{(0)\dagger}U^{(0)} = U^{(0)}U^{(0)\dagger} = 1$ permits relating the time evolution in either representation.

Key aspect: maintain the order of the BS column vector, the effect of the evolution operator is applied to the row vector defining the quantum state, i.e. in the expression $C_j(\Omega, t_0)U(t, t_0)\Psi_{\mathrm{j}}(\mathbf{q}, \mathbf{Q})$ that is equal to $C_j(\Omega, t_0)\Sigma_m U_{jm}(t, t_0)\Psi_m(\mathbf{q}, \mathbf{Q})$ the base function is relabeled once a sum over the index j is carried out (see equation (5)). Thus, applied to a quantum state prepared at time t_0, $U(t, t_0)\Omega(\mathbf{q}, \mathbf{Q}, t_0)$ is given by [19]

$$\begin{aligned}\Omega(\mathbf{q}, \mathbf{Q}, \mathrm{t}) = U(t, t_0)\Omega(\mathbf{q}, \mathbf{Q}, t_0) &= \Sigma_j C_j(\Omega, t_0)\mathrm{U}(t, t_0)\Psi_j(\mathbf{q}, \mathbf{Q})\\ &= \Sigma_j C_j(\Omega, t)\ \Psi_j(\mathbf{q}, \mathbf{Q}).\end{aligned} \tag{5}$$

The problem is solved once we get $\{C_j(\Omega, t)\}$, i.e. once the matrix elements $U_{mj}(t, t_0)$ are determined. The matrix elements of the time evolution operator depend upon the spectra of the system. Thus, whatever the level at which $U_{mj}(t, t_0)$ is calculated, determining the coefficients at a given time imply a full portrait of the state taken as the initial one since: $C_j(\Omega, t) = \Sigma_m C_m(\Omega, t_0)U_{mj}(t, t_0)$. Correlation functions of different types can be defined with these amplitudes [9].

Amplitude different from zero signals the possibility an experimenter has to activate the response related to that BS. In principle, all base states having non-zero amplitude at a given time can be measured simultaneously. No population interpretation is adequate in the present context [9].

The correlation function for the h-state $D_h(t_0, t)$ is given by the scalar product of $\Omega(\mathbf{q}, \mathbf{Q}, t)$ with the base state $C_h(\Omega, t_0)\Psi_h(\mathbf{q}, \mathbf{Q})$, namely,

$$D_h(t) = \langle C_h(\Omega, t_0)\Psi_h(\mathbf{q}, \mathbf{Q})|\Omega(\mathbf{q}, \mathbf{Q}, t)\rangle = C_h^*(\Omega, t_0)C_h(\Omega, t). \tag{6}$$

The square modulus for the hth channel is its cross-section at time t; complex conjugation indicated by *. Any spectroscopic experiment involving the $\Psi_h(\mathbf{q}, \mathbf{Q})$-BS as the origin for the excitations (UV, IR, Raman, etc.) is modulated in amplitude at time t by the value of $D_h(t) = C_h^*(\Omega, t_0)C_h(\Omega, t)$. If the amplitude were to be zeroing at all times, no spectroscopic feature related to the h-state will be visible. The intensity regime is given by $I_h(t) = |D_h(t)|^2$. If at $t = t_0$ the system has zero amplitude at the hth base state, the response in intensity starts from zero; as the time evolution puts some amplitude at that state, this will be detected as a time dependent intensity picture. Pump–probe experiments [20, 21] are examples.

The correlation amplitude measuring how much of the initial linear superposition state remains at time t is given by the scalar product:

$$D(t, t_0) = \langle\Omega(\mathbf{q}, \mathbf{Q}, t_0)|\Omega(\mathbf{q}, \mathbf{Q}, t)\rangle = \Sigma_j C_j^*(\Omega, t_0)C_j(\Omega, t). \tag{7}$$

This correlation function is different from zero for those states having non-zero amplitudes at the beginning of the experiment. If one is able to follow a specific state, say, $C_j^*(\Omega, t_0)\, C_j(\Omega, t)$, the square modulus of function $D(t, t_0)$ will measure the decrease in intensity as state amplitudes at new channels become different from zero (norm conservation); the state vector is normalized to one at all times.

In actual experiments that use electromagnetic radiation, this is filtered so that only one or a few base states are probed in equation (7). For a pump/probe experiment, the correlation function of interest is not equation (7) but the quantum state at an intermediate time t' just before the probe is switched on; this latter is the state making the spectral response. It is convenient to define the correlation function by taking out the part corresponding to the pumping step:

$$\begin{aligned} D(t, t') - D(t', t_0) &= \langle \Omega(\mathbf{q}, \mathbf{Q}, t') | (U - \mathbf{1}) \Omega(\mathbf{q}, \mathbf{Q}, t_0) \rangle \\ &= \Sigma_j C_j^*(\Omega, t') C_j(\Omega, t) - \Sigma_j C_j^*(\Omega, t_0) C_j(\Omega, t') = \Sigma_j' C_j^*(\Omega, t') C_j(\Omega, t). \end{aligned} \tag{8}$$

The symbol Σ' stands for a sum over all j that are different from those amplitudes appearing at time t_0. One focus on new features developed by pumping. The intensity for this case is $I = |D(t, t') - D(t', t_0)|^2$ [9]. Thus, all elementary base states present at initial time are subtracted away. No response can be expected for all those amplitudes $C_j^*(\Omega, t')$ that are zero at time t'. Sensing a response based on equation (8) after t' while it was zero at t_0 means that the previous time evolution lead to non-zero amplitude for the BSs involved.

The interpretation of a quantum state differs from the orthodox view [21]. Here, all amplitudes are required to define the quantum state; no population concept is implied until a measurement in intensity is made in post-mortem conditions. The response is from one system not from an ensemble. The 1-system is not to be considered as “wandering” around and staying at the diverse BSs for finite times. For some measurements in the intensity regime, the amplitudes in square modulus just signals relative intensity. The more complete measurement will be a holographic detection [9]. The weirdness of a quantum system comes from the idea that one is directly treating BSs as if they were actual molecules. The particle picture imposed in the standard QM description is at the origin of most of the paradoxes found so far. Similar comments apply to the classical wave picture.

1.3. Separability, molecular species and time evolution

The physical quantum state wave functions $\Phi(\mathbf{q}, \mathbf{Q})$ are non-separable. On the contrary, we will show that the base functions $\{\Psi_{jk}(\mathbf{q}, \mathbf{Q})\}$ can be separable. The condition is to form a new complete set.

Note, in a rigorous quantum mechanical setting, an electronic base function parametrically dependent on nuclear configuration space cannot be. Such dependence would imply that the electronic quantum number of the base function depends upon the particular selected region of nuclear configuration space. The proof comes with the scrutiny of the exact electronuclear BS function $\Psi_{jk}(\mathbf{q}, \mathbf{Q})$ solution of: $\mathcal{H}_0(\mathbf{q}, \mathbf{Q})\ \Psi_{jk}(\mathbf{q}, \mathbf{Q}) = E_{jk}\Psi_{jk}(\mathbf{q}, \mathbf{Q})$; it is obvious that the electronic quantum number does not depend at all on the domain of $\mathbf{Q}$ that we might have selected to look at (if we could do that); the eigen value equation with $\mathcal{H}_0(\mathbf{q}, \mathbf{Q})$ is valid for all $\mathbf{Q}$-values, the quantum number derives from symmetry/boundary conditions.

In the quantum number separable base functions a time dependent amplitude can now be written in a way that differs from standard form [22] as given by

$$
\begin{aligned}
C_{jk}(t) = {} & \Sigma_{j'k'} C_{j'k'}(t_0)\delta_{j',j}\delta_{k',k} - i\,\Sigma_{j'k'} \int_{t_0}^{t} \mathrm{d}t' C_{j'k'}(t_0) V_{j'k',jk}(t') \\
& + i^2 \Sigma_{j'k'} \Sigma_{j''k''} \int_{t'}^{t} \mathrm{d}t' \int_{t_0}^{t'} \mathrm{d}t'' C_{j'k'}(t_0) V_{j'k',j''k''}(t') V_{j''k'',jk}(t'') - i^3 \Sigma_{j'k'} \Sigma_{j''k''}\ \Sigma_{j'''k'''} \\
& \int_{t'}^{t} \mathrm{d}t' \int_{t_0}^{t'} \mathrm{d}t'' \int_{t_0}^{t''} \mathrm{d}t'''\ C_{j'k'}(t_0) V_{j'k',j''k''}(t')\ V_{j''k'',j'''k'''}(t'')\ V_{j'''k''',jk}(t''') + \cdots \quad (9)
\end{aligned}
$$

The amplitude $C_{jk}(t)$ is the one multiplying the fixed BS $\Psi_{jk}(\mathbf{q}, \mathbf{Q})$; the set of equation is infinite. The relative simplicity of this type of equation is due to the fact that the base set ordering is maintained fixed and all changes are performed on the space of amplitudes; it is the quantum state that is changing.

The key to transforming the general framework into a more practical approach resides in actual calculation of the matrix elements of the time evolution operator. A rather complete treatment of this issue is given in [23]. In section 2.3. further discussions are presented.

1.4. Parity, spin dependence and electromagnetic coupling

Parity or space inversion is a discrete symmetry where $\mathbf{x} \rightarrow -x, y \rightarrow -y, z \rightarrow -z$ or $q_1 \rightarrow -q_1, q_2 \rightarrow -q_2, q_3 \rightarrow -q_3$. The parity operator and the position operator anticommute, $\mathbf{x} = -\mathbf{x}$ as it does with the momentum $\mathbf{p}$. Thus $\mathbf{x}(|x'\rangle) = -\mathbf{x}|x'\rangle = -x'|x'\rangle = -x'(|x'\rangle)$ and the vector $|x'\rangle$ has a negative eigenvalue $-x'$.

A distinction must be made between global quantum state and base function. A BS function is an eigen function of parity. It is either odd or even, i.e. it changes sign or it does not. A physical quantity, in general, does not depend on the way the axes are signed. Any of such quantities are numbers. If a change of sign is detected under parity operation, the quantity must be zero. This is parity selection rule to be used in the analysis of chemical reaction mechanisms [24, 25].

To complete the characterization of the base functions and check for parity, spin must be introduced. The operator is not only unitary but also hermitian; it commutes with **L**, **S** and **J**. For further details (see [7, p. 251]).

In the present context, for relativistic QM the law of conservation of number of particles is not true in general. The relativistic description of an electron in an e/m. field implies the existence of a spin $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$ for this particle-state. The Pauli matrices $\boldsymbol{\sigma} = (\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3)$ are usually related to a special blend of operators appearing in the Dirac hamiltonian that are introduced without any reference to spin [26]. The non-relativistic limit leads to the 2-spinor representation for electron states.

The molecular (Coulomb) hamiltonian H commutes with S^2. The base wave functions are hence factored. The global base functions are represented as direct products of space and spin functions. The space part was discussed above. The spin dependent part of base functions is represented in a direct product space of n 2-spinors appropriately symmetrized [17].

The hamiltonian $\mathscr{H}$ contains the kinematic couplings, namely, spin–orbit so that this operator commutes with the total angular momentum $F = S+L+I$; the sum of spin, orbital and nuclear spin operators. For the molecular case it is common to use $J = L + S$ as quantum operators and neglect nuclear spin.

The irreducible representations of J^2, or those for S^2 and L^2 can be used to label BSs of H. One can follows the chemical change with BSs of the kind $|J, M_J; L, M_L, S, M_S\rangle$. The basis for the quantum theory of angular momentum can be found in [27]; for details see standard QM books, (e.g. [7], see also [28]).

For a 1-electron system, the BSs are column vectors $\alpha = [1\ 0]$ and $\beta = [0\,1]$ and the spin state is the linear superposition: $\Xi(a,b) = (a\ b)[\alpha\ \beta] = a\,\alpha + b\,\beta$ and with $|a|^2 + |b|^2 = 1$. A rotation in 3-D space with Euler angles ϕ, θ, ζ as defined in [7, p. 172] induces a unitary transformation in this 2-D spin space with matrix elements: $S_{11} = \exp(-\mathrm{i}(\phi + \zeta)/2)\cos(\theta/2)$, $S_{12} = -\exp(-i(\phi - \zeta)/2)\sin(\theta/2)$, $S_{21} = -S_{12}^*$ and $S_{22} = S_{11}^*$.

The I-frame is selected so that for the spin vector operator $\mathbf{S} = (S_1, S_2, S_3)$, the eigen value equations are: $\boldsymbol{S}^2|S\ M_S\rangle = S(S+1)|SM_S\rangle$ and $S_3|SM_S\rangle = (M_S)|SM_S\rangle$. A frame rotation moving away the 3-axis, induces spin polarization without charge polarization [29]. In general, electronic calculations must be carried out in the same, or equally oriented, frame. Otherwise, the results cannot be put together as the pieces may be incommensurable.

In quantum chemistry one uses a special form: $a = 1$, $b = 0$ corresponding to $\Xi(1,0) = \alpha$; the case $\Xi(0,1) = \beta$. It is an unfortunate practice to take these latter states as if they were properties of a given electron. Here, only $\Xi(a,b)$ makes sense. Information is stored in amplitudes [30].

The molecular hamiltonian in presence of an electromagnetic transverse potential $\mathbf{A}(\mathbf{r}, t)$ is given in equation (10) [23].

$$
\begin{aligned}
H' = H_c + K_\mathrm{N} + H_\mathrm{RAD} + V_\mathrm{dyn} &= H + H_\mathrm{RAD} + \Sigma_i \mathbf{p}(\mathbf{q}_i)\cdot\mathbf{A}(\mathbf{q}_i) - \Sigma_k (q_k/M_k)\mathbf{p}(\boldsymbol{\xi}_k)\cdot\mathbf{A}(\boldsymbol{\xi}_k) \\
&\quad + \Sigma_i g_i/2\mathbf{S}_i\cdot\mathbf{B}(\mathbf{q}_i) - \Sigma_k (g_k\, q_k/2M_k)\mathbf{S}_k\cdot\mathbf{B}(\boldsymbol{\xi}_k) \\
&\quad + \Sigma_i \mathbf{A}(\mathbf{q}_i)\cdot\mathbf{A}(\mathbf{q}_i) + \Sigma_k (q_k^2/2M_k)\mathbf{A}(\boldsymbol{\xi}_k)\cdot\mathbf{A}(\boldsymbol{\xi}_k), \qquad (10)
\end{aligned}
$$

g_a is the Landé factor of the ath state-particle; in the atomic unit system the factor e/m for electrons is implicit in corresponding coupling terms. The radiation hamiltonian H_{RAD} equals to $(\varepsilon_0/2)\int d^3r\,(\mathbf{E}_\perp(\mathbf{r}) + \mathbf{B}(\mathbf{r}))$; the magnetic field $\mathbf{B}(\mathbf{r})$ is multiplied by $c^2 = 1$ in the present units, ε_o is vacuum permittivity. The dynamic coupling operators, V_{dyn}, are defined in equation (10). The transverse electric and magnetic fields are related to $\mathbf{A}$ in equation (10) by: $\mathbf{E}_\perp(\mathbf{r}, t) = -(1/c)\int \mathbf{A}(\mathbf{r}, t)/\int t$ and $B = \nabla \times \mathbf{A}$. The system is quantized with the base functions for a Fock-space $|\boldsymbol{\kappa}, n\rangle$; n is the number of quanta in the normal mode (photons), the vector κ has a modulus proportional to the circular radiation frequency $\omega = 2\nu$, i.e. $|\boldsymbol{\kappa}| = \omega/c$. Note that photons are characterized by spin one where only two components express themselves experimentally (see [23, p. 44]). The base states can sometimes be label as $|n\boldsymbol{\kappa}\varepsilon\rangle$, where ε is the polarization state of light.

The hamiltonian $H = H_{\mathrm{C}} + K_{\mathrm{N}}$ and S^2 (total electronic spin operator) commute themselves as well as with one component that conventionally is taken to be along the third component of the spin-vector, S_3 or S_z. In this scheme, H also commutes wit L^2 and L_3 (L_z). At low energy, the non-relativistic 2-spinor formalism follows from the 4-spinor one [10]. Equation (10) represents Breit–Pauli hamiltonian [31].

Summing up. The electronic quantum numbers and response to external fields identify molecular species. Molecular change is elicited by time evolution involving the electronic quantum number. This process is akin to a chemical change. Dirac's conjecture is then, partially at least, fulfilled.

2. From physics to physical chemistry

Once the core of a chemical process is formally obtained as time evolution of quantum amplitudes, the generator of time evolution $\mathcal{H}$ must be given an explicit form. If one were to use a base set where the operator is diagonal, unless an external field is present, no actual change of electronic base state amplitude is possible. The objective now is to examine whether or not the molecular (Coulomb) hamiltonian H can be used as a faithful model to $\mathcal{H}$ or it should take the place of $\mathcal{H}_0$. The answer has an import for all those models constructed around the hamiltonian H to describe time evolution in quantum chemistry.

2.1. The Coulomb hamiltonian and dynamics

For the electro-nuclear model, it is the charge the only homogeneous element. Thus, it has always been natural to use the Coulomb hamiltonian $H_{\mathrm{C}}(\mathbf{q}, \mathbf{Q})$ as an entity to work with. In fact this is a key operator for describing molecular physics events [3]. Let us consider the exact problem first.

The Coulomb hamiltonian H_C includes the electronic kinetic energy (K_e) and all electrostatic interaction operators ($V_{ee}+V_{eN}+V_{NN}$). Define the functional $E(\mathbf{Q};[\Psi])=\langle\Psi(\mathbf{q})|H_C(\mathbf{q},\mathbf{Q})|\Psi(q)\rangle$. The variational principle applied to the function space $\Psi(\mathbf{q})$ leads to the Euler–Lagrange equation:

$$H_C(\mathbf{q},\mathbf{Q})\Psi(\mathbf{q}) = \mathrm{E}(\mathbf{Q})\Psi(\mathbf{q}). \tag{11}$$

For a self-adjoint $H_C(\mathbf{q},\mathbf{Q})$, Kato's theorem [18] ensures the existence of a complete set of eigenfunctions, $\{\phi_j(\mathbf{q})\}$ [32, 33]. But, the problem is to find a complete set of solutions to the molecular hamiltonian H:

$$H(\mathbf{q},\mathbf{Q})\Phi(\mathbf{q},\mathbf{Q}) = (H_C(\mathbf{q},\mathbf{Q}) + K_N(\mathbf{Q}))\Phi(\mathbf{q},\mathbf{Q}) = E\Phi(\mathbf{q},\mathbf{Q}). \tag{12}$$

This is the standard molecular physics problem that is usually handled with algorithms such as the Born–Oppenheimer scheme [34, 35]; for modern developments along this direction see [3]. Here, an exact solution to equation (12) is required via the construction of a complete separable set of base functions. Remember that the general quantum states wave functions $\Phi(\mathbf{q},\mathbf{Q})$ are not separable.

The procedure to solve equation (12) uses of a complete set of electronic diabatic wave functions $\{\phi_j(\mathbf{q})\}$ that diagonalize H_C in equation (11); this is the GED (generalized electronic diabatic) set. For any point $\mathbf{Q}$, energy obtains from the diabatic potential energy functional $\mathrm{E}(\mathbf{Q};[\phi_k])$.

For a system of n-electrons, the number of nodal planes, permutation symmetries, parity, etc. help characterize a complete set of electronic base functions; properties that are independent from the $\mathbf{Q}$-point selected from the nuclear configuration space. Herzberg and Teller [36] and Longuet-Higgins [37] have used this idea too. If one departs from the BO ideology, the complete set obtained from equation (11) at say $\mathbf{Q}_0$ permits classifying the electronic base functions. These functions are isomorphic to those obtained from a diagonalization of the electron kinetic energy operator plus self-repulsion [33] in the sense of conserving nodal planes albeit the energy is in the continuum; see also work recently reported by Martín [38] on B-splines. Asymptotic states appear as solutions to the super molecule at $\mathbf{Q}_0$ albeit they are not apparent due in part to actual computing limitations. The problem that must be solved is the incorporation of asymptotic states (see below) in the global Hilbert space. The qualitative solution to this problem opens a way to understanding a little better those processes related to chemical bond breaking and forming. Asymptotic states are basic elements in beams reactive scattering.

The pattern used to perform separability is well known and we follow it to see its limitations. The diabatic potential is used to define equations for the nuclear wave functions leading to the product set $\{\phi_k(\mathbf{q})\zeta_{km}(\mathbf{Q})\}$ by solving for each electronic diabatic potential the corresponding equation (13):

$$\{K_N + E(\mathbf{Q};[\phi_k]) - E_{km}\}\zeta_{km}(\mathbf{Q}) = 0. \tag{13}$$

These equations show that, at least, one can find infinite dimensional subspaces (with fixed k) where the molecular hamiltonian $H{=}K_{\mathrm{N}} + H_{\mathrm{C}}$ is diagonal. The problem is that there are infinite nuclear hamiltonian operators thereby annihilating the procedure as a general one.

Yet, the result obtained above differs from previous schemes; the reason for this is that all electronic diabatic base wave functions can be obtained from only one electronic Schrödinger equation (see [39–41]). The Born–Oppenheimer scheme [3, 42] applied to chemical reactions is based on solving infinite electronic Schrödinger equations with or without non-adiabatic couplings [43] thereby transforming the procedure in an algorithm instead of an electronic structure theory.

The set of functions $\{\zeta_{km}(\mathbf{Q})\}$ for different electronic quantum numbers has the same limitation as the BO scheme. Although the functions in $\{\phi_k(\mathbf{q})\zeta_{km}(\mathbf{Q})\}$ are linearly independent there is no way to show that they form a complete set.

To do away with these objections, use instead the complete set of functions diagonalizing the nuclear kinetic energy operator K_{N}. The set, to within normalization factors, is $\{f_k(\mathbf{Q})\cdot \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{Q})\}$; $\mathbf{k}$ is a vector in reciprocal space. Including the system in a box of volume $\mathcal{V}$, the reciprocal vectors are discrete, $\mathbf{k}_i$, and the functions $f_{kl}(\mathbf{Q}) = (1/\sqrt{\mathcal{V}})\exp(i\mathbf{k}_l\cdot\mathbf{Q})$ form an orthonormal set with the completeness relation $\delta(\mathbf{Q}-\mathbf{Q}') = \sum_i f_i(\mathbf{Q}) f_i(\mathbf{Q}')$. For an $3m$-dimensional nuclear base states, the product functions $f_k(\mathbf{Q}_1,\ldots,\mathbf{Q}_m)\Pi_{i=1,m} f_{ki}(\mathbf{Q}_i)$ provides a complete base set.

The direct product set $\{\phi_j(\mathbf{q})\mathrm{f}_{kl}(\mathbf{Q})\}$ is complete. The problem now is to render diagonal equation (12) in this base set. The index $\mathbf{k}$ is made discrete by using periodic boundary conditions and, at the end, taking the limit of infinite box; this method permits handling the problems in a smooth manner (see p. 280 in [44]; consult also [38] and references therein). The matrix elements of equation (12) reads

$$\begin{aligned}&\langle\phi_j(\mathbf{q})f_{k'}(\mathbf{Q})|(H_{\mathrm{C}}(\mathbf{q},\mathbf{Q}) + K_{\mathrm{N}}(\mathbf{Q}))|\phi_g(\mathbf{q})f_k(\mathbf{Q})\rangle\\&= \langle f_{k'}(\mathbf{Q})|(K_{\mathrm{N}} + E(\mathbf{Q};[\phi_j])|f_k(\mathbf{Q})\rangle\delta_{jg}.\end{aligned}\tag{14}$$

Equation (14) is factored as a function of the electronic quantum number via δ_{jg} (Kronecker symbol). Each sub-matrix of infinite dimension relates to one electronic label only; in this subspace $\mathbf{Q}$-dynamics is modulated by the electronic state with m-product base functions $f_k(\mathbf{Q}_1,\ldots,\mathbf{Q}_m)$. Observe that there is no coupling between electronic states generated by the standard molecular hamiltonian; these states are diabatic.

Although the plane wave base set is most useful to establish general mathematical results, in practice, the local representations derived for each electronic state of equation (13) can be used; contact with and exploiting of standard molecular quantum chemical schemes is hence made clear. For each electronic subspace equations (14) and (13) differ only by a local (j-dependent) linear transformation: $\zeta_{jm}(\mathbf{Q}) = \Sigma_{k'}\mathrm{A}_{k'}(\zeta_{jm})f_{k'}(\mathbf{Q})$. The coefficients $\mathrm{A}_{k'}(\zeta_{jm})$ are fixed for each jm-index. And, as it is implied by equation (14), connection between different electronic states is not allowed by electronic orthogonality.

The set $\{\phi_j(\mathbf{q})\zeta_{jm}(\mathbf{Q})\}$ considered as base functions that makes the hamiltonian H (cf. equation (12) block-diagonal in the electronic space; the functions $\zeta_{jm}(\mathbf{Q})$ are not orthogonal in $\mathbf{Q}$-space for arbitrary electronic states; the overlap integrals $\int \mathrm{d}^{3m}\mathbf{Q}\zeta_{jm}(\mathbf{Q})\zeta_{j'm'}(\mathbf{Q})$ are the well known Franck–Condon factors, $S_{jm,j'm'}$.

A quantum state $\Gamma(\mathbf{q}, \mathbf{Q})$ can be represented as a linear superposition in the electro-nuclear base:

$$\Gamma(\mathbf{q}, \mathbf{Q}) = \Sigma_{jm}\mathrm{C}_{jm}(\Gamma)\phi_j(\mathbf{q})\zeta_{jm}(\mathbf{Q}). \tag{15}$$

The j-index runs over robust electronic species; the m-index corresponds to nuclear dynamics always in the same electronic state. The average value of the energy for this quantum state is $\langle\Gamma(\mathbf{q}, \mathbf{Q})|H|\Gamma(\mathbf{q}, \mathbf{Q})\rangle$. Replacing equation (15) and using equation (14) with (13) one gets the standard QM formula:

$$E(\Gamma) = \langle\Gamma(\mathbf{q}, \mathbf{Q})|H|\Gamma(\mathbf{q}, \mathbf{Q})\rangle = \Sigma_{jm}|C_{jm}(\Gamma)|^2\mathrm{E}_{jm}. \tag{16}$$

This result is valid for the molecular hamiltonian H. Each BS identifies a molecular state in the sense given in [39]. For diabatic attractor states the result would be self-evident. For asymptotic states, the representation must be completed; this is discussed in section 3.

The separable base set is referred to as generalized electronic diabatic molecular (GEDM) base set. Observe that no structural features are implied yet. Thus, separability via electronic quantum numbers is achieved although the general quantum states are not separable (see the author's comments in [45] p. 95, 120, 374).

As a matter of fact, equation (15) highlight a specific aspect of the present approach: All chemistry would be given as time evolution of a 1-system quantum state. The set of amplitudes $\{C_{jm}(\Gamma)\}$ is the key element when chemical processes come into sight. No wandering on potential energy surfaces is required as a matter of principle.

2.2. *Time evolution: molecular change*

In the GEDM space, the molecular hamiltonian H cannot by itself be a generator of time evolution. The GEDM and Hilbert spaces are isomorphic. This result is rigorous and put in jeopardy the claim of those schemes based on H with base functions of BO-type [3, 46, 47] as genuine quantum mechanical approaches [22]; they would qualify instead as numerical algorithms and/or models.

The molecular hamiltonian H is a part of the total hamiltonian $\mathcal{H}(\mathbf{q},\mathbf{Q})$. Kinematic coupling terms are required to make possible time evolution. The mapping looks like

$$\mathcal{H}(\mathbf{q},\mathbf{Q}) \to H_{\mathrm{C}}(\mathbf{q},\mathbf{Q}) + K_{\mathrm{N}}(\mathbf{Q}) + V = H + V. \tag{17}$$

The operator V besides the electron–phonon couplings, $V_{\mathrm{e}\otimes\mathrm{ph}}$, includes the spin–orbit operator V_{SO} [see equation (18)] whenever the magnetic field has a molecular origin only; external fields generate dynamic couplings. $V_{\mathrm{e}\otimes\mathrm{ph}}$ operator is characteristic of Jahn-Teller [48–50] and Renner effects [51, 52]. In the base $\{\phi_j(\mathbf{q})f_k(\mathbf{Q})\}$ the operator $V_{\mathrm{e}\otimes\mathrm{ph}}$ is non-diagonal. Different electronic states are henceforward coupled to each other.

The chemical processes and, in general, molecular processes (relaxation, energy reshuffling, etc.) can be sensed via particular change of the amplitudes of a linear superposition on the electronuclear base set derived from the molecular hamiltonian. We take a simple case where the electron–phonon coupling is on. The matrix elements of $\mathcal{H}$ in this base set look like

$$\left\{\int d\mathrm{Q}\zeta^{*}_{j'm'}(\mathbf{Q})\{(K_{\mathrm{N}}+E(\mathbf{Q};[\phi_j]))\delta_{jj'}+\langle\phi_{j'}|V_{e\otimes ph}(\mathbf{q},\mathbf{Q})|\phi_j\rangle_q\}\zeta_{km}(\mathbf{Q})\right\}=\mathcal{H}_{j'm',jm} \tag{18}$$

$\mathcal{H}$ would be diagonal in this basis were it not for electron–phonon coupling operators. The time evolution operator $U(t,t_0)$ propagates an arbitrary quantum state thanks to the non-zero matrix elements $(V_{e\otimes ph})_{j'm',jm}$. The set $\{\phi_j(\mathbf{q})\zeta_{jm}(\mathbf{Q})\}$ is fixed while the amplitudes of the linear superposition equation (15) can change as a function of time; this is indicated in equation (9). However, because a connection to standard chemical representation is sought we will move on to consider diabatic potential energy hyper-surfaces to give a first cue; such procedure corresponds that include a particular model that include real space features.

The diabatic potential energy hypersurfaces $E(\mathbf{Q};[\phi_j])$ are of use to decode energy reshuffling in neighborhoods of a point $\mathbf{Q}\#$ where $E(\mathbf{Q}\#;[\phi_j]) = E(\mathbf{Q}\#;[\phi_{j'}])$. This is a conic intersection and the domain where this condition holds can be named a seam as it is common practice in the adiabatic scheme [53]; the crux of the matter is the degeneracy involved. In the neighborhood there is a zone where $j(\mathbf{Q})<j'(\mathbf{Q})$ and another $j(\mathbf{Q})>j'(\mathbf{Q})$, at the conic intersection another $j(\mathbf{Q}) = j'(\mathbf{Q})$. There is an energy inversion. Take the secular equation: $|\mathcal{H}_{j'm',jm} - \mathrm{E}|$. The determinant has dimension 2 in the electronic quantum number; we assume m and m' fixed so that we get almost degeneracy at the conic intersection. In the domain where the lower state is $j(\mathbf{Q})$, the wave function has amplitudes dominated by this state for energy gaps sufficiently large. The opposite holds when $j'(\mathbf{Q})$ is the lowest energy base state. The chemical change is sensed by the change in the corresponding amplitudes. Such neighborhoods would determine the contributions to $\mathcal{H}_{j'm',jm}$. This opening of the matrix element helps introduce mechanistic ideas that belong to a real space description.

The quantum evolution is controlled by the operator $U(t, t_0)$ appearing in equation (5); the amplitudes evolve with equation (9). For a quantum state having $C_{j'm'}(t_0) \neq 0$ and $C_{jm}(t_0) = 0$, equation (9) tells that $C_{jm}(t)$ will become different from zero if there are chains of connecting matrix element all different from zero: $U_{j'm',jm} \cdots U_{k'l'.k''l''} U_{k''l''.kl} U_{kl,jm} \neq 0$. For the first-order term, $U_{j'm'.jm}$, the integral responsible for the process will be peaked in the region around the conic intersection as defined here. We see that the mapping $\mathrm{E}(\mathbf{Q}; [\phi_j])$ might induce structural-like features if we use an appropriate space to discuss such issues. The configuration space $\mathbf{Q}$ is not appropriate.

Thus, in principle, $\mathcal{H}(\mathbf{q}, \mathbf{Q})$ given by (17) should be sufficient to describe chemistry and help set up the stage to describe chemical processes as quantum dynamical evolution. Besides, signals of possible structural element start to show up. We are again in line with Dirac's statement [2].

2.3. Time evolution in electromagnetic fields

Time evolution is illustrated with two graphs in figure 1. The key elements are the amplitudes. Two "histories" are depicted. In equation (9), the energy spectra appears explicitly; the operators in the interaction representation are $V(t) = \exp(i\mathcal{H}_0 t) V \exp(-i\mathcal{H}_0 t)$ in atomic units (Dirac representation). Furthermore, first order contributions to the amplitude $C_{jk}(t)$ can only originate from those base states in the initial quantum state with amplitudes different from zero; higher order terms (in $V(t)$) elicit newly emergent amplitudes; these amplitudes are also rooted in the initial quantum state. If no interaction is effected on the system within the time gap $t - t_0$, measuring the complete set $\{C_{jk}(t)\}$ at time t would provide a determination of the initial state, $\{C_{j'k'}(t_0)\}$. An amplitude different from zero at time t_0 opens a possibility for the system to respond under the perturbing source reflected by the operator V. Note that possibility has nothing to do with probability; if the amplitude is different from zero, an experiment will show a response.

As a model, take $V = -(e/c)\mathbf{A} \cdot \mathbf{p} + (e/c)^2 \mathbf{A} \cdot \mathbf{A}$ from equation (10). For the time being, retain the term linear in $\mathbf{A}$. Experimentalists can tailor quantum states with appropriate dynamic couplings. We need a base set for the e/m system in order to complete the quantum description.

The base functions are direct products of molecular and photon base states, with $\boldsymbol{\varepsilon}$ signaling light polarization vector: $|\mathrm{ij}\rangle|\boldsymbol{\kappa\varepsilon}\mathrm{n}\rangle \rightarrow |\mathrm{ij}; \boldsymbol{\kappa\varepsilon}\mathrm{n}\rangle$. Ortho normality conditions: $\langle \boldsymbol{\kappa}'\boldsymbol{\varepsilon}' | \boldsymbol{\kappa\varepsilon} \rangle = \delta_{\boldsymbol{\varepsilon}'\boldsymbol{\varepsilon}}\delta(\boldsymbol{\kappa}' - \boldsymbol{\kappa})$. The volume element in $\boldsymbol{\kappa}$-space in terms of the density of states (DOS) $\rho(\mathrm{E})$ is given by: $\mathrm{d}^3\boldsymbol{\kappa} = \boldsymbol{\kappa}^2 \mathrm{d}\kappa \mathrm{d}\Omega = \rho(E)\mathrm{d}E\,\mathrm{d}\Omega$. For a cubic box of length L, $\rho(E) = (L/2\pi)^3 (E^2/\hbar^3 \mathrm{c}^3)$ and $E = \hbar \mathrm{c}\kappa$ [54].

The time dependent field in the dipolar model, $\mathbf{A}(\mathbf{x}, t) \rightarrow \mathbf{A}(\mathbf{o}, t) = \mathbf{A}(t)\mathrm{A}_0\boldsymbol{\varepsilon}\ \cos\omega t$. The matrix element of the evolution operator reads as

$$\begin{aligned}\langle \mathrm{ij};\, \boldsymbol{\kappa\varepsilon} n|V(t)|i'j';\, \boldsymbol{\kappa}'\boldsymbol{\varepsilon}n'\rangle &= -{<}\boldsymbol{\kappa\varepsilon}n|\mathbf{A}(t)|\kappa'\boldsymbol{\varepsilon}n'\rangle\boldsymbol{\varepsilon}\cdot\langle i|\mathbf{p}|i'\rangle S_{ij,i'j'}\\ &= \delta_{\varepsilon'\varepsilon}\delta(\boldsymbol{\kappa}'-\boldsymbol{\kappa})\langle n|\mathbf{A}(t)|n'\rangle\boldsymbol{\varepsilon}\langle i|\mathbf{p}|i'\rangle \mathrm{S}_{ij,i'j'}. \qquad (19)\end{aligned}$$

Only the electronic part of $\mathbf{p}$ may have non-zero matrix elements, the nuclear part contributes with the Franck–Condon factor, $S_{ij,i'j'}$. The operator $\mathbf{A}(t)$ is linear in photon creation ($a^{\dagger}$) and destruction (a) operators [54]:

$$\mathbf{A}(\mathrm{t}) = \Sigma_{\kappa}(1/2)A_{\boldsymbol{\kappa}}\varepsilon_{\kappa}(a_{\boldsymbol{\kappa}}\exp(-t\omega_{\boldsymbol{\kappa}}t) + a_{\boldsymbol{\kappa}}^{\dagger}\exp(+t\omega_{\boldsymbol{\kappa}}t)). \qquad (20)$$

The photon field labels n and n' differ at most in one unit. The molecular transition must involve a change in parity for the product wave function of -1 because the associated 1-photon base state transition has parity -1. Thus, s→s, p→p, d→d, etc. transitions are (dipole) forbidden. In photo-electron ionization, the s-state electron must be connected to a p-state of the continuum (vice versa). We write now the first order term of equation (9) as

$$\begin{aligned}&\int_{t_0}^{t}\mathrm{d}t' C_{j'k'}(t_0)\langle\{n_{\kappa}\}|V_{j'k',jk(t')}|\{n_{\kappa}\}\rangle\\ &= C_{j'k'}(t_0)\Sigma_{\kappa}\mathrm{A}_{\kappa}\,\varepsilon_{\kappa}\cdot\langle i|p|i'\rangle S_{ij,i'j'}\int_{t_0}^{t}\mathrm{d}t'\{\sqrt{n}_{\kappa}\exp i(E_{i'k'}-E_{ik}-\omega_{\kappa})(t'-t_0)\\ &\quad +\sqrt{(}n_{\kappa}+1)\exp +i(E_{i'k'}-E_{ik}+\omega_{\kappa})(t'-t_0))\}. \qquad (21)\end{aligned}$$

Equation (20) use the relations: $a_{\boldsymbol{\kappa}}|\mathrm{n}_{\boldsymbol{\kappa}}\rangle = \sqrt{n}_{\boldsymbol{\kappa}}|n_{\boldsymbol{\kappa}} - 1\rangle$ and $a_{\boldsymbol{\kappa}}^{\dagger}|\{\mathrm{n}_{\boldsymbol{\kappa}}\}\rangle = \sqrt{(}\mathrm{n}_{\boldsymbol{\kappa}} + 1)|\mathrm{n}_{\boldsymbol{\kappa}} + 1\rangle$; $\mathrm{n}_{\boldsymbol{\kappa}}$ is the photon number in the κ-mode. The first term in the curly bracket corresponds to the absorption of a photon with exponent $E_{i'k'} - E_{ik} - \omega\kappa = 0$; the second is the emission with the condition $E_{i'k'} - E_{ik} - \omega\kappa = 0$; we assume $E_{i'k'} > E_{ik}$. These conditions cannot simultaneously be fulfilled for a given pair of molecular levels. For the time being, off resonance effects are not considered. Energy exchange between the molecular system and the field fulfils the principle of energy conservation.

Except for the amplitude $C_{j'k'}(t_0)$ and the occupation numbers, the integral is standard in time-dependent perturbation approach [7]. This amplitude makes the difference. For, if the initial base state has zero amplitude, even if the matrix elements of the evolution operator are different from zero, no intensity associated to the transition $ik \rightarrow i'k'$ will be measured.

The terms appearing in equation (9) and made explicit in equation (21) can be related to a number of processes elicited with lasers and masers: two-photons processes connect to the second order term [54–57]; three-photon processes would appear in third order of V. In figure 1 Feynman-like graphs are depicted to help visualize the intermediate steps.

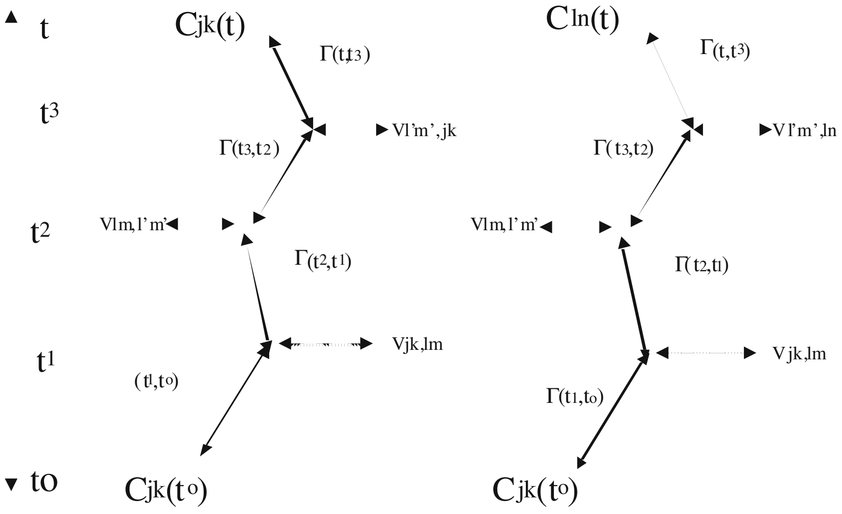

Figure 1. A modified 3rd order term in equation (9) is graphically depicted for the special case where only one base state amplitude is different from zero at time t_o. Implicit is the use of a time-ordering operator that by ordering the intermediate times allows for a series expansion of the exponential form given to $U(t, t_0)$. The case where one follows time evolution of $C_{jk}(t_0)$ is depicted to the left; at the right, a system having $C_{\mathrm{ln}}(t_0) = 0$ is followed from the initial state $C_{jk}(t_0)$. Read from top-to-bottom: $\Gamma(t_1, t_0)V_{jk,lm}\Gamma(t_2, t_1)V_{lm,l'm'}\Gamma(t_3, t_2)V_{l'm',jk}\Gamma(t, t_3)$; this term goes into: $\exp\{-i(t_{ojk} - t_1)E_{jk}\}V_{jk,lm}\exp\{-i(t_1 - t_2)E_{lm}\}V_{lm}\exp\{-i(t_1 - t_2)\mathrm{E}_{l'm}\}V_{l'm',jk}\exp\{-i(t_3 - t)E_{jk}\}$. Now, because sums are to be taken at intermediate points, it is the complete spectra of the system, which determines the emergence of non-zero amplitudes at specific base sets positions. Integration over time makes appear the energy differences in the denominators. In general, resonance conditions favor emergence of non-zero amplitudes. The field giving or taking energy at a given frequency appears in the time dependent terms. The graph on the right can be used to describe a two-photon process.

A pump–probe experiment would function as follows. For an external pulse lasting sufficiently long, time-evolution would produce non-zero coefficients at base states different from the initial one. The necessary condition is the existence of chains of transition moments different from zero relating the initial state to the one of interest, e.g. $V_{j'k',j''k''}(t')V_{j''k'',j'''k'''}(t'')V_{j'''k''',jk}(t''')$. The probe laser would then have now as initial state the set of amplitudes $\{C_m(\Omega, t = t_0 + \Delta)\}$ where Δ is the time-delay between pump and probe pulses. Solving an equation similar to equation (9) where $t_0 + \Delta$ replaces t_0, one would expect that many of the amplitudes that were zero at the beginning (t_0) are changed into non-zero ones. Time-resolved probing put in evidence the spectra of selected components. The intensity of the corresponding spectra will be dependent upon products of amplitudes as well as transition moment integrals. A common shape starts from zero, raises with typical slope and attains a plateau [58]; the shape would look like a titration profile.

The electronuclear system provides the ground for the mechanism to act; the non-zero amplitudes reflect what can be prepared and/or measured in the laboratory.

The diabatic electronic base states cannot be changed as if they were a property of a "molecule". This is a key factor. The linear superpositions will show up the effects because the base set is complete. Whatever the laser intensity might be, the time evolution will produce wave packets with amplitudes at the totally (or partially) ionized base states.

So far, Chemistry seen as physical processes in a quantum mechanical setting is fairly well documented. The point now is to get more of the structural and "objectual" (analytes) aspects.

3. Toward chemistry

The QM scheme developed so far is taken now, with the help of special algorithms, into a form where real space features are explicit. Two aspects are important to bear in mind: (1) chemistry is carried out in real space; (2) structure and shape are important ingredients of the chemical theory. We relate them to QM via appropriate algorithms because Hilbert and Real spaces are incommensurable. Adiabatic Born–Oppenheimer (BO) [35] and generalized electronic diabatic (GED) [39, 40] algorithms are two examples.

3.1. Confining and asymptotic GED states. A hint at molecular structure

The construction of a picture leading to structural appearance requires the introduction of a mapping assigning some physical meaning to the nuclear configuration space. Up till now, this space is the support for the nuclear electronic wave function only. This point must be stressed. Most of the models used to calculate wave functions do not realize the difference between the support of a nuclear wave function and the space indicating the locations of positive charges.

The nuclear configuration space has been exclusively used to stand for the domain of the nuclear wave function. The nature of the Coulomb hamiltonian suggests the introduction of the isometric mapping that changes the meaning of $\mathbf{Q}$ without changing its metric so that distances remain unchanged [59]. Thus, the common view where the coordinates $\mathbf{Q}_1, \mathbf{Q}_2, \ldots, \mathbf{Q}_m$ stand for the position of nuclear charge and mass can be taken into the present approach as no deep mathematical change is introduced with. The inertial frame remains invariant. In this case, the ordering of the energy eigen values depends upon the particular value of the nuclear configuration space chosen: $E_{j(\mathbf{Q})} \equiv E_{j(\mathbf{Q})}$. The "quantum number" $j(\mathbf{Q})$ only indicates the base state energies order depend upon the point selected to calculate the functional $E_{j(Q)}$; the electronic base functions are defined already and should not change. The functional $E_{j(Q)}$ corresponds to a diabatic potential energy because the index j is independent from $\mathbf{Q}$ (see [32, 39, 40]).

The picture following the isometry-mapping may help now describing the classes of diabatic base functions with the help of the diabatic potential energy hypersurface $E(\mathbf{Q}; [\phi_j])$. The GED functions have either confinement or asymptotic properties. Such representation can be introduced because one induces a picture of nuclear charges as if they could be seen in real 3-D space. A confining diabatic electronic state can be seen as inducing an attractor towards the positive charge background. This attractor in real space permits defining one fixed point at which the gradient of $E(\mathbf{Q}; [\phi_j])$ is zero. This is the nearest one can get to the structure concept on rigorous QM basis.

To avoid misunderstandings, because we are using the vector **Q** as if it were the position vector of the positive charge background (PCB), it is convenient to introduce the symbol $\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots, \xi_m)$ instead; this Greek symbol represents a set of positive charges in real space. The model corresponds to a quantum electronic system interacting with a PCB. This is an algorithm now as much as BO is. The gradient can hence be calculated: $\partial \mathrm{E}(\boldsymbol{\xi}; [\phi_j])/\partial\boldsymbol{\xi}$.

For a given electronic state showing a confining property, there is a PCB for which the gradient is zero; this point is identified as $\boldsymbol{\xi}^j$. The second order tensor, $G_{kk'} = \partial^2 \mathrm{E}(\boldsymbol{\xi}; [\phi_j])/\partial\boldsymbol{\xi}_k\partial\boldsymbol{\xi}_k$ at $\boldsymbol{\xi}^j$ (the Hessian) has all the eigenvalues positive.

3.2. Chemical species and graphs

We showed how to describe chemical reactions with the help of $\mathcal{H}(\mathbf{q},\mathbf{Q})$. Now, we apply the isometry and write $\mathcal{H}(\mathbf{q},\mathbf{Q}) \longrightarrow \mathcal{H}(\mathbf{q},\boldsymbol{\xi})$. For systems where no particular change of spin-state is sensed, the universal kinematic electron–phonon coupling will control the chemical evolution. For reactions where different electronic states have different spin, the spin–orbit term will open the channels accessible to the system. In some cases both operators may be active [52]. The thing is to watch (experimentally) amplitudes different from zero at those base functions describing different molecular states in the linear superposition.

A chemical species is hence defined by the electronic quantum number for a confining diabatic state. The total angular momentum J, spin S and orbital L with projections along the 3-axis are used to identify the quantum base state; in spectroscopy, spin multiplicity and total angular momentum are indicated. Molecular graphs, as defined in [39], are useful to discuss issues of chemical reactivity.

In the motionless I-frame the number of nodal planes, surfaces and hypersurfaces, the parity, local symmetries, permutation symmetries, etc. characterize the diabatic electronic base functions once completed with the spin component (see below). The ground electronic state has no nodal planes, as usual, it is assumed to be the state of lowest energy. The Coulomb hamiltonian is bounded below [60].

In between plasma states and super-molecules, there are all types of partitioning determined by base functions related to local confinement. The number of electrons can be decomposed into sums of subsystem such that $n = \Sigma_i n_i$. To each n_i a partitioning of the positive background is possible, $\Sigma_k Z_k(n_i)$; the sum must be equal to the total charge of the PCB. Positive ions correspond to $\Sigma_k Z_k(n_i) > n_i$. Negative ions have $\Sigma_k Z_k(n_i) < n_i$. Neutral fragments have $\Sigma_k Z_k(n_i) = n_i$.

An important point: a free-electron state is always correlated to the continuum of a specific system. We assume that the global system is electrically neutral. The total mass and charge is conserved for all possible partitioning of the arguments of the electronic and nuclear space coordinates. These represent all possible products for all possible dissociation and ionization reactions involving the ground and excited states. From this point of view, the base functions (BS) represent all possible chemical products. The fragments $\{\Sigma_k Z_k(n_i); i = 1, n\}$ can be seen as molecular species at infinite distance. Each one of them ought to have an infinite set of electronic diabatic states. Reactive scattering can hence be represented [40, 61] with no difficulty.

The Coulomb hamiltonian being diagonal in the electronuclear basis, each electronic quantum number assign a chemical species in a unique way. Observe that we can now speak of molecules in the chemical structural sense.

Using the isometry based on point nuclear charges discussed above, a particular diabatic base function can be characterized by an invariant graph [39]. A nodal plane (local) appears as an absence of link between the points standing for the nuclei. It is at this level that qualitative ideas about chemical bond become quantitative. In figure 2 we display the graphs of a simple subset for base functions in reactions involving formaldehyde chemistry [24]. The nodal plane corresponds to an anti-bonding situation. The nature of the connectivity in the graphs of figure 2 is a fundamental invariant. The use of valence bond graphs in the diabatic sense is appropriate.

The quantum state $(0100\cdots)$ corresponds to the collision between a hydrogen molecule (H_2) and carbon monoxide (CO); the specific electronic states for the fragments are not given just for the sake of simplicity; this is a representation in Hilbert space. Another example is given by the quantum state $(0010\cdots)$ in the base set $[\Phi_1\Phi_2\Phi_3\Phi_4\cdots]$ that corresponds to a water molecule interacting with a carbon atom. It is easy to see that the graph H–C–O–H would correspond to another base function, say, Φ_5 (not indicated in figure 2). Free atoms correspond to another class of graphs. In plain words, all possible chemical species for a set of n-electrons (in this case 16) and m-nuclei (four in this case with total charge 16) form an infinitely denumerable set of base functions.

Hilbert space stands for all physical states a system may have. Chemistry is a subset of such states that can be made visible if one distill the information with adequate algorithms.

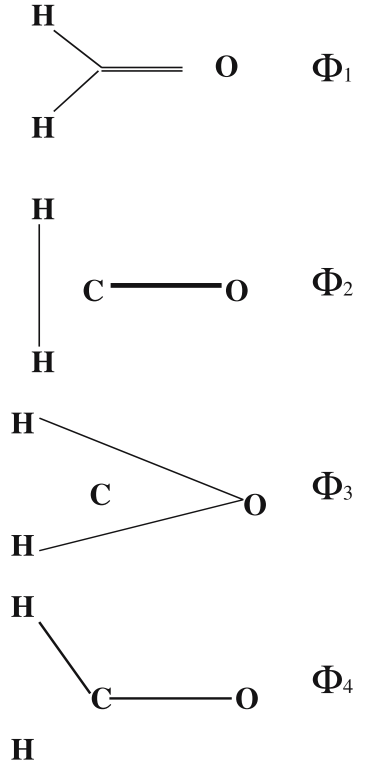

Figure 2. Topologic graphs signaling different diabatic chemical species discussed in the text. Take the geometry of the PCB to be the same for all diabatic electronic states, ξ^1.$E(\xi^1; [\Phi_1]) \ll E(\xi^1; [\Phi_2]) \ll E(\xi^1; [\Phi_4]) \ll E(\xi^1; [\Phi_3])$. Local frames can be defined for the connected graphs species by using a corresponding electronic attractor geometry. Di-hydrogen and carbon monoxide molecules are asymptotic elements compared to formic aldehyde (supermolecule); water and carbon atoms form another pair of asymptotic states. Intermolecular distance and orientation can be defined with the help of the local inertial frames.

3.3. Chemical species and change

The structural property of molecular systems is hidden in the electronic wave function. There is no need to go all the way down to mechanical representations of molecular structure to get the picture of robust stable electronuclear species. The questions, where are the "nuclei" and what are their classical mechanical motions? are wrongly posit in a QM setting. The important thing is to know those electronuclear quantum states most involved in the time evolution process and therefrom construct semi classical models.

Whatever the "positions" of the nuclei might be if they are trapped by an electronic state the system would be found in a high energy region of the diabatic potential energy derived from the electronic wave function. Such regions become accessible via vibration–rotation excitations. Most of them appear as conic intersections.

Consider the states jk and $j'k'$. The diabatic potential energy functions cross in a neighborhood $\boldsymbol{\xi}\sharp$, i.e. $E(\boldsymbol{\xi}\sharp; [\Phi_{\mathrm{j}}])$ and $E(\boldsymbol{\xi}\sharp; [\Phi_{\mathrm{j}'}])$ are equal. The quantum state has $C_{jk} \neq 0$ and $C_{j'k'} = 0$ as initial state; if the available energy E is smaller than the electronic energy at the conic intersection, the amplitudes will not change and the chemical change is frozen.

A conical intersection only signals a domain around it (a neighborhood) wherein the linear superposition may change. And this can be done assisted by either electron–phonon coupling or by spin–orbit coupling. What is meaningful is that there is a change of amplitudes characterizing the evolution of the quantum state. There is no climbing on the hypersurfaces; these latter are helpful algorithms not physical objects.

The introduction of the electronic spin is essential to construct correct symmetry adapted base states. In what follows, the base functions include the spin part for electrons and nuclei, $\sigma_{jk}(\mathrm{spin}) = \Xi_j(1, \ldots, n)\Xi_{jk}(1, \ldots, m)$ [17].

For the set of product functions $\phi_j(\mathbf{q})\zeta_{jk}(\Xi)\sigma_{jk}(\mathrm{spin})$, there are molecular states that correspond to confining electronic base states. A spin singlet-state is anti-symmetric, the space function is symmetric, to odd permutations. These spin states involve only two 2-spinor functions. For higher spin multiplicity the analysis is made with the tools from angular momentum theory [17].

To keep inertial frames fixed helps constructing base states for molecular systems that are wholly confined (a super-molecule) or correlated to asymptotic fragments. The latter are the reactants in common chemical terms.

3.4. Laboratory chemistry

Chemists, control pressure, prepare adiabatic walls enclosure, or control the temperature or use containers. Processes are thus controlled via adequate manipulation of these variables. Two mathematical elements are necessary to define adequate base sets for the global system that, so far, it is referred to an I-frame. This is the rest mass frame for all quantum states defined so far. In an inertial system, there is no experiment defined within the frame states that can show evidence for global dynamics (motion). As in Newton's approach, the state of motion is to be changed by external agents to the system.

3.4.1. Take the system in an enclosure: rectangular (cubic) box

The description in an appropriate (rigged) Hilbert space requires the construction of complete base function sets first. Thereafter, quantum states are represented by linear superpositions and changes thereon appear as variations in the amplitudes of the linear superposition.

The simplest model for a container is a rectangular box of volume $\mathcal{V} = \mathcal{L}_1\mathcal{L}_2\mathcal{L}_3$; $\mathcal{L}_i$ being the ith side length; a similar model was implicit in the construction of a complete base set for the nuclear wave functions above. We have to handle a transformation from an inertial frame used to determine the electro-nuclear quantum states to a laboratory fixed frame. Consider the quantum state $\Psi(\mathbf{q}, \boldsymbol{\xi})$ for a system in an inertial frame that is in uniform motion with velocity $\mathbf{v}$ with respect to a fixed in the box (laboratory frame). The origin change results in a phase factor added to the wave function already calculated; the phase includes the total classical kinetic energy $((1/2)\mathbf{M}\mathbf{v}^2)$ and momentum $(\mathbf{M}\mathbf{v})$; $\mathbf{M}$ being the total mass of the system embodied in the initial I-frame. These quantities gauge the momentum and energy scales in the laboratory frame. At this point one can either use the semi-classical picture assigning a global velocity to the frame and a particular rotational angular momentum or move on to a quantum mechanical description. In all circumstances, the inertial frames are classical devices related to the real world.

Let $\mathbf{R} = (R_1, R_2, R_3)$ be the coordinate of the inertial frame origin measured from the laboratory fixed frame. Because an inertial frame belongs to the "classical" world, a first model may be a particle of mass M in a cubic box. Even at this semi-classical level, $\boldsymbol{\lambda}_{\mathrm{deBroglie}} = (2M|\mathbf{v}|/h)$ is related to the a wave function of the frame, namely, the phase factors, $\exp(-iM\mathbf{v}\cdot\mathbf{R})$ and $\exp(-iM\mathbf{v}^2t/2)$ in units of $h/2\pi = \hbar$. These phase factors affect all internal states in the same manner. Now, the introduction of base states for the "particle in a box" supersedes the semi-classical model. The hamiltonian is given in the laboratory frame by

$$\mathcal{H}(\mathbf{K}) = -(h/2\pi)^2/(2M)\mathbf{K}^2 = (-(h/2\pi)^2/2M)\nabla^2_{\mathbf{R}}. \tag{22}$$

The energy levels depend upon the box length and consequently, by changing the external pressure a change in length can be made if the material device is so constructed. The reciprocal vector $\mathbf{K}$ is (K_1, K_2, K_3). The base functions are given by $\Psi_{K_1K_2K_3}(\mathbf{R}) = (1/\mathcal{L}_1\mathcal{L}_2\mathcal{L}_3)^{1/2}\exp(\mathrm{i}\cdot\mathbf{K}\cdot\mathbf{R}) = \Psi_{\mathbf{K}}(\mathbf{R}) = (1/\mathcal{V})^{1/2}\exp(\mathrm{i}\mathbf{K}\cdot\mathbf{R})$. Boundary conditions yield as usual $K_1\mathcal{L}_1 = 2\pi n_1$; $K_2\mathcal{L}_2 = 2\pi n_2$; $K_3\mathcal{L}_3 = 2\pi n_3$. The energy eigenvalue $\mathrm{E}_{n_1n_2n_3}$ for this specific case are known to be $(\hbar^2/(2M))(n_1^2/\mathcal{L}_1^2 + \mathrm{n}_2^2/\mathcal{L}_2^2 + \mathrm{n}_3^2/\mathcal{L}_3^2)$. The quantum numbers can be collected in one vector symbol in 3D: $\mathbf{n} = (n_1, n_2, n_3)$; $\mathbf{K}_{\mathbf{n}}/2 = (\mathrm{n}_1/\mathcal{L}_1, \mathrm{n}_2/\mathcal{L}_2, \mathrm{n}_3/\mathcal{L}_3)$. The energy is then also given by: $\mathrm{E}_{n_1n_2n_3} = \mathrm{E}_{\mathbf{K}} = (4)^2(h/2\pi)^2/(2\mathrm{M})\mathbf{K}_{\mathbf{n}} \cdot \mathbf{K}_{\mathbf{n}}$.

$\mathbf{K}$ acts as a 3-D discrete label. The energy eigenvalues can be changed after a variation in box-length (e.g. pressure effects). The eigenfunctions satisfy new boundary conditions. The number of nodal planes is invariant. In the limit $\mathcal{V}_i \to \infty$ for $i = 1, 2$ and 3, the system becomes invariant to rotations and origin translations. The trick was to impose periodic boundary conditions.

Invariance to rotations of the laboratory frame imposes global angular momentum conservation, $\mathbf{D} = (D_1, D_2, D_3)$ is a vector operator; as usual, the base function fulfilling $\mathbf{D}^2|D, M_{\mathrm{D}}\rangle = D(D+1)|D, M_{\mathrm{D}}\rangle$and$D_3|D, M_{\mathrm{D}}\rangle = M_{\mathrm{D}}|D, M_{\mathrm{D}}\rangle$; $-D \leqslant M_{\mathrm{D}} \leqslant +D$ and $D = 0, 1, 2, \ldots$ Taking now as E the energy eigenvalue of $\mathcal{H}(\mathbf{K})$ and noting that $\mathcal{H}(\mathbf{K}), \mathrm{D}^2$ and D_3 commute, $\{|E, D, M_{\mathrm{D}}\rangle\}$ is a complete base set. The connection with the $|\mathbf{K}\rangle$-base is given by the amplitudes $\langle E, D, M_{\mathrm{D}}|\mathbf{K}\rangle = \langle E = (h/2\pi)^2/(2M)K^2, D, M_{\mathrm{D}}|K\rangle(h/2\sqrt{MK})Y_{\mathrm{D}}^{M_{\mathrm{D}}}(\mathbf{k})$ in terms of spherical harmonic functions with $\mathbf{k} = \mathbf{K}/|\mathbf{K}|$ a unit vector in the direction of the wave vector $\mathbf{K}$, and $K = |\mathbf{K}|$. The normalization is characteristic of continuum states: $\langle E', D', M'_{\mathrm{D}}|E, D, M_{\mathrm{D}}\rangle = \delta(\mathrm{E}\text{-}\mathrm{E}')\delta_{\mathrm{DD'}}\delta_{\mathrm{MDMD'}}$. The angular momentum base set is useful to describe stationary situations. The amplitude $\langle \mathbf{R}|\mathbf{K}\rangle = \Psi_{\mathrm{K}}(\mathbf{R})$. In the energy base one gets $\langle \boldsymbol{R}|\boldsymbol{K}\rangle = \Sigma_{\mathrm{D}=0,\infty}\Sigma_{\mathrm{D\cdot MD\cdot +D}} <\mathbf{R}|\boldsymbol{E}, \boldsymbol{D}, \boldsymbol{M}_{\mathrm{D}}><\boldsymbol{E}, \boldsymbol{D}, \boldsymbol{M}_{\mathrm{D}}|\mathbf{K}\rangle$ and the energy constraint $E = (h/2\pi)^2/(2M)\mathbf{K}^2$. The change of basis, if necessary, is then simple.

In the **K**-representation, the set $\{\Lambda_{\mathbf{K}jk}(\mathbf{R}, \mathbf{q}, \boldsymbol{\xi}, \sigma) = \Psi_{\mathbf{K}}(\mathbf{R})\phi_j(\mathbf{q})\boldsymbol{\zeta}_{jk}(\boldsymbol{\xi})\sigma_{jk}$ (spin) provides a base to represent quantum states internal to the I-frame in uniform motion as it were. Note that the real variable **R** stands for the origin of the I-frame. An arbitrary quantum state of the system is a linear superposition

$$\Theta(\mathbf{R}, \mathbf{q}, \boldsymbol{\xi}, \sigma) = \Sigma_{\mathbf{K}jk}\mathrm{S}_{\mathbf{K}jk}[\Theta]\Psi_{\mathbf{K}}(\mathbf{R})\phi_j(\mathbf{q})\boldsymbol{\zeta}_{jk}(\boldsymbol{\xi})\sigma_{jk}(\mathrm{spin}) = \Sigma_{\mathbf{K}jk}\mathrm{S}_{\mathbf{K}jk}\Lambda_{\mathbf{K}jk}(\mathbf{R}, \mathbf{q}, \boldsymbol{\xi}, \sigma). \tag{23}$$

In general, this is an internal–external entangled system. For a non -entangled state the set of amplitudes can be factored, i.e. $\{\mathrm{S}_{\mathbf{K}jk}[\Theta] = \mathrm{B}_{\mathbf{K}}\mathrm{C}_{jk}\}$. Spin amplitudes are implicit in order to simplify notations. Quantum states for complete entanglement of the box and I-frame system cannot be separated as simple products of internal and frame components.

In equation (23), amplitude different from zero opens the possibility to experimentally probe the transitions rooted in the specific base state. Either emission or absorption or inelastic scattering spectra can be used to detect amplitudes different from zero. If a quantum base state has zero amplitude always, no experimental probe would sense its spectra. In a pump probe experiment, at initial time the state to be probed has zero amplitude (see section 2.3).

The mapping $\mathrm{S}_{\mathbf{K}'jk}(t) \to |\mathrm{S}_{\mathbf{K}'jk}(t)|^2$ corresponds to measure in intensity signals rooted in the base state $|\mathbf{K}'_{jk}\rangle$; see section 1.2 for correlation functions. The question is now to get an algorithm that allows us to put internal states in a way adapted to speak on analytically pure chemical substances, e.g. analytes. Chemistry and chemical kinetics are normally described as changes of concentration: reactants, products and intermediates analyte mixtures. The problem is to introduce descriptions based on this concept of “concentration”, e.g. number of elements per unit volume. A reagent put in a bottle must find out a representation in the present approach.

3.5. From molecular states to chemical compounds

The ansatz $\mathcal{H}(\mathbf{q},\mathbf{Q}) \rightarrow \mathcal{H}(\mathbf{q},\boldsymbol{\xi})$ is the key to get a concept for reagents (analytes). The PCB exists in real space; if only a different interpretation is retained (isometry) then the ansatz can be reverted. Otherwise, as seen now, for any local transformation related to particular electronic states, the results can be useful but no claim as to their quantum mechanical soundness can be made.

Let us consider a confining electronic state $\phi_k(q)$; this defines a molecular species. If instead of equation (14) we take Schrödinger equation (13), the diabatic potential energy hypersurface $E(\boldsymbol{\xi};[\phi_k])$ shows the attractor geometry $\xi^k = (\xi_1^k, \dots, \xi_m^k)$. At this point in real space, the gradient is zero. The relative coordinates $\delta\boldsymbol{\xi}^k = (\boldsymbol{\xi} - \boldsymbol{\xi}^k)$ can easily be used to get a model to equation (13) because the Hessian can be calculated at any convenient attractor.

$$\{K_{\mathrm{N}}(\delta\boldsymbol{\xi}) + E(\delta\boldsymbol{\xi};[\boldsymbol{\xi}^k])\}\boldsymbol{\zeta}^0_{km}(\boldsymbol{\xi}) = E^0_{km}\zeta^0_{km}(\boldsymbol{\xi}) = 0, \tag{24}$$

$\delta\boldsymbol{\xi} = (\delta\boldsymbol{\xi}^1, \dots, \delta\boldsymbol{\xi}^m)$. The harmonic oscillator model obtains in a rather direct manner; for the kth normal mode with frequency ω^k: for a simple case we get, $E^0_{km} = (n + 1/2)\omega^k$ and $n = 0, 1, 2 \dots$

The rigid model to molecular rotation becomes electronic base state dependent. In the laboratory fixed frame the system can be identified by the attractor geometry. Inertia tensors and principal axis frames are properties, as it were, of the diabatic electronic base function. The general case corresponds to the asymmetrical top model. Of interest to us is the construction of the base set. This is done with the help of the base functions for the symmetrical top. This latter is exactly solved so that the complete set of eigen functions provides the base set. See [63] for further details. Observe that there will be a frame rotation in passing from our I-frame to the principal moment of inertia frame. An incompatibility arises at this point because the semi classical approach treat a tumbling "molecule", that is to say, an accelerated frame that requires of a third quantum number. Here, we quote the energy eigen values of the angular momentum that are related to a fixed frame (albeit with origin shifted to the center of mass). The base functions are those related to the symmetric top.

Thus, for the kth attractor the inertia tensor C^k can now be calculated and diagonalized. The set of energy levels for this model is well known; for the simplest case for a rotation angular momentum $\mathbf{D}$: Each D-level is $2D + 1$ degenerate, i.e.$-D \leqslant K \leqslant +D$, and the quantum number K is the component of angular momentum along the symmetry axis of the top. When we refer to the I-frame 3-axis (z-axis) one has m_{D} to be the projection. This procedure can be applied to all relevant attractors. The energy terms (wave number divided by hc) are then

$$F(D, K) = D(D + 1)B^k + (A^k - B^k)K^2, \tag{25}$$

$B^k = (h/c8)/\mathcal{C}_{\perp}^{k}$; $A^k = (h/c8)/\mathcal{C}_{\parallel}^{k}$. The energy levels are then $E_{\mathrm{DK}} = hcF(D, K)$. A selection rule applies for the unsymmetrical top: $D = M_{\mathrm{D}}$ in this model (see ref. [63]).

The equations (24) and (25) shift the grounds we have been using. The electronic state and its vibration and rotation spectra are seen as representing a molecular object tumbling and fluctuating around the nuclear equilibrium configuration; a situation similar to that found in physical chemistry textbooks.

Transforming the molecular state into a "thing", objectification that does not belong to Hilbert space, permits describing the state as a molecule occupying particular vibration–rotation states. This would be fine if we do not realize that following upward on the energy ladder sooner or later situations of almost resonance with the energies characteristic of electronic conic intersection obtain. The chemist knows how to operate to avoid the decomposition. For a chemical change to go, E must be about and above $E(\boldsymbol{\xi}\sharp; [\phi_j]) = E(\boldsymbol{\xi}\sharp; [\phi_{j'}])$, that is, an energy barrier opposes the change (kinetics). The transition state approach also emerges from the diabatic description although modified by quantum features.

Transition amplitudes are integrals over the whole configuration space. Thus, selectivity can be seen to reflect the space properties of the wave functions. The GED-nuclear algorithm opens a practical way to analyze reaction paths and, at the end of the calculation, return to a rigorous quantum mechanical framework. As a matter of fact, it helps introducing real space restraints that are translated in Hilbert space via domain restrictions in **Q**-space. The obvious example is separating two analytes in different bottles.

A chemist that sets an experiment cannot expect results to depend upon the way the laboratory axes are signed. A parity operation must leave the quantum state invariant; this imposes constraints on the base functions that must remain invariant to parity operation when the global system is considered.

To analyze this property it is convenient to work in the angular momentum base for the I-frame. Mathematically, parity is given by $(-1)^{D+L+S+I}$. If we take $L = 0$ and $S = 0$, for $I =$ even then D must be even too; for $I =$ odd then D must be odd so that the exponent sum is even and parity invariance holds. This is a general selection rule that, for the case examined here, applies to ortho-para hydrogen system.

The total angular momentum **G** labels the base functions. A linear superposition includes base functions that have different angular momentum signatures. From the example of figure 2, many of the base states are products of spin doublets and formaldehyde has base states that are either spin singlet or triplet. The GED algorithm helps seeing that superpositions will be in effect at the relevant conical intersections; the kinematic operators mediating the mixing of base states and changing the amplitudes.

3.6. Chemical mechanisms

Chemistry without reaction mechanism would not be chemistry. There are two complementary ways to find out mechanistic aspects in this context: (1) Analyses of equation (9) and/or (21); (2) Diabatic potential energy hyper-surfaces.

Inter system-crossing reaction (simplest case) concerns two base states having different values of S, say, a singlet and a triplet spin state. The base states are coupled by spin–orbit effects; replace electron–phonon by spin–orbit interaction operator in the matrix elements of equation (10). The energy gap between the diabatic potential energy hypersurfaces is zero at the crossing between these hypersurfaces. A domain in $\boldsymbol{\xi}$-space around the conical intersection will contribute to the mixing, e.g. for a system prepared with zero amplitude at the triplet if the system is allowed to reach the bottleneck then non-zero amplitudes at the triplet are expected. For a chemical system, there is a possibility to control the mixing [32, 33, 61].

A second, important example relates to a bond breaking (singlet state) and the probing of two free radicals ($S = 1/2$, each). The electronic state of the asymptotic radical species corresponds to a nodal plane between the centers that were involved in the covalent bond. This state is anti-bonding in the familiar language of molecular orbitals; in other words it correlates to two fragments at infinite distance. The diabatic potential energy hypersurface, shown schematically in figure 3 is repulsive for any finite distance between the fragments. The bonding state corresponds to a confined state. Therefore, above the dissociation limit, the free radical potential curve intersects the confined state associated to the bonding state. We see that any bond making between non-bonded radical fragments must have a positive energy barrier measured from the energy of dissociated partners. The opposite process, dissociation, obviously has activation energy. This result is independent of particular computing schemes provided all relevant base states are taken into account.

What is the role played by nodes? Basically, any space displacement leading to shortening in the distance between the asymptotic centers implies an increase of repulsive forces. These forces are responsible for the molecular shape. The role of antibonding orbitals is enhanced. We knew already on LUMOS $(0, +1, +2, \dots)$ in chemical reactivity. Now they will help understanding structural features [64].

The effects, measured by a change of quantum amplitudes, will be more sensible at the crossing regions (conic intersections, seams) between the relevant diabatic potential energy functions $\mathrm{E}(\boldsymbol{\xi}; [\phi_j])$. This part corresponds to a mechanistic descriptions; the matrix elements in equation (10) are obtained by integration over the full electronuclear space and the mechanistic aspects fade away without their help.

Ionization has to be handled within Hilbert space; for further analyses see ref. [40, 61].

Catalysts enter via new base states that can be treated with direct product techniques. We can even consider the electromagnetic field (quantized) as a catalyst. The reason is simple. At the conic intersection domain, rotation-vibration energy levels with small energy gaps, e.g. microwave domain, will increase the number of coupled states in the reactant channels fulfilling energy conservation (cf. equation (21)); the electron–phonon operator linearly depends upon the electron momentum in a tensor product with the nuclear one.

The mathematics of these models has been examined in our group (see e.g. [24, 25, 32, 33]).

Summarizing. Full chemical processes are presented at the 1-system QM level; conservation of material elements (electrons and nuclei) making part of the 1-system is required, i.e. a non-relativistic approach suffices. A measurement in intensity regime on such system will translate on nearly vanishing signals. In chemistry, a sample of N non-interacting copies of the 1-system would do to give decodable signals. This intensity amplification aspect will be treated elsewhere.

Discussion

Following an old suggestion by Dirac, we have used contemporary quantum mechanics to construct conceptual bases to chemistry in its dynamical and structural aspects. The principle of linear superposition played a central role and a new concept to interpret the amplitudes has been introduced. A clear-cut distinction is made between a base set and the general quantum state characterizing the system. Any physical state is a set of complex numbers; these amplitudes

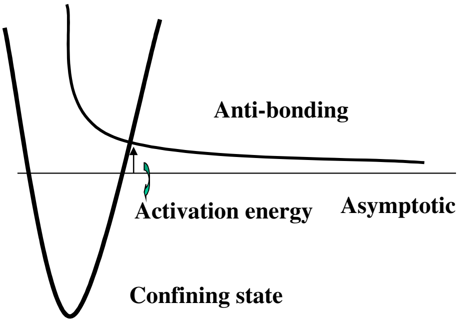

Figure 3. Schematic diabatic potential energy surfaces. The anti-bonding state is usually associated to nodal planes (cf. figure 2)The asymptotic states are not directly related to supermolecule states in the standard approach. Here, the anti-bonding state in a given supermolecule is identified first and henceforward related to the asymptotic state using the diabatic potential energy hypersurface. As a rule of thumb, for a simple covalent bond, the double excitation in the anti-bonding orbital would suffice to get a model q.

are the mathematical objects that would sustain the changes a given system may undergo. A quantum state is experimentally measurable.

A clear conclusion is that the chemical reactions elicit Hilbert space processes. Note that this result may have been obvious to Dirac, but it has never been shown before. We have now the essentials of chemistry and chemical processes in Hilbert space. A connection with real space was established with the help of a generalized electro-nuclear separability theorem. At this point, a reader may measure the differences the present approach has with respect to the extraordinary work by Primas [8]. For the time being, we leave this issue here, we recommend a thorough study of the mathematics given in [8].

The standard Coulomb hamiltonian can be diagonalized in the generalized electronic diabatic scheme; nuclear quantum states can also be found on general planar wave bases. The problem of multiple nuclear Schrödinger equations was overcome. The direct products of such functions diagonalize the total molecular hamiltonian but not $\mathcal{H}$. Time evolution is hence driven by kinematic coupling operators, e.g. spin–orbit and/or electron–phonon coupling operators. Control with external electromagnetic fields can be achieved.

On the technical side, diabatic schemes have been extensively used in the literature (see our own work and references therein [24, 41, 65–67]; for a recent overview on non-adiabatic effects in chemical dynamics refer to the proceedings [45]). From the analysis presented around equations (13) and (22), the BO scheme by diagonalizing infinite electronic hamiltonians (**Q** as a parameter) produces for most **Q** a complete set; state crossings spoil the generality of the method. The different **Q**-sets can only be defined in a "frozen nuclei" algorithm i.e. they are in place of our $\boldsymbol{\xi}$-space. Under these circumstances, there is no mathematical way to go back to the configurational space **Q** where the exact nuclear wave function must be defined. We have therefore an algorithm. And, from an algorithm one cannot prove theorems [68, 69] showing that the exact electronic diabatic separability does not exist.

The nature of the electronic wave function for radical reactions is an important issue. The antibonding situation, e.g. state Φ_4 in figure 2, can be constructed by using a base function where two-electron occupies the CH antibonding orbital. The energy as a function of the distance between the C- and the H-centers is therefore repulsive as illustrated in figure 3. Standard calculations using the LCAO model usually, if not always, miss this point. A molecular calculation must include a "double excited" configuration with the LUMO involved in the bond breaking. Besides, the LCAO bonding orbital behaves badly with the interatomic distance. As in figure 3, a bonding base state does not dissociate. The criticism by Langhoff of the BO scheme is pertinent [70]. Therefore, if a QM study of the kind described here is sought, one must be extremely careful with the use of current computing packages.

Moreover, it was shown that the harmonic oscillator and rigid rotor are useful models that handle molecules as "things" (see a discussion [21, chapter

4]). They are not approximations to the nuclear Schrödinger equation. A similar status has the BO-scheme. In fact, both the BO and the GED are algorithms designed to obtain model base functions. The difference between them is that the GED algorithm is related to a hierarchy of approximations that connects to the exact problem while BO-scheme does not. At the algorithm level, one may take full advantage of contemporary computing methods with modifications easy to implement. The interpretation ought to be made in the diabatic frame.

How does bonds get broken or formed? In the present context, this is the wrong question. Bonds are not objects that form or break. Although a persistent idea has it that some nuclear motion corresponds to chemical process, from the present paper one can see a mixing of the vibration activation process with the chemical change itself. There are base quantum states where what we call a bond is in the graph; some others where it is not. The linear superposition over these states determines the situation referring to a process in Hilbert space. A chemical process does not occur on a potential energy surface, being this diabatic or adiabatic. Potential energy surfaces provide a communication language. They help sense regions where linear superpositions (amplitudes over fixed base functions) can vary and base functions overlap locally to diverse extents. Reaction coordinates can be meaningfully defined at the PCB level. Nuclear dynamics must be added before time evolution can be implemented; semi-classical wave packet propagation [71] is only a model that due to the large number of parameters might be successful in giving agreement to experimental data (cf. chapter 5[8]). Still, the projection in real space is important because experimental techniques are now closing into observation of molecular motion induced by femtosecond laser pulses [72]. To get the maximum of such experiment, a clear perception of what is dependent on Hilbert space evolution and what is visible in real space must be gained (see [40] for discussions).

The electronuclear system in the GED scheme got coupled via electron–phonon interactions or via spin–orbit interactions or both as the case may be. These are the internal sources for time evolution in molecular quantum space as defined here. Summarizing. The diabatic electronic base function derived here in Hilbert space maps on to a molecular system in chemical (real) space. The chemical process corresponds to a time evolution from a particular quantum state; this is given as a linear superposition, and driven by the total hamiltonian that includes kinematic coupling operators. To make the contact with chemical processes in laboratory space, the available energy must be assigned to help discard all states in Hilbert space that at the end of the study do not conserve energy. The amplitudes for them are hence put equal to zero.

So far, there are sufficient mathematical elements that sustain Dirac's statement quoted in the introduction. Hilbert space speaks about possibilities the system has to evolve. Real space is the place where events (facts) can be recorded and systems prepared [9]; the amplitudes of the linear superposition are involved at this level: no events if the amplitude is zero or too weak intensity to be detectable. These real space systems must be mapped onto the corresponding Hilbert space. This dichotomy is essential to understand the mechanism of chemical reactions. Blurring the borders only leads to fuzzy descriptions.

Acknowledgments

The author thanks Dr. P. Perez (U. Andrés Bello), Director of The Millennium Nucleus for Applied Quantum Mechanics and Computational Chemistry, for inviting him to Chile, and Profs. R. Contreras and P. Fuentealba (U. of Chile) for fruitful discussions and valuable information. Long, productive and friendly discussions with Prof. G. Arteca are gratefully acknowledged.

References

[1] G.C. Schatz and M.A. Ratner, *Quantum Mechanics in Chemistry* (Prentice Hall, Englewood Cliffs, 1993).
[2] P.A.M. Dirac, Proc. Roy. Soc. (London) 123 (1929) 714.
[3] H. Meyer, Ann. Rev. Phys. Chem. 53 (2002) 141.
[4] B.O. Roos, *Lecture Notes in Quantum Chemistry* (Springer-Verlag, Berlin, 1992).
[5] P.A.M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1947).
[6] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, 1955).
[7] J.J. Sakurai, *Modern Quantum Mechanics* (Benjamin/Cummings, Menlo Park, 1994).
[8] H. Primas, *Chemistry, Quantum Mechanics and Reductionism* (Springer-Verlag, Berlin, 1981).
[9] H. Fidder and O. Tapia, Int. J. quantum chem. 97 (2004) 670.
[10] W. Greiner, *Relativistic Quantum Mechanics. Wave Equations* (Springer-Verlag, Berlin, 1987).
[11] W. Greiner and B. Müller, *Quantum Mechanics. Symmetries* (Springer, Heidelberg, 1994).
[12] E. Wigner, Ann. Math. 40 (1939) 149.
[13] E. Wigner, *Group Theory* (Academic Press, New York, 1959).
[14] L.E. Ballentine, *Quantum Mechanics: A Modern Development* (World Scientific, Singapore, 1998).
[15] S. Weinberg, *The Quantum Theory of Fields* (Cambridge Univerty Press, New York, 1995).
[16] S. Cohen, D.L. Judd and J.J.R. Rindell, Phys. Rev. 119 (1960) 384.
[17] R. Pauncz, *Spin Eigenfunctions* (Plenum Press, New York, 1979).
[18] T. Kato, Trans. Am. Math. Soc. 70 (1951) 195.
[19] H.D. Zeh, Found. Phys. 1 (1970) 69.
[20] A.H. Zewail, *Femtochemistry. Ultrafast Dynamics of the Chemical Bond* (World Scientific, Singapore, 1994).
[21] C.J. Isham, *Quantum Theory* (Imperial College Press, London, 1995).
[22] S. Mukamel, *Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
[23] C. Cohen-Tannoudji, J. Dupont-Roc and G. Grynberg *Photons and Atoms. Introduction to Quantum Electrodynamics* (Wiley & Son Inc., New York, 1989).
[24] O. Tapia and P. Braña, J. Mol. Str. (Theochem) 580 (2002) 9.
[25] O. Tapia, H. Fidder, V.S. Safont, M. Oliva and J. Andres, Int. J. Quantum Chem. 88 (2002) 154.

[26] E. Elbaz, *Quantum. The Quantum Theory of Particles, Fields, and Cosmology* (Springer-Verlag, Berlin, 1998).
[27] L.C. Biedenharn and H. Van Dam, *Quantum Theory of Angular Momentum* (Academic Press, New York, 1965).
[28] E.U. Condon and G.H. Shortley *The Theory of Atomic Spectra* (Cambridge University Press, London, 1977).
[29] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnár, M.L. Roukes, A.Y. Chtchelkanova and D.M. Treger, Science 294 (2001) 1488.
[30] J. Preskill, Nature 402 (1999) 357.
[31] R.P. Feynman, *Quantum Electrodynamics* (Benjamin, Inc., New York, 1961).
[32] G.A. Arteca and O. Tapia, J. Math. Chem. 35 (2004) 1.
[33] G.A. Arteca and O. Tapia, J. Math. Chem. 35 (2004) 159.
[34] M. Born and J. Oppenheimer, Ann. Physik. 84 (1927) 457.
[35] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
[36] G. Herzberg and E. Teller, Z. Physik. Chem. B21 (1933) 410.
[37] H.C. Longuet-Higgins, Adv. Spectry. 2 (1961) 429.
[38] F. Martín, J. Phys. B. 32 (1999) R197.
[39] O. Tapia and G.A. Arteca, Internet Electron. J. Mol. Des. 2 (2003) 454.
[40] O. Tapia, Int. J. Quantum Chem. 97 (2004) 637.
[41] O. Tapia and G.A. Arteca, Adv. Quantum Chem. 47 (2004) 273.
[42] A.A. Kiselev, J. Phys. B: Atom. Molec. Phys. 3 (1970) 904.
[43] A.W. Jasper, C. Zhu, S. Nangia and D.G. Truhlar, Faraday Discuss. 127 (2004) 1.
[44] F.W. Byron Jr. and R.W. Fuller, *Mathematics of Classical and Quantum Physics* (Dover Publications, Inc., New York, 1970).
[45] M.S. Child (ed.), Faraday Discussions 127 (2004) 473.
[46] O. Goscinski and V. Mujica in: *Density Matrices and Density Functionals*, eds. R. Erdahl and V.H. Smith Jr, (Reidel, Dordrecht 1987) p. 597.
[47] R.G. Woolley and B.T. Sutcliffe, Chem. Phys. Lett. 45 (1977) 393.
[48] W. Moffitt and A.D. Liehr, Phys. Rev. 106 (1957) 1195.
[49] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover Publications, Inc., New York, 1986).
[50] F.S. Ham and G.A. Slack, Phys. Rev. B. 4 (1971) 777.
[51] J.A. Pople and H.C. Longuet-Higgins, Mol. Phys. 1 (1958) 372.
[52] J.A. Pople, Mol. Phys. 2 (1959) 16.
[53] D.R. Yarkony, Acc. Chem. Res. 31 (1998) 511.
[54] R. Loudon, *The Quantum Theory of Light* (Clarendon Press, Oxford, 1986).
[55] D.M. Friedrich and W.M. McClain, Ann. Rev. Phys. Chem. 31 (1980) 559.
[56] M. Shapiro and P. Brumer, Adv. Atom. Mol. Opt. Phys. 42 (2000) 287.
[57] E. Courtade, M. Anderlini, D. Ciampini, J.H. Müller, O. Morsch, E. Arimondo, M. Aymar and E.J. Robinson, J. Phys. B: At. Mol. Opt. Phys. 37 (2004) 967.
[58] A.H. Zewail, Science 242 (1988) 1645.
[59] E. Kreyszig, *Introductory Functional Analysis with Applications* (John Wiley & Sons, New York, 1978).
[60] W.E. Thirring, in: Schrödinger, C.W. Kilmister ed. (Cambridge University Press, Cambridge, 1987) p. 65.
[61] O. Tapia, Int. J. Quantum Chem. 99 (2004) 373.
[62] L. Pauling, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).
[63] H.W. Kroto, *Molecular Rotation Spectra* (Dover Publications Inc., New York, 1992).
[64] F. Aparicio, J. Ireta, A. Rojo, L. Escobar; A. Cedillo and M. Galván, J. Phys. Chem. B. 107 (2003) 1692.

[65] O. Tapia, in: *Quantum Systems in Chemistry and Physics, Vol II: Advanced Problems and Complex Systems*, eds. A. Hernandez-Laguna, J. Maruani, R. McWeeny and S. Wilson (Kluwer, Dordrecht, 2000) p. 193.
[66] O. Tapia, in: *New Trends in Quantum Systems in Chemistry and Physics*, eds. J. Maruani, S. Wilson and Y. G. Smeyers (Kluwer, Dordrecht, 2000) p. 23.
[67] O. Tapia, Adv. Quantum Chem. 40 (2001) 103.
[68] C.A. Mead and D.G. Truhlar, J. Chem. Phys. 77 (1982) 6090.
[69] H. Nakamura and D.G. Truhlar, J. Chem. Phys. 115 (2001) 10353.
[70] P.W. Langhoff, R.H. Hinde, J.A. Boatz and J.A. Sheehy, Chem. Phys. Lett. 358 (2002) 231.
[71] J.E. Bayfield, *Quantum Evolution* (John Wiley & Sons, New York, 1999).
[72] L. Bartels, F. Wang, D. Möller, E. Knoesel and T. Heinz, Science 305 (2004) 648.