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Preface

Since it's inception in 1967, the *Advances in Quantum Chemistry* series has attempted to present various aspects of atomic, molecular, and solid state theory at the cutting edge. The contributions have taken various forms, from longer review articles to conference proceedings, and most of them have been well received. In this issue, we continue in this trend, and address some of the fundamental issues in density functional theory (DFT). DFT is extremely popular these days in its applied form: It is almost impossible to read an experimental article where explanation of the results does not involve a DFT calculation using one or another commercial program and implementing one or another parameterized potential scheme. However, the success of applied DFT seems to be that it works, rather than the result of critical analysis of the fundamentals of the theory. However, the community also needs to explore the limits of the theory itself, and it is with this that the first four contributions in this issue concern themselves.

The question of the locality of density-functional potentials of Kohn-Sham type, a central issue of the foundations of DFT, has been controversial for some time. Robert Nesbet has argued in several articles in the literature, in opposition to most of the DFT community, that the locality of DFT potentials has never been rigorously proven and he claims by means of a counter example that a local potential cannot exist for a system with more than two electrons. His conclusion is that a consistent density functional theory does not exist and that the only rigorous way to proceed is by constructing an orbital functional theory (OFT). This result has been challenged in the scientific literature by several authors; criticisms that have been vigorously refuted by Nesbet. In the present volume four chapters appear on the subject.

In the first chapter Nesbet summarizes his arguments against standard DFT and presents his alternative orbital functional theory. In the second chapter, Robert van Leeuwen presents an extensive review of DFT and confirms and substantiates the generally accepted result that a large class of density functionals is in fact differentiable with the derivative in the form of a local potential. The third chapter by Ingvar Lindgren and Sten Salomonson applies a different technique of DFT to demonstrate the existence of a local derivative of an even larger class of density functionals. Lindgren and Salomonson also criticize Nesbet's approach explicitly and claim to have found the point where the arguments of Nesbet fail. In the final DFT chapter, Roman Nalewjaski presents some connections between DFT and information theory.

In the present volume the controversial issues concerning the fundamentals of DFT can be followed in great detail and the readers can judge for themselves. We think it is an excellent and stimulating issue, as it explores the fundamentals of DFT.

In addition to the DFT chapters, there are two chapters by John and James Avery; the first time a father and son team has published in Advances. In the first, a new and more general type of symmetry-preserving pair creation operator is proposed and extended to cases where orthonormality of orbitals of different configurations cannot be assumed.

Together with Osvaldo Goscinski they examine in their second chapter whether it is possible to generate natural orbitals for a system from an initial calculation using generalized Sturmians.

Finally the contention "Was H_2^- observed in solid H_2? A Theoretical answer" by H.U. Suter, B. Engels and S. Lunell, *Adv. Quant. Chem.* 40 is revisited by T. Miyazaki.

We wish you a pleasant read.

Erkki Brändas and John R. Sabin
Editors

Local and Nonlocal Potential Functions in Density Functional Theory

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1. INTRODUCTION

In Kohn–Sham (KS) density functional theory (DFT), the occupied orbital functions of a model state are derived by minimizing the ground-state energy functionals of Hohenberg and Kohn. It has been assumed for some time that effective potentials in the orbital KS equations are always equivalent to local potential functions. When tested by accurate model calculations, this locality assumption is found to fail for more than two electrons. Here this failure is explored in detail. The sources of the 'locality hypothesis' in current DFT thinking are examined, and it is shown how the theory can be extended to an orbital functional theory (OFT) that removes the inconsistencies and paradoxes.

This article is based on the First Annual John C. Slater Lectures, given by the author at the University of Florida, Quantum Theory Project, on February 15, 16, and 20, 2001.

2. THESIS: ARE DENSITY FUNCTIONAL DERIVATIVES REALLY LOCAL FUNCTIONS?

2.1. Density functional derivatives in DFT

2.1.1. *Notation and definitions*

The N-electron Hamiltonian is $H = \hat{T} + \hat{U} + \hat{V}$, where $\hat{T}$ is kinetic energy, $\hat{U}$, the interelectronic Coulomb interaction, and $\hat{V}$, the external potential term. A system of N interacting electrons is modeled by a system of N noninteracting electrons moving in a self-consistent mean field. This requires a postulated mapping rule $\Psi \rightarrow \Phi$ by which any N-electron wave function Ψ determines a model or reference state Φ, a Slater determinant with orthonormal occupied orbital functions $\phi_i(\mathbf{r}), i = 1, \ldots, N$. Φ is determined only up to a unitary transformation of the occupied orbitals. All quantities here are spin-indexed. Spin indices and summations are suppressed but considered to be implicit in notation.

For simplicity, only nondegenerate nonrelativistic ground states will be considered. The reference-state density function is $\rho = \sum_i n_i \rho_i = \sum_i n_i \phi_i^* \phi_i$, where the occupation numbers n_i are one or zero and $\sum_i n_i = N$. Because ρ has this orbital decomposition, any density functional $F[\rho]$ is also an orbital functional $F[\{\phi_i, n_i\}]$. This implies a natural definition of an energy functional $E = E_0 + E_c$, such that $E_0 = (\Phi|H|\Phi)$ and E_c is an orbital functional that approximates the correlation energy $\langle H\rangle - E_0$. $E_0 = T + U + V$ is an explicit orbital functional. Defining $U = E_h + E_x$,

$$T = \sum_i n_i(i|\hat{t}|i); \quad E_h = \tfrac{1}{2}\sum_{i,j} n_i n_j (ij|u|ij)$$

$$E_x = -\tfrac{1}{2}\sum_{i,j} n_i n_j (ij|u|ji); \quad V = \sum_i n_i(i|\hat{v}|i) \tag{1}$$

where $u = 1/r_{12}$ and $\hat{t} = -\frac{1}{2}\nabla^2$. For most applications, the general nonlocal external potential $\hat{v}$ reduces to a local function $v(\mathbf{r})$.

It is assumed that E_c is so defined that the functional E is minimized for ground states. Ground-state orbital functions and the density function are determined by Euler–Lagrange equations expressed in terms of functional derivatives of E. For any density or orbital functional, with fixed n_i, infinitesimal orbital variations determine the functional variation

$$\delta F = \int d^3\mathbf{r} \sum_i n_i\{\delta\phi_i^* \hat{v}_F \phi_i + \mathrm{cc}\} \tag{2}$$

where $\hat{v}_F$ is a linear operator that may reduce to a multiplicative local function $v_F(\mathbf{r})$ in each particular case. The orbital functional derivative is $\delta F/n_i\delta\phi_i^* = \hat{v}_F\phi_i$. If the density functional derivative $\delta F/\delta\rho$ of $F[\rho]$ is a local function $v_F(\mathbf{r})$, then

$$\delta F = \int d^3\mathbf{r} v_F(\mathbf{r})\delta\rho(\mathbf{r}) = \int d^3\mathbf{r} \sum_i n_i\{\delta\phi_i^* v_F(\mathbf{r})\phi_i + \mathrm{cc}\} \tag{3}$$

since $\delta\rho = \sum_i n_i\{\delta\phi_i^*\phi_i + \mathrm{cc}\}$. This definition corresponds to that of a Fréchet functional derivative [1,2], the generalization in functional analysis of an analytic total derivative. If this definition fails, an extended definition $(\delta F/\delta\rho)\phi_i = \hat{v}_F\phi_i$ is consistent with the variation of the equivalent orbital functional. It will be shown here that this extended definition corresponds to that of a Gâteaux functional derivative [1,2], the generalization in functional analysis of an analytic partial derivative. Consistency is ensured by the chain rule

$$\frac{\delta F}{\delta\rho}\phi_i = \frac{\delta F}{n_i\delta\phi_i^*} = \hat{v}_F\phi_i \tag{4}$$

2.1.2. *Outline of DFT for an N-electron system*

Hohenberg and Kohn [3] proved for nondegenerate N-electron states that the ground-state density function $\rho(\mathbf{r})$ uniquely determines the external potential function $v(\mathbf{r})$ and all properties of the ground state. Kohn and Sham [4] showed that a mapping $\Psi \longrightarrow \Phi$ onto a model state could be defined by applying the Hohenberg–Kohn theory to a noninteracting system. The Kohn–Sham construction (KSC) minimizes the kinetic energy orbital functional $T = \sum_i n_i(i|\hat{t}|i)$ subject to $\rho = \rho_\Psi$.

This determines a model state Φ for any N-electron ground state Ψ if the construction can be carried out (*noninteracting v-representability*), and defines a ground-state density functional $T_s[\rho]$. It should be noted that the rule $\Psi \rightarrow \Phi$ is not unique. $T = \sum_i n_i(i|\hat{t}|i)$ is a density functional for ground states for all such rules, because the orbital functions ϕ_i are themselves determined by the density. A total energy functional $E = T + E_\mathrm{h} + E_\mathrm{xc}[\rho] + V$ is defined by any postulated model of the exchange-correlation energy.

In KS theory [4], the occupied orbital functions of the model state are determined by the KS equations

$$\{\hat{t} + v_h(\mathbf{r}) + v_\mathrm{xc}(\mathbf{r})\}\phi_i = \{\epsilon_i - v(\mathbf{r})\}\phi_i \tag{5}$$

Defining $F = E - V = T + E_\mathrm{h} + E_\mathrm{xc}$, the expected orbital Euler–Lagrange (OEL) equations are

$$\frac{\delta F}{\delta \rho}\phi_i = \{\epsilon_i - v(\mathbf{r})\}\phi_i \tag{6}$$

if the required functional derivatives can be defined consistently. These two equations are equivalent if functional derivatives exist such that

$$\frac{\delta T}{\delta \rho}\phi_i = \hat{t}\phi_i; \quad \frac{\delta E_\mathrm{xc}}{\delta \rho}\phi_i = v_\mathrm{xc}(\mathbf{r})\phi_i \tag{7}$$

These conditions could be consistent if a Fréchet functional derivative $v_F(\mathbf{r}) = \delta F/\delta\rho(\mathbf{r})$ exists for every well-defined density functional $F[\rho]$. The *locality hypothesis* assumes this to be true. Various tests of this hypothesis are considered here.

2.1.3. Hohenberg–Kohn theorems for orbital functionals

The Hohenberg–Kohn theorems make no assumptions about functional derivatives, and in fact can be shown to be valid for ground states in any OFT [5]. This extension of Hohenberg–Kohn theory is important in establishing necessary conditions for the existence of Fréchet functional derivatives (the locality hypothesis). With fixed occupation numbers $n_i = 1$, $i \le N$, an orbital functional is a functional of a model state Φ. Consider a model system defined by the orbital functionals $E_\mathrm{xc}[\Phi]$ and $F = T + E_\mathrm{h} + E_\mathrm{xc}$, such that $\min(F + V) = E[v]$ approximates an N-electron ground state energy. Consider a specified density function ρ in the class of functions ρ_Φ. Then minimize the functional $F[\Phi]$ subject to $\rho_\Phi = \rho$, using the Levy construction [6]. The density constraint can be enforced using a Lagrange-multiplier field $v(\mathbf{r})$. For any given $v(\mathbf{r})$, a functional of ρ is defined by

$$F_v[\rho] = \min_{\Phi_t}\left\{F[\Phi_t] + \int v(\rho_t - \rho)\,\mathrm{d}^3\mathbf{r}\right\} = E[v] - \int v\rho\,\mathrm{d}^3\mathbf{r} \tag{8}$$

A ground-state functional $F_s[\rho]$ is defined by $F_v[\rho]$ when v is chosen such that $\rho_v = \rho$. The minimizing model function Φ_v determines ρ_v. This determines v

for any given ρ if the variational problem has a solution (*v-representability*). $E_v[\rho] = F_s[\rho] + \int v\rho\, \mathrm{d}^3\mathbf{r}$ defines an energy functional for arbitrary v. When $\rho = \rho_v$, $E_v[\rho_v] = E[v]$, its minimum value. When $\rho \neq \rho_v$, $E_v[\rho] = F[\Phi] + \int v\rho\, \mathrm{d}^3\mathbf{r}$ for some $\Phi(\rightarrow\rho) \neq \Phi_v$. Hence $E_v[\rho] \geq E_v[\rho_v]$. This establishes the variational property of $E_v[\rho]$, verifying the Hohenberg–Kohn theorems.

2.2. Kinetic energy in Thomas–Fermi theory

For more than two electrons, it has been shown [7] that any local kinetic energy 'potential' is inconsistent with exact KS equations, which use the nonlocal operator of Schrödinger: $\hat{t} = -\frac{1}{2}\nabla^2$.

2.2.1. *Model: Atom with N noninteracting electrons*

The argument can be specialized to an atom with N noninteracting electrons, with the Hamiltonian $H = \hat{T} + \hat{V}$, whose mean value $(\Phi|H|\Phi)$ in a single-determinant reference state Φ defines the orbital energy functional $E = T + V = \sum_i n_i(i|\hat{t} + v|i)$, where $v(\mathbf{r}) = -Z/r$. The OEL equations, just the Schrödinger equation for each occupied orbital ($i \leq N$),

$$\hat{t}\phi_i = \{\epsilon_i - v(\mathbf{r})\}\phi_i \tag{9}$$

are derived using the orbital functional derivatives

$$\frac{\delta T}{n_i \delta\phi_i^*} = \hat{t}\phi_i; \quad \frac{\delta V}{n_i \delta\phi_i^*} = v(\mathbf{r})\phi_i \tag{10}$$

The hydrogenic orbital eigenfunctions, energy eigenvalues, and density function are determined unambiguously.

Since Hohenberg–Kohn theorems can be proved for the ground state of any orbital-functional model[5], the orbital functional $T = \sum_i n_i(i|\hat{t}|i)$ is a density functional $T_s[\rho]$ for such ground states. A Thomas–Fermi equation is determined if $\delta T_s/\delta\rho$ is equivalent to a local potential function $v_T(\mathbf{r})$:

$$\frac{\delta T_s}{\delta\rho} = v_T(\mathbf{r}) = \mu - v(\mathbf{r}) \tag{11}$$

If $\hat{t}$ in the OEL equations could be replaced by a local function $v_T(\mathbf{r})$, as in the Thomas–Fermi equation, the trace sum over occupied orbitals $\sum_i n_i(i|\hat{t} - v_T|i)$ would have to vanish. Otherwise the reference state Φ would not be the ground state of the noninteracting model, contrary to the Hohenberg–Kohn theorems. But if this condition is satisfied, subtracting the two equations, after multiplying the OEL equation by $n_i\phi_i^*$, summing, and integrating and after multiplying the Thomas–Fermi equation by $\rho(\mathbf{r})$ and integrating, implies the sum rule

$$\sum_i n_i(\epsilon_i - \mu) = \int \mathrm{d}^3\mathbf{r} \sum_i n_i\phi_i^*(\hat{t} - v_T)\phi_i = 0 \tag{12}$$

or $\sum_i n_i \epsilon_i = N\mu$. Because $\epsilon_i \leq \mu$ for $n_i = 1$, this sum rule fails unless all occupied ϵ_i are equal. This would violate the exclusion principle in general for any compact system with more than two electrons.

It can be concluded that the locality hypothesis fails for the functional derivative of T_s. Thus there is no exact Thomas–Fermi theory for $N > 2$. In contrast, as will be shown below, use of the linear operator $\hat{t}$ in the KS equations is variationally correct.

2.3. Exchange energy in the Hartree–Fock model

If variational theory does not imply the existence of a local potential function equivalent to the kinetic energy operator $\hat{t}$ in ground-state OEL equations, one must also question the validity of the locality hypothesis for exchange and correlation. This question can be examined for the exchange energy and exchange potential in the unrestricted Hartree–Fock (UHF) model of closed-shell atoms, for which Hohenberg–Kohn theorems can be proved [5,8]. Occupied orbitals, orbital energies, and the ground-state density are known to high accuracy. Computed results for He, Be, and Ne test several distinct necessary conditions for the locality hypothesis, that the Fock exchange operator $\hat{v}_x$ can be replaced in the UHF equations by an exact local exchange potential $v_x(\mathbf{r})$. These tests succeed for He, with only two electrons, but fail in general for heavier atoms, and in particular for Be and Ne [9,10]. Requiring locality of the exchange potential imposes a true variational constraint for more than two electrons.

2.3.1. Model: unrestricted Hartree–Fock

The model state Φ is identical to the UHF ground state, for which Hohenberg–Kohn theorems are valid. The energy mean value $E = (\Phi|H|\Phi) = T + E_h + E_x + V$ is an orbital functional. The occupied orbitals ϕ_i satisfy the OEL (UHF) equations

$$\frac{\delta(E - V)}{n_i\,\delta\phi_i^*} = \{\hat{t} + v_h(\mathbf{r}) + \hat{v}_x\}\phi_i = \{\epsilon_i - v(\mathbf{r})\}\phi_i \tag{13}$$

where $\hat{v}_x$ is the Fock exchange operator. Suppose that E_x has a local density functional derivative $v_x(\mathbf{r})$. Then the KS equations would be

$$\frac{\delta(E - V)}{\delta\rho(\mathbf{r})}\phi_i = \{\hat{t} + v_h(\mathbf{r}) + v_x(\mathbf{r})\}\phi_i = \{\epsilon_i - v(\mathbf{r})\}\phi_i \tag{14}$$

If the UHF and KS equations were equivalent, on multiplying by ϕ_i^* and summing, they would imply $v_x(\mathbf{r})\rho(\mathbf{r}) = \sum_i n_i\phi_i^*(\mathbf{r})\hat{v}_x\phi_i(\mathbf{r})$, which defines the local exchange potential of Slater [11]. It is well known that the Slater potential gives relatively poor results for atoms [10]. It is clearly not equivalent to the Fock exchange operator in UHF equations for more than two electrons. It can be concluded that the locality hypothesis fails for E_x in the UHF model for typical atoms. The restriction to a local exchange potential $v_x(\mathbf{r})$ in the KS equations is inconsistent with an exact theory.

2.4. Exchange and correlation energy in linear-response theory

It has recently been shown [12] that time-dependent or linear-response theory based on local exchange and correlation potentials is inconsistent in the pure exchange limit with the time-dependent Hartree–Fock theory (TDHF) of Dirac [13] and with the random-phase approximation (RPA) [14] including exchange. The DFT-based exchange-response kernel [15] is inconsistent with the structure of the second-quantized Hamiltonian.

2.4.1. *Linear-response theory of excitation energies*

In the linear-response limit of the time-dependent DFT [16], excitation frequencies are determined by

$$\sum_{q'} \left\{ \delta_{qq'} - \frac{M_{qq'}(\omega)}{\omega - \omega_{q'} + i\eta} \right\} \xi_{q'}(\omega) = 0 \tag{15}$$

where q denotes a virtual excitation $i \rightarrow a$. This depends on the parameters $\omega_q = \epsilon_a - \epsilon_i$ and $\alpha_q = n_i - n_a$. A second transition is indexed by $q' {:} j \rightarrow b$. In the exchange-only limit $M_{qq'}(\omega) = \alpha_{q'}(aj|u + f_{\mathrm{x}}|ib)$. This can be compared with the well-established RPA in the same limit [14] (p. 89), $M_{qq'}(\omega) = \alpha_{q'}(aj|u - u\mathcal{P}|ib)$, using the exchange operator $\mathcal{P}(\mathbf{r}, \mathbf{r}')\delta(m_s, m_s')$. These equations agree if the exchange response kernel $f_{\mathrm{x}} = -u\mathcal{P}$, is a linear operator. If expressed in the same notation, the result of Dirac's (1930) [13] derivation of the TDHF is the linear operator in the RPA formula $f_{\mathrm{h}} + f_{\mathrm{x}} = u\{I - \mathcal{P}\} = \bar{u}$. This is an exact result in the exchange-only limit. It is a direct consequence of the structure of the second-quantized electron Hamiltonian[12].

It can be shown that the response kernel is a functional second derivative. Assuming that the functional first derivative $\delta E_{\mathrm{x}}/\delta\rho$ is a local function (the locality hypothesis for v_{x}), Petersilka *et al.* [15] have derived the approximate formula

$$f_x^{\mathrm{OEP}}(\mathbf{r}\mathbf{r}') \simeq -2\frac{|\sum_k n_k \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|\rho(\mathbf{r})\rho(\mathbf{r}')} \tag{16}$$

This result cannot be reconciled with that of Dirac [13] and with the structure of the second-quantized Hamiltonian [12,14]. The implication is that the locality hypothesis fails for E_{x} and probably for E_{c}, which can be incorporated in a formally exact extension of Dirac's derivation. [17] Thus restriction to local exchange and correlation potentials is inconsistent with exact linear-response theory.

2.5. Counterarguments

The original formulation of DFT by Kohn and Sham appeared to imply that an exact orbital theory could be expressed in terms of a local exchange-correlation potential[4] ('note added in proof', p. A1138). This conclusion would follow from variational theory if $E_{xc}[\rho]$ always had a Fréchet functional derivative $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta\rho(\mathbf{r})$. The problem is that the existence of such a local function has not been proved in general, and is disproved in specific cases when tested. Any counter example negates the general assertion that locality is a consequence of the variational theory.

Alternatively, it might be that any well-defined density functional necessarily has a Fréchet functional derivative, so that the locality property is inherent in the definition $v_F(\mathbf{r}) = \delta F/\delta\rho$ [18,19] and can be assumed without detailed proof. The mathematical object so defined must be proven to exist if this 'definition' is to have any meaning. Counterexamples show that a 'local functional derivative' does not exist in cases for which it can be tested. Either the theory must be abandoned or the definition must be generalized.

It has been asserted that a valid theory can be established by proving 'noninteracting v-representability', equivalent to showing that a local potential function exists for which the KS equations have a solution that reproduces a given $\rho(\mathbf{r})$ [19] (p. 44). This would be true if the locality hypothesis were true, otherwise not. Accurate calculations of the KSC establish noninteracting v-representability [20], but do not reproduce the model ground state for more than two electrons. These calculations show that minimizing T by itself, subject to a density constraint, is not equivalent to minimizing $E - V$.

It might be argued that the error of constraint computed in accurate KSC calculations can be defined out of existence by calling it a 'correlation energy' [20]. This amounts to adding an arbitrary number to the mean energy computed for the UHF variational model, so as exactly to cancel out the residual error imposed by the locality constraint. Such an adjustment of computed results amounts to adding an arbitrary constant to the variational Hamiltonian, which cannot be justified. In contrast, the optimized effective potential (OEP) method involves no such *post hoc* adjustment, and very straightforwardly obtains the best possible local effective potential for the same variational model. Accurate calculations show that the differences between the KSC and OEP wave functions and energies are very small compared with the difference of both of these methods from computationally exact UHF results [10].

A deeper argument is that local density functional derivatives appear to be implied by functional analysis [2,21,22]. The KS density function has an orbital structure, $\rho = \sum_i n_i\rho_i = \sum_i n_i\phi_i^*\phi_i$. For a density functional F_s, strictly defined only for normalized ground states, functional analysis implies the existence of functional derivatives of the form $\delta F_s/n_i\delta\rho_i = \epsilon_i - v(\mathbf{r})$, where the constants ϵ_i are undetermined. On extending the strict ground-state theory to an OFT in which OEL equations can be derived, these constants are determined and are just the eigenvalues of the one-electron effective Hamiltonian. Since they differ for each different orbital energy level, the implied functional derivative depends on a 'direction' in the function-space of densities. Such a Gâteaux derivative [1,2] is equivalent in the DFT context to a linear operator that acts on orbital functions [23].

This argument leads back to the OEL equations of OFT, which contain nonlocal potentials in general.

2.6. Implications

The locality hypothesis is not a general consequence of functional analysis and cannot be assumed without proof in any particular case. The many technical arguments that appear to support this hypothesis in existing literature should be reexamined. Secondary consequences of the locality hypothesis such as electronic self-interaction and the lack of physical significance of one-electron energy eigenvalues should be reconsidered. Computational methodology based on strictly local potential functions must be reconsidered and extended to some degree of nonlocality.

3. ANTITHESIS: ORBITAL FUNCTIONAL DERIVATIVES DEFINE LINEAR OPERATORS

3.1. Functional derivatives in orbital functional theory

In practical applications of DFT, some postulated explicit functional $E_{\mathrm{xc}}[\rho]$ is used to derive KS equations, which are then solved to determine the density function ρ. Since ρ is constructed from orbital densities, the assumed functional E_{xc} is also an orbital functional. This implied orbital functional coincides with the density functional for ground states, but is in fact much more general. Given some formula for E_{xc}, the N-electron energy is defined as a functional in the orbital Hilbert space, not confined to ground states, and not restricted by normalization. Because this is exactly the context of the standard variational derivations of Schrödinger's equation and of the Hartree–Fock equations, the OEL equations that make this energy functional stationary can be derived by a straightforward analysis using orbital functional derivatives. Since restriction to ground states of the more general OFT produces the corresponding DFT, valid results of both theories must be compatible. The implied relationship is used here to analyze the inconsistencies summarized in the preceding Section.

3.1.1. Derivation of the orbital Euler–Lagrange equations

Given the N-electron Hamiltonian $H = \hat{T} + \hat{U} + \hat{V}$, and postulating some rule $\Psi \rightarrow \Phi$ that determines a reference state, this defines an orbital functional $E = T + U + V + E_{\mathrm{c}}$, where $T + U + V = (\Phi|H|\Phi)$ is explicit, as defined previously, and $E_{\mathrm{c}} \simeq E_{\mathrm{exact}} - (\Phi|H|\Phi)$ is an orbital functional defined for a particular approximate model. It is assumed that E is minimized in the ground state of the model. $V = \sum_i n_i(i|\hat{v}|i)$ if $\hat{v}$ is a general nonlocal external potential.

The Schrödinger variational principle can be applied directly: for fixed occupation numbers n_i, E is required to be stationary subject to $(i|j) = \delta_{ij}$. To simplify the derivation, trial orbitals can be required to be orthogonal, but diagonal Lagrange multipliers ϵ_i are used for the normalization constraint. The variational condition is

$$\delta\left[E - \sum_i n_i\{(i|i) - 1\}\epsilon_i\right] = \int d^3\mathbf{r} \sum_i n_i\left(\delta\phi_i^*\left\{\frac{\delta E}{n_i\delta\phi_i^*} - \epsilon_i\phi_i\right\} + \mathrm{cc}\right) = 0 \quad (17)$$

The required orbital functional derivatives are

$$\frac{\delta T}{n_i\,\delta\phi_i^*} = \hat{t}\phi_i; \quad \frac{\delta U}{n_i\,\delta\phi_i^*} = \hat{u}\phi_i; \quad \frac{\delta V}{n_i\,\delta\phi_i^*} = \hat{v}\phi_i; \quad \frac{\delta E_\mathrm{c}}{n_i\,\delta\phi_i^*} = \hat{v}_\mathrm{c}\phi_i \qquad (18)$$

using $\hat{u} = v_h(\mathbf{r}) + \hat{v}_x$, where v_h is the classical Coulomb potential, and $\hat{v}_\mathrm{x}$ is the Fock exchange operator. Defining $\mathcal{G}\phi_i = \delta E/n_i\delta\phi_i^*$, the variational equation is

$$\int d^3\mathbf{r} \sum_i n_i(\delta\phi_i^*\{\mathcal{G} - \epsilon_i\}\phi_i + \mathrm{cc}) = 0 \qquad (19)$$

For unconstrained variations of (orthogonal) orbitals in the usual Hilbert space this implies the OEL equations

$$\{\mathcal{G} - \epsilon_i\}\phi_i = 0, \qquad i = 1,\dots,N \qquad (20)$$

Equivalently, if $F = E - V$,

$$\frac{\delta F}{n_i\,\delta\phi_i^*} = \{\hat{t} + \hat{u} + \hat{v}_\mathrm{c}\}\phi_i = \{\epsilon_i - \hat{v}\}\phi_i, \qquad i = 1,\dots,N \qquad (21)$$

For most applications, the external potential operator $\hat{v}$ reduces to a local potential $v(\mathbf{r})$, and the Hohenberg–Kohn theory is valid for the ground state. The present derivation follows exactly the logic of standard Hartree–Fock theory. It is not restricted to ground states and remains valid for fractional occupation numbers.

3.2. The optimized effective potential

For any orbital-functional model, an optimal effective (local) potential (OEP) can be constructed following a well-defined variational formalism [24,25]. If a Fréchet derivative existed for the exchange-correlation energy E_xc for ground states, it would be obtained in an OEP calculation, while the minimum energy and corresponding reference state would coincide with OFT results. Thus numerically accurate OEP calculations test the locality hypothesis.

As in the Hartree–Fock theory, the OEL equations for a given orbital functional E are equivalent to the conditions $(a|\mathcal{G}|i) = 0, i \le N < a$, assuming orthonormal orbitals, where $\mathcal{G}$ is the effective Hamiltonian defined by orbital functional derivatives. Equivalently, $(\delta\phi_i|\mathcal{G}\phi_i) = 0, i \le N$. If a local potential $v_\mathrm{xc}(\mathbf{r})$

was equivalent to $\hat{v}_{\mathrm{xc}}$ in the OEL equation, it would satisfy the condition $(\delta\phi_i|v_{\mathrm{xc}} - \hat{v}_{\mathrm{xc}}|\phi_i) = 0,\ i \leq N$. The OEP method requires this condition to be satisfied for all orbital variations generated by an external local potential,

$$\delta\phi_i(\mathbf{r}) = -\int g_i(\mathbf{r},\mathbf{r}')\delta v(\mathbf{r}')\phi_i(\mathbf{r}')\mathrm{d}^3\mathbf{r}' \tag{22}$$

where

$$g_i(\mathbf{r},\mathbf{r}') = \sum_a (1-n_a)\phi_a(\mathbf{r})(\epsilon_a - \epsilon_i)^{-1}\phi_a^*(\mathbf{r}') \tag{23}$$

is the Green's function of the OEP orbital equation. This is derived by first-order perturbation theory, subject to orthogonality of the set of occupied orbitals. Such restricted variations imply the OEP variational condition, for arbitrary $\delta v(\mathbf{r})$,

$$\sum_i n_i \int \mathrm{d}^3\mathbf{r}\phi_i^*(\mathbf{r})\delta v(\mathbf{r})\sum_a (1-n_a)\phi_a(\mathbf{r})(\epsilon_a - \epsilon_i)^{-1}(a|v_{\mathrm{xc}} - \hat{v}_{\mathrm{xc}}|i) = 0 \tag{24}$$

OEP imposes one variational constraint on OFT: (a) v_{xc} must be a local function. Hence in general $E_{\mathrm{OEP}} \geq E_{\mathrm{OFT}}$. Because of the Green's function weighting, OEP does not imply $(a|v_{\mathrm{xc}} - \hat{v}_{\mathrm{xc}}|i) = 0,\ i \leq N < a$, and the computed densities may differ [26,27]. In the UHF model, accurate calculations find that $E_{\mathrm{OEP}} > E_{\mathrm{UHF}}$ [27–29] for more than two electrons. Table 1 shows computed values of several criteria that test the locality hypothesis by comparing the densities and wave functions:

$$\begin{aligned}
RS^2 &= \tfrac{1}{2}\sum_i n_i \sum_a (1-n_a)(i|v_x - \hat{v}_{\mathrm{x}}|a)(\epsilon_a - \epsilon_i)^{-1}(a|v_x - \hat{v}_{\mathrm{x}}|i) = 0 \\
ZP &= \tfrac{1}{2}\int \mathrm{d}^3\mathbf{r}_1 \int \mathrm{d}^3\mathbf{r}_2 \delta\rho(1) r_{12}^{-1}\delta\rho(2) = 0 \\
R_2 &= \int r^2 \Delta\rho\, \mathrm{d}^3\mathbf{r} = 0 \\
S &= (\Phi_{\mathrm{OEP}}|\Phi_{\mathrm{UHF}}) = 1
\end{aligned} \tag{25}$$

where $\delta\rho = \rho_{\mathrm{OEP}} - \rho_{\mathrm{UHF}}$ [30]. Results of variational OEP calculations [27] are shown, using $v_x(\mathbf{r}) = v_{\mathrm{Slater}}(\mathbf{r}) + \sum_q \pi_q(\mathbf{r})c_q$, in a basis of product functions π_q. The optimized local exchange potential does not reproduce the Hartree–Fock ground state for more than two electrons. These results confirm the failure of the locality hypothesis for v_x.

Table 1. OEP criteria for locality of v_x (Hartree units)

Atom	RS	SZP	R_2	S
He	1.0−9	1.0−7	1.0−9	1.000000
Be	0.111−1	0.246−3	0.491−2	0.999987
Ne	0.193−1	0.115−3	−0.280 to 2	0.999991

Signed integers indicate powers of 10.

3.3. The Kohn–Sham construction

When $E_{\mathrm{xc}}[\rho]$ is specified, the relevant ground-state density for Hohenberg–Kohn theory is ρ_0, computed using the equivalent orbital functional E_{xc} in the OEL equations, $(\mathcal{G} - \epsilon_i)\phi_i = 0$. The local potential $w(\mathbf{r})$ in the corresponding KS equations is determined by the KSC by minimizing T for $\rho = \rho_0$. Assuming the locality hypothesis, that $w - v$ is the Fréchet derivative of the model ground-state functional $F_s[\rho] - T_s[\rho]$, this implies that $w = v_h + v_{\mathrm{xc}} + v$ is a sum of local potentials. If $\hat{v}_{\mathrm{xc}}$ in the OEL equations was equivalent to a local potential $v_{\mathrm{xc}}(\mathbf{r})$, the KS and OEL equations would produce the same model wave function.

As an application of the Hohenberg–Kohn theory to a noninteracting system, the KSC can be carried out using the Levy construction [6] with a Lagrange-multiplier field $w(\mathbf{r})$ for the density constraint,

$$\delta\left[\sum_i n_i\{(i|\hat{t}|i) - [(i|i) - 1]\epsilon_i\} + \int \mathrm{d}^3\mathbf{r}\, w(\mathbf{r})(\rho(\mathbf{r}) - \rho_0(\mathbf{r}))\right]$$
$$= \int \mathrm{d}^3\mathbf{r} \sum_i n_i(\delta\phi_i^*\{\hat{t} + w - \epsilon_i\}\phi_i + \mathrm{cc}) = 0 \tag{26}$$

This implies the KS equation $\{\hat{t} + w - \epsilon_i\}\phi_i = 0$ if the orbitals ϕ_i can vary freely in the orbital Hilbert space. The Lagrange multiplier field $w(\mathbf{r})$ is to be chosen so that $\rho(\mathbf{r}) = \rho_0(\mathbf{r})$. If $w(\mathbf{r})$ exists, ρ is said to be *noninteracting v-representable.*

The KSC imposes two variational constraints on OFT: (a) v_{xc} must be a local function; and (b) $\rho = \rho_0$. These nested constraints imply $E_{\mathrm{KSC}} \geq E_{\mathrm{OEP}} \geq E_{\mathrm{OFT}}$. [20] In the UHF model, a particular case of OFT, for typical atoms [29,20,10], $E_{\mathrm{KSC}} \geq E_{\mathrm{OEP}} > E_{\mathrm{UHF}}$ for more than two electrons, and the KSC local exchange potential does not reproduce the Hartree–Fock ground state. These results confirm the failure of the locality hypothesis for v_x, and demonstrate that noninteracting v-representability does not imply locality.

3.4. Exact linear-response theory

The failure of the DFT linear-response theory to reduce to the exact formalism of Dirac [13] in the exchange-only limit [12] is symptomatic of the inadequacy of the locality hypothesis. It will be shown here that on dropping this hypothesis a linear-response theory can be derived that is formally exact for both exchange and correlation. As will be discussed in more detail in the following Section, an exact but implicit orbital functional exists for the correlation energy E_{c} [31]. This produces a formally exact correlation term in the OEL equations, defined by the orbital functional derivative

$$\frac{\delta E_{\mathrm{c}}}{n_i\,\delta\phi_i^*} = \hat{v}_{\mathrm{c}}\phi_i \tag{27}$$

The derivation by Dirac [13] of TDHF can be expressed in terms of orbital functional derivatives [12]. This derivation can be extended directly to a formally exact time-dependent orbital-functional theory (TDOFT). The Hartree–Fock operator $\mathcal{H}$ is replaced by the OFT operator $\mathcal{G} = \mathcal{H} + \hat{v}_c$ throughout Dirac's derivation. In the linear-response limit, this generalizes the RPA equations [14] to include correlation response [17].

Dirac defines an idempotent density operator $\hat{\rho}$, such that the kernel is $\sum_i \phi_i(\mathbf{r}) n_i \phi_i^*(\mathbf{r}')$. The OEL equations are equivalent to

$$[\mathcal{G}, \hat{\rho}] = 0 \tag{28}$$

The corresponding time-dependent equations are

$$i\hbar \frac{\partial}{\partial t} \hat{\rho}(t) = [\mathcal{G}(t), \hat{\rho}(t)] \tag{29}$$

Dirac proved, for Hermitian $\mathcal{G}$, that the time-dependent equation

$$i\hbar \frac{\partial}{\partial t} \phi_i(\mathbf{r}t) = \mathcal{G}(\mathbf{r}t) \phi_i(\mathbf{r}t) \tag{30}$$

implies that $\hat{\rho}(t)$ is idempotent. Hence $\hat{\rho}(t)$ corresponds to a normalized time-dependent reference state. For $t \geq 0$, a weak perturbing potential $\Delta v(\mathbf{r}t)$ induces a screening potential such that

$$\Delta G = \Delta v + \Delta \mathcal{G}_s \tag{31}$$

The first-order perturbation equations are

$$i\hbar \frac{\partial}{\partial t} \Delta\hat{\rho}(t) = [\mathcal{G}(0), \Delta\hat{\rho}(t)] + [\Delta\mathcal{G}, \hat{\rho}(0)] \tag{32}$$

$\Delta\phi_i(t) = \sum_a (1 - n_a) \phi_a c_i^a(t)$ in this orbital representation. Hence the kernel of $\Delta\hat{\rho}(t)$ is

$$\Delta\rho(\mathbf{r}, \mathbf{r}'; t) = \sum_i \sum_a n_i (1 - n_a) [\phi_a(\mathbf{r}) c_i^a(t) \phi_i^*(\mathbf{r}') + \phi_i(\mathbf{r}) c_i^a(t)^* \phi_a^*(\mathbf{r}')] \tag{33}$$

Using $(p|\mathcal{G}(0)|j) = \epsilon_p \delta_{pj}$ and $(j|\hat{\rho}(0)|q) = n_q \delta_{jq}$, in the basis of eigenfunctions of $\mathcal{G}(0)$,

$$\begin{aligned} (p|[\mathcal{G}(0), \Delta\hat{\rho}]|q) &= (\epsilon_p - \epsilon_q)(p|\Delta\hat{\rho}|q); \\ (p|[\Delta\mathcal{G}, \hat{\rho}(0)]|q) &= (n_q - n_p)(p|\Delta G|q) \end{aligned} \tag{34}$$

The equation of motion implied for $c_i^a(t)$ is

$$i\hbar \dot{c}_i^a(t) = (\epsilon_a - \epsilon_i) c_i^a(t) + (n_i - n_a)(a|\Delta\mathcal{G}|i) \tag{35}$$

for $i \leq N < a$.

3.4.1. *Definition of the response kernel*

If $\hat{v}\phi_i = \delta F/(n_i \delta\phi_i^*)$, a response kernel $\hat{f}$ is defined by the second functional derivative

$$\hat{f}\phi_j(\mathbf{r}) = \frac{\delta\hat{v}}{n_j\,\delta\phi_j^*} \tag{36}$$

Then $\Delta\phi_j(t)$ induces

$$\Delta\hat{v} = \sum_j n_j[(\Delta\phi_j|\hat{f}\phi_j) + hc] = \sum_j n_j \sum_b (1 - n_b)[(j|\hat{f}|b)c_j^b(t) + c_j^{b*}(t)(b|\hat{f}|j)] \tag{37}$$

The response kernel for the Hartree and the exchange energy functionals is $\hat{f}_\mathrm{h} + \hat{f}_\mathrm{x} = (\bar{u} = (1/r_{12})(1 - \hat{P}_{12})$, in agreement with Dirac [13] and with the second-quantized Hamiltonian. The response kernel $\hat{f}_\mathrm{c}$ is a linear operator such that

$$\hat{f}_\mathrm{c}\phi_j = \frac{\delta\hat{v}_\mathrm{c}}{n_j\,\delta\phi_j^*} \tag{38}$$

Variations of unoccupied orbitals $\delta\phi_a\,(N < a)$ in the functional E_c are induced by variations of occupied orbitals $\delta\phi_i\,(i \leq N)$ through unitarity. The combined total response kernel is the linear operator

$$\hat{f}_\mathrm{hxc} = \hat{f}_\mathrm{h} + \hat{f}_\mathrm{x} + \hat{f}_\mathrm{c} = \bar{u} + \hat{f}_\mathrm{c} \tag{39}$$

The equations of motion for the coefficients $c_i^a(t)$ (for indices $i, j \leq N < a, b$) are

$$\begin{aligned} i\hbar\dot{c}_i^a(t)i = (\epsilon_a - \epsilon_i)c_i^a(t) + (n_i - n_a)[(a|\Delta v(t)|i) + \sum_j \sum_b \{(aj|\hat{f}_\mathrm{hxc}|ib)c_j^b(t) \\ + (ab|\hat{f}_\mathrm{hxc}|ij)c_j^b(t)^*\}]. \end{aligned} \tag{40}$$

If $\Delta v(\mathbf{r}t) = 2\Delta w(\mathbf{r})\Re(\mathrm{e}^{-\mathrm{i}\omega t})$ for complex frequency ω, and $c_i^a(t) = X_i^a \mathrm{e}^{-\mathrm{i}\omega t} + Y_i^{a*}\mathrm{e}^{\mathrm{i}\omega^* t}$,

$$\begin{aligned} (\epsilon_a - \epsilon_i - \hbar\omega)X_i^a + (n_i - n_a)\sum_j \sum_b [(aj|\hat{f}_\mathrm{hxc}|ib)X_j^b \\ + (ab|\hat{f}_\mathrm{hxc}|ij)Y_j^b] = -(n_i - n_a)(a|\Delta w|i), \\ (\epsilon_a - \epsilon_i - \hbar\omega)Y_i^a + (n_i - n_a)\sum_j \sum_b [(ij|\hat{f}_\mathrm{hxc}|ab)X_j^b \\ + (ib|\hat{f}_\mathrm{hxc}|aj)Y_j^b] = -(n_i - n_a)(i|\Delta w|a) \end{aligned} \tag{41}$$

In the exchange-only limit, these are the TDHF or RPA equations ([14], p. 89).

3.4.2. *Excitation energies and energy gaps*

If there is no driving term $\Delta v(\mathbf{r}t)$ in these TDOFT equations, discrete excitation energies are determined by values of $\hbar\omega$ for which the determinant of the residual homogeneous equations vanishes. The simplest internally consistent approximation to an excitation energy is obtained by limiting the summation to the diagonal term $j, b = i, a$. The second line vanishes because of antisymmetry, $(ii|\hat{f}_{\mathrm{hxc}}|aa) \equiv 0$, and the first line reduces to a single equation

$$\{\epsilon_a - \epsilon_i - \hbar\omega - (ai|\hat{f}_{\mathrm{hxc}}|ai)\}X_i^a = 0 \tag{42}$$

Neglecting correlation response, this implies $\hbar\omega = \epsilon_a - \epsilon_i - (ai|\bar{u}|ai)$, a well-known formula for first-order hole–particle excitation energies [32,33].

The two-electron integral depends strongly on orbital localization. Separate localization transformations of occupied and unoccupied orbitals should be carried out to minimize the excitation energy. This provides a mechanism to reduce the Hartree–Fock band gaps. The correlation response kernel has the physical effect of screening the Hartree–Fock exchange terms, as is well known from many-body theory. Such direct effects on energy gaps are evident from the OFT formalism.

3.5. Implications

DFT is the ground-state limit of a more general OFT. The OEL equations of OFT do not necessarily contain local potential functions. Tests of locality fail for the effective exchange potential in the UHF exchange-only model. Dirac's derivation of TDHF theory can readily be extended to a TDOFT that includes electronic correlation. The exchange-only limit of this theory is consistent with TDHF and with the RPA in many-body theory.

4. SYNTHESIS: ALL EXACT THEORIES ARE THE SAME

The preceding discussion has considered the 'locality hypothesis' in DFT: that density functionals in this theory have Fréchet functional derivatives which take the form of local potential functions $\delta F/\delta\rho(\mathbf{r}) = v_F(\mathbf{r})$. Counterexamples from Thomas–Fermi theory (kinetic energy), from Hartree–Fock as a model theory (exchange energy), and from linear-response theory (failure in the pure-exchange limit) appear to contradict the implications of modern functional analysis [2,21,22]. It will be shown here that this apparent inconsistency can be resolved by extending the definition of such density functional derivatives to the more general class of Gâteaux derivatives [1,2,23], which are the generalizations in functional analysis of analytic partial derivatives. This has the very important implication that if DFT is strictly limited to normalized ground states it cannot determine the variational equations required for specific applications. Following well-established variational theory, as used for example by Schrödinger [34], it is necessary to extend the definition of any density functional to include unconstrained densities in an infinitesimal neighborhood of each ground-state density in the Banach space of densities. The OFT discussed above defines such an extension for all practical applications of the theory. When this extended definition is used, 'exact' DFT and OFT become alternative statements of the same theory. This underlying theory is itself simply a particular formal model of the many-body theory of interacting electrons.

4.1. Implications of functional analysis

The mathematical issues relevant to the definition of density functional derivatives can be considered in the simple model of noninteracting electrons. As in the KSC [4], this singles out the kinetic energy. The N-electron Hamiltonian operator is $H = \hat{T} + \hat{V}$. Orbital functional derivatives determine the noninteracting OEL equations

$$\hat{t}\phi_i = \{\epsilon_i - v\}\phi_i \tag{43}$$

which just restate the orbital Schrödinger equation for a given external local potential $v(\mathbf{r})$. When restricted to ground states, the orbital functional $T = E - V$ becomes a density functional $T_s[\rho]$. The density functional derivative is defined such that

$$\delta T_s = \int d^3\mathbf{r} \sum_i n_i \left\{ \delta\phi_i^* \frac{\delta T_s}{\delta\rho} \phi_i + \mathrm{cc} \right\} \tag{44}$$

The symbol T_s here refers to an extended definition, valid in any infinitesimal function-neighborhood of a normalized ground state, such that

$$\delta T_s = \int d^3\mathbf{r} \sum_i n_i (\delta\phi_i^* \hat{t}\phi_i + \mathrm{cc}) = \int d^3\mathbf{r} \sum_i n_i (\delta\phi_i^* \{\epsilon_i - v\}\phi_i + \mathrm{cc}) \tag{45}$$

In terms of partial densities $\left(\rho = \sum_i n_i\rho_i\right)$,

$$\delta T_s = \int d^3\mathbf{r} \sum_i n_i \{\epsilon_i - v(\mathbf{r})\}\delta\rho_i(\mathbf{r}) \tag{46}$$

The eigenvalue terms drop out for variations constrained by normalization.

The implied functional derivative is $\delta T_s / n_i \delta\rho_i = \epsilon_i - v(\mathbf{r})$. Since $\rho = \sum_i n_i\rho_i$, this implies the elementary chain rule

$$\frac{\delta T_s}{n_i\,\delta\rho_i} = \frac{\partial\rho}{n_i\,\partial\rho_i}\frac{\delta T_s}{\delta\rho} = \frac{\delta T_s}{\delta\rho} \tag{47}$$

This is a *Gâteaux* derivative, whose value varies with 'direction' in the function space [1,2]. An explicit orbital index is not needed if $\delta T_s/\delta\rho$ is considered to be the linear operator $\mathcal{H} - v = \hat{t}$. This confirms the chain rule for functional derivatives

$$\frac{\delta T_s}{\delta\rho}\phi_i = \frac{\delta T}{n_i\,\delta\phi_i^*} = \hat{t}\phi_i \tag{48}$$

4.1.1. *Is there an exact Thomas–Fermi theory?*

For fixed normalization the Lagrange multiplier terms in δT_s vanish. If these constants are undetermined, it might appear that they could be replaced by a single global constant μ. If so, this would result in the formula [22] $\delta T_s = \int d^3\mathbf{r}\{\mu - v(\mathbf{r})\}\delta\rho(\mathbf{r})$. Then the density functional derivative would be a local function $v_T(\mathbf{r})$ such that $\delta T_s/\delta\rho = v_T(\mathbf{r}) = \mu - v(\mathbf{r})$. This is the Thomas–Fermi equation, so that the locality hypothesis for v_T implies an exact Thomas–Fermi theory for noninteracting electrons.

However, as shown above, comparison with the orbital Schrödinger equations implies a sum rule $\sum_i n_i\epsilon_i = N\mu$. This sum rule requires all $\epsilon_i = \mu$, in violation of the exclusion principle for more than two electrons [7]. Thus it is incorrect to assume that the undetermined constants in ground-state theory can be set to the same value for different orbital energy levels. In contrast, Kohn and Sham [4] were correct in substituting $\hat{t}$ for $\delta T/\delta\rho$ in the KS-equations. There is no equivalent exact Thomas–Fermi theory.

4.1.2. *Atoms with noninteracting electrons*

For hydrogenic wave functions,

$$\frac{\partial T}{\partial Z} = \frac{2T}{Z} = \int d^3\mathbf{r}\frac{Z}{r}\frac{\partial\rho}{\partial Z} \tag{49}$$

If an exact local potential $v_T(\mathbf{r})$ did exist, it could be constructed by the sum rule

$$v_T(\mathbf{r})\rho(\mathbf{r}) = \sum_i n_i\phi_i^*(\mathbf{r})\hat{t}\phi_i(\mathbf{r}) = \sum_i n_i\phi_i^*(\mathbf{r})\epsilon_i\phi_i(\mathbf{r}) + \frac{Z}{r}\rho(\mathbf{r}) \tag{50}$$

If $v_T(\mathbf{r})$ were a functional derivative, then

$$P_T = \frac{\partial T}{\partial Z} - \int d^3\mathbf{r}v_T(\mathbf{r})\frac{\partial\rho}{\partial Z} = 0 \tag{51}$$

Values computed for He, Be, and Ne, respectively, are $P_T = 0.00000$, 1.38904, 9.23714 (Hartree units). This confirms that a Fréchet derivative of the functional $T_s[\rho]$ does not exist for more than two electrons.

4.1.3. *Interacting electrons*

For $E = T + U + V + E_c$, define the orbital functional $F = E - V$. The OEL equations are

$$\frac{\delta F}{n_i\delta\phi_i^*} = \{\mathcal{G} - \hat{v}\}\phi_i = \{\hat{t} + \hat{u} + \hat{v}_c\}\phi_i = \{\epsilon_i - \hat{v}\}\phi_i \tag{52}$$

For ground states, F reduces to a density functional $F_s[\rho]$ if the external potential is local. The symbol F_s here refers to a definition extended to infinitesimal function-neighborhoods of normalized ground-state densities. The density functional derivative is defined by

$$\delta F_s = \int d^3\mathbf{r} \sum_i n_i \left\{ \delta\phi_i^* \frac{\delta F_s}{\delta\rho} \phi_i + \mathrm{cc} \right\} \tag{53}$$

For orbital variations about ground-state solutions of the OEL equations,

$$\begin{aligned} \delta F_s &= \int d^3\mathbf{r} \sum_i n_i (\delta\phi_i^* \{\hat{t} + \hat{u} + \hat{v}_c\} \phi_i + \mathrm{cc}) \\ &= \int d^3\mathbf{r} \sum_i n_i (\delta\phi_i^* \{\epsilon_i - \hat{v}\} \phi_i + \mathrm{cc}) \end{aligned} \tag{54}$$

When $\hat{v}$ is a local function this becomes $\delta F_s = \int d^3\mathbf{r} \sum_i n_i \{\epsilon_i - v(\mathbf{r})\} \delta\rho_i(\mathbf{r})$. The partial functional derivatives are local functions $\delta F_s / n_i \delta\rho_i = \epsilon_i - v(\mathbf{r})$, where the Lagrange multipliers are determined by normalization. $\delta F_s / \delta\rho$ is a *Gâteaux* derivative [1,2], equivalent [23] to the linear operator $\mathcal{G} - v$.

The argument has come full circle, reproducing the chain rule

$$\frac{\delta F_s}{\delta\rho} \phi_i = \frac{\delta F}{n_i \, \delta\phi_i^*} = \{\hat{t} + \hat{u} + \hat{v}_c\} \phi_i \tag{55}$$

There is no implication that the effective potentials are local functions.

4.2. Exact orbital functionals for exchange and correlation

By a suitable definition of correlation energy, the N-electron variational energy can be expressed as a sum of the orbital functionals $E = T + V + E_h + E_x + E_c$ [5]. Given any rule $\Psi \longrightarrow \Phi$, define $E_c = E - E_0$, where $E_0 = (\Phi|H|\Phi)$ is a sum of explicit orbital functionals. E_c can be expressed as a formally exact but implicit functional of the occupied orbitals of Φ. [17] In practice, E_c must be approximated. However, any proposed formula for $E_{xc}[\rho]$ or $E_c[\rho]$ defines an OFT in which the KS functional $F_s[\rho]$ is generalized to an orbital functional F that is equivalent for ground states. The OEL equations that minimize the energy functional always take the form $\delta E / n_i \delta\phi_i^* = \mathcal{G}\phi_i = \epsilon_i \phi_i$, $i \leq N$. Spin indices and sums are implied here as in the preceding sections.

4.2.1. Exact explicit orbital functionals

E_0 is a sum of explicit orbital functionals, $T + V + E_h + E_x$, with explicit orbital functional derivatives. Defining $\hat{t} = -\frac{1}{2}\nabla^2$ for kinetic energy,

$$T = \sum_i n_i (i|\hat{t}|i); \qquad \frac{\delta T}{n_i \, \delta\phi_i^*} = \hat{t}\phi_i \tag{56}$$

For a general nonlocal external potential,

$$V = \sum_i n_i (i|\hat{v}|i); \qquad \frac{\delta V}{n_i \delta \phi_i^*} = \hat{v}\phi_i \tag{57}$$

Defining $u = 1/r_{12}$, for the Hartree energy,

$$E_\mathrm{h} = \tfrac{1}{2}\sum_{i,j} n_i n_j (ij|u|ij); \quad \frac{\delta E_\mathrm{h}}{n_i\,\delta\phi_i^*} = \sum_j n_j (j|u|j)\phi_i = v_h \phi_i \tag{58}$$

For the exchange energy,

$$E_\mathrm{x} = -\tfrac{1}{2}\sum_{i,j} n_i n_j (ij|u|ji); \quad \frac{\delta E_\mathrm{x}}{n_i\,\delta\phi_i^*} = -\sum_j n_j (j|u|i)\phi_j = \hat{v}_\mathrm{x}\phi_i \tag{59}$$

There is no self-interaction.

4.2.2. *Correlation energy as an exact orbital functional*

Using unsymmetric normalization, $(\Phi|\Psi) = (\Phi|\Phi) = 1$, $(H - E)\Psi = 0$ implies $E = (\Phi|H|\Psi) = (\Phi|H|\Phi) + (\Phi|H|Q\Psi) = E_0 + E_\mathrm{c}$, where $Q = I - \Phi\Phi^\dagger$ and $E_\mathrm{c} = (\Phi|H|Q\Psi)$. A formal simplification results from using the Brueckner reference state Φ, defined by maximum projection onto a given N-electron state Ψ (subsequently renormalized as indicated above) [35–37]. Because $(\delta\Phi|Q\Psi) = 0$ implies $(\Phi_i^a|Q\Psi) = 0$ for all particle–hole virtual excitations, $i \leq N < a$, one-electron matrix elements are eliminated from matrix elements $(\Phi|H|Q\Psi)$ in the Brueckner–Brenig orbital basis [36]. The Brueckner condition $(\delta\Phi|\Psi) = 0$ implies that $(\delta\Phi|H|\Psi) = 0$ for any energy eigenstate Ψ, which must be compatible with the OEL equations for occupied orbitals [37].

The correlation energy is given implicitly by

$$E_\mathrm{c} = -(\Phi|H[Q(H - E_0 - E_\mathrm{c} - i\eta)Q]^{-1}H|\Phi) \tag{60}$$

an exact 'optical potential' derived by partitioning [31]. The coefficients of two-particle/two-hole virtual excitations Φ_{ij}^{ab} $(i,j \leq N < a,b)$ in $Q\Psi$ are

$$c_{ij}^{ab} = (ab|\bar{c}|ij) = (\Phi_{ij}^{ab}|Q\Psi) = -(\Phi_{ij}^{ab}|[Q(H - E_0 - E_\mathrm{c} - i\eta)Q]^{-1}H|\Phi) \tag{61}$$

This defines an exact but implicit formula,

$$\begin{aligned} E_\mathrm{c} &= \sum_{i<j} n_i n_j \sum_{a<b} (1 - n_a)(1 - n_b)(\Phi|H|\Phi_{ij}^{ab})c_{ij}^{ab} \\ &= \sum_{i<j} n_i n_j \sum_{a<b} (1 - n_a)(1 - n_b)(ij|\bar{u}|ab)(ab|\bar{c}|ij) \end{aligned} \tag{62}$$

The orbital functional derivative $\delta E_\mathrm{c}/(n_\mathrm{i}\delta\phi_\mathrm{i}^*) = \hat{v}_\mathrm{c}\phi_i$ is derived taking variations of unoccupied orbitals induced by unitarity into account. This gives an explicit formula for any orbital-functional model of E_xc (e.g. LDA [4] or Colle–Salvetti. [38]) In an iterative loop with specified $(ab|\bar{c}|ij)$, the effective correlation 'potential' is a linear operator $\hat{v}_c$ whose kernel is

$$\begin{aligned} v_c(\mathbf{r},\mathbf{r}') = {} & \tfrac{1}{2}\sum_j n_j \sum_{b,c}(1-n_c)(1-n_b)(j|\bar{u}|b)\phi_c(\mathbf{r})\phi_c^*(\mathbf{r}')(b|\bar{c}|j) \\ & -\tfrac{1}{2}\sum_{j,k} n_k n_j \sum_b (1-n_b)(b|\bar{c}|j)\phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')(j|\bar{u}|b). \end{aligned} \qquad (63)$$

This operator is consistent with the leading terms in quasiparticle self-energies implied by many-body perturbation theory (e.g. [14], p. 68). Because of the antisymmetric form of all matrix elements, there is no self-interaction.

4.3. Quasiparticles and Landau theory

4.3.1. Nonintegral occupation numbers

If occupation numbers are treated as parametric variables, the OFT functional $E[\{\phi_i; n_i\}]$ interpolates between the physical states with integral occupation numbers. The OEL equations of the theory are well-defined for fractional occupation numbers $0 \le n_i \le 1$. This purely mathematical interpolation procedure was exploited by Slater and Wood [39] to provide a smooth connection between the different physical states. Janak [40] used this concept of nonintegral occupation numbers to prove that one-electron energies in DFT are parametric partial derivatives $\epsilon_i = \partial E/\partial n_i$. Janak's theorem is proven below for a general OFT. The key idea of Slater and Wood is that physical energy differences can be obtained by integrating these partial derivatives as functions of fractional occupation numbers. A similar idea was proposed by Landau [41,42] in the context of a free-energy function of occupation numbers described by Fermi–Dirac statistics, with orbital energies ϵ_i parametrized as functions of $\{n_i\}$.

4.3.2. Janak's theorem

In OFT, E is a functional of Φ, expressed as integrals over the Dirac matrix $\sum_i \phi_i(\mathbf{r}) n_i \phi_i^*(\mathbf{r}')$. For $n_i \neq 0$ this implies two chain rules:

$$\begin{aligned} \frac{\delta E}{\delta \phi_i^*} &= n_i \mathcal{G}\phi_i = n_i \frac{\delta E}{\delta(n_i\phi_i^*)} \\ \frac{\partial E}{\partial n_i} &= \int \mathrm{d}^3\mathbf{r}\,\phi_i^* \frac{\delta E}{\delta(n_i\phi_i^*)} \end{aligned} \qquad (64)$$

Hence if n_i is allowed to vary,

$$\delta E = \sum_i \delta n_i \int \mathrm{d}^3\mathbf{r}\,\phi_i^* \mathcal{G}\phi_i + \sum_i n_i \int \mathrm{d}^3\mathbf{r}\{\delta\phi_i^* \mathcal{G}\phi_i + \mathrm{cc}\} \qquad (65)$$

For variations of normalized solutions of OEL equations, $\int \phi_i^* \mathcal{G} \phi_i = \epsilon_i$ and $\int \mathrm{d}\phi_i^* \mathcal{G} \phi_i = \epsilon_i \int \mathrm{d}\phi_i^* \phi_i = 0$. This implies Janak's theorem:

$$\mathrm{d}E = \sum_i \frac{\partial E}{\partial n_i} \mathrm{d}n_i = \sum_i \epsilon_i \, \mathrm{d}n_i \tag{66}$$

The eigenvalues ϵ_i are Landau quasiparticle energies [37].

4.3.3. Landau quasiparticles

Landau [41–43] proposed that interacting electrons can be described as a collection of Fermi–Dirac quasiparticles, 'dressed' electrons modified by a self-consistent interaction. Landau postulates a variational energy function of occupation numbers, whose partial derivatives $\epsilon_i = \partial E / \partial n_i$ define the quasiparticle energies for Fermi–Dirac statistics. In Landau's theory, interactions are represented by the parametrized dependence of one-electron energies on occupation numbers. For example, electronic self-interaction is characterized by $\partial \epsilon_i / \partial n_i$, which should vanish in an exact theory. Since the quasiparticles are Fermions, entropy and free energy are defined. When applied to an electron gas, this provides a conceptual basis for Fermi-liquid theory. The parametrized electronic interactions can describe strongly correlated systems, such as magnetic impurities in metals. Although the Landau theory can be derived from many-body theory [43], it is not based on an effective one-electron Hamiltonian and is not adapted to first-principles calculations.

This concept is essentially the same as that of modelling an interacting N-electron system by a reference state constructed from one-electron orbital functions determined by a self-consistent field. Janak's theorem for a general OFT suggests that Landau's parametric quasiparticle energies can be identified with eigenvalues of the OEL equations. The present extension of OFT to include formally exact correlation energy may provide a formalism within which Landau theory can be implemented as an *ab initio* computational method, even for strongly correlated systems.

5. CONCLUSIONS

The principal conclusion of the present analysis is that an 'exact' DFT is not possible if restricted to local potential functions. This excludes an exact Thomas–Fermi theory for more than two electrons, but it is shown here that DFT in the local density approximation (LDA) and the optimimized effective potential (OEP) model are sound variational theories. An exact OFT exists, but must be implemented using nonlocal potentials.

Computational methods based on multiple scattering theory (MST) are currently formulated only for local potential functions [44]. New formalism may be necessary in order to extend such methods to nonlocal potentials, but this appears to be necessary if electronic self-interaction is to be eliminated systematically. A *caveat* is that nonlocal exchange by itself produces a well-known Fermi-surface anomaly in metals, which must be cancelled by electronic correlation. The challenge to theory is to devise a formalism that retains nonlocal exchange and correlation, but exactly removes the singularity at the Fermi level [45].

The validity of Janak's theorem in OFT opens up the prospect of incorporating *ab initio* methods into Landau theory for applications to strongly correlated systems, especially when combined with the procedure of integrating over fractional occupation numbers to obtain physical energy differences.

Exact linear-response theory based on TDOFT is a potentially powerful methodology for treating excitations and polarization response.

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Density Functional Approach to the Many-Body Problem: Key Concepts and Exact Functionals

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Abstract

We give an overview of the fundamental concepts of density functional theory. We give a careful discussion of the several density functionals and their differentiability properties. We show that for nondegenerate ground states we can calculate the necessary functional derivatives by means of linear response theory, but that there are some differentiability problems for degenerate ground states. These problems can be overcome by extending the domains of the functionals. We further show that for every interacting v-representable density we can find a noninteracting v-representable density arbitrarily close and show that this is sufficient to set up a Kohn–Sham scheme. We finally describe two systematic approaches for the construction of density functionals.

Contents

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1. INTRODUCTION

In this paper we give an overview of the foundations of density functional theory for stationary systems. In the discussion we try to be as precise as possible, and we therefore carefully discuss several exact density functionals and the domains of densities on which they are defined. At the heart of almost any application of density functional theory lies the Kohn–Sham equations. These equations describe a noninteracting system that is required to produce the ground state density of an interacting system. Therefore, any discussion of the validity of these equations has to focus on how well we can approximate a density of an interacting system with that of a noninteracting system. Closely related to this question is whether or not the exact functionals that we defined have functional derivatives. This is because the various potentials, such as the Kohn–Sham potential, in density functional theory appear as functional derivatives of the energy with respect to the density. The investigation of the existence of functional derivatives will form a central theme of this review.

A large part of this work will follow the proofs of the fundamental papers by Lieb [1] and Englisch and Englisch [2,3]. In this paper we try to make these two important works more accessible by providing some background on the mathematics involved. We further show, from a more physical viewpoint, how to calculate functional derivatives by response theory and show that for nondegenerate ground states the static density response function is invertible. We also show that for every interacting v-representable density there is a noninteracting v-representable density arbitrarily close to it and that this is sufficient to set up a Kohn–Sham scheme. We finally discuss two systematic approaches for the construction of the exchange–correlation functional and provide an outlook and conclusions.

2. DEFINITION OF THE PROBLEM

Density functional theory in its earliest formulation by Hohenberg, Kohn and Sham [5,8] aims at a description of the description of ground state properties of many-electron systems in terms of the electron density. One may wonder why this is possible. Let us therefore investigate this point more closely. Consider a Hamiltonian of a stationary many-body system

$$\hat{H}_v = \hat{T} + \hat{V} + \hat{W} \tag{1}$$

where $\hat{T}$ is the kinetic energy of the electrons, $\hat{V}$ the external potential, and $\hat{W}$ the two-particle interaction. We denote the Hamilton operator $\hat{H}_v$ with a subindex v to indicate that we will consider the Hamiltonian as a functional of the external potential v. The constituent terms are explicitly given as:

$$\hat{T} = \sum_{i=1}^{N} -\tfrac{1}{2}\nabla_i^2 \tag{2}$$

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{3}$$

$$\hat{W} = \sum_{i>j}^{N} w(|\mathbf{r}_i - \mathbf{r}_j|) \tag{4}$$

where $w(|\mathbf{r}|) = 1/|\mathbf{r}|$ will in our discussion always be the Coulomb potential. We are interested in electronic systems, i.e., molecules and solids. For all these systems the kinetic energy operator $\hat{T}$ and two-particle interaction $\hat{W}$ are identical. They only differ in the form of the external potential $v(\mathbf{r})$ and the number of electrons N. The properties of all these systems can therefore be regarded as a functional of the external potential v. This is in particular the case for the ground state wavefunction $|\Psi[v]\rangle$ and the ground state energy $E[v]$, which are of course related by the Schrödinger equation

$$(\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \tag{5}$$

At first sight we have not gained much by this viewpoint, the problem looks as difficult as before. However, the problem will have a different appearance once we eliminate the potential in favor of the electron density. One may wonder what is so particular about the relation between the density and the potential. Let us therefore look specifically at the term that describes the external potential. It can be written as:

$$\hat{V} = \int \mathrm{d}^3 r \, v(\mathbf{r})\hat{n}(\mathbf{r}) \tag{6}$$

where we defined the density operator by

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{7}$$

The expectation value of $\hat{V}$ is given by

$$\langle \Psi|\hat{V}|\Psi\rangle = \int \mathrm{d}^3 r \, n(\mathbf{r})v(\mathbf{r}) \tag{8}$$

where $n(\mathbf{r})$ the electron density. The electron density is obtained from the many-body wavefunction, which in our case will usually be the ground state wavefunction of Hamiltonian $\hat{H}_v$, by

$$n(\mathbf{r}_1) = \langle \Psi|\hat{n}(\mathbf{r}_1)|\Psi\rangle = N \sum_{\sigma_1 \cdots \sigma_N} \int \mathrm{d}^3 r_2 \cdots \mathrm{d}^3 r_N |\Psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N)|^2 \tag{9}$$

In this expression σ_i is the spin variable for electron i. The physical interpretation of the density is that $n(\mathbf{r})\Delta V$ is proportional to the probability of finding an electron in an infinitesimal volume ΔV around $\mathbf{r}$. Note that in the definition equation (9) we sum over the spin coordinate σ_1 so we do not distinguish between the probabilities of finding up or down spin electrons at $\mathbf{r}$. We see from equation (8) that the external potential $v(\mathbf{r})$ and the electron density $n(\mathbf{r})$ are conjugate variables. With this we mean that they occur as a simple product in the contribution of the external potential to the energy. It is exactly this property that allows us to prove the Hohenberg–Kohn theorem, which establishes a 1–1-correspondence between the density and the external potential. We can therefore go from a functional $E[v]$ of the external potential to a functional $E[n]$ of the density. We can ask ourselves whether there is any reason that $E[n]$ would be easier to calculate than $E[v]$. *A priori* there is no reason to expect this. However, we will see that the determination of $E[n]$ is equivalent to the solution of a set of one-particle equations, known as the Kohn–Sham equations, with a potential $v_s[n]$ that is also a functional of the density. By now we know that we can find practical and useful approximations for this potential $v_s[n]$ and that the Kohn–Sham equations have been successfully applied to the calculation of properties of many electronic systems. However, as in any physical theory, there are a number of assumptions made in the transformation to the Kohn–Sham one-particle equations. The aim of this paper is to discuss these assumptions and thereby the validity of the Kohn–Sham equations.

3. CONDITIONS ON THE ELECTRON DENSITY AND THE EXTERNAL POTENTIALS

We begin by giving a discussion of the properties of the two key objects in density functional theory, the density n and the external potential v. The density has the obvious properties

$$n(\mathbf{r}) \geq 0, \qquad \int \mathrm{d}^3 r\, n(\mathbf{r}) = N \tag{10}$$

These properties follow directly from the definition of the density and the usual normalization condition on the wavefunction. If we take into account that the density is obtained as the density of a bound eigenstate of Hamiltonian (1) we can derive further conditions. For this we put the physical constraint on the many-body system that it has a finite expectation value of the kinetic energy, i.e.,

$$T[\Psi] = \tfrac{1}{2} \sum_{i=1}^{N} \sum_{\sigma_1 \cdots \sigma_N} \int \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N |\nabla_i \Psi|^2 < \infty \tag{11}$$

At this point it is useful to introduce a new space of functions. We say that a function f is in $H^1(\mathcal{R}^n)$ ($\mathcal{R}$ denotes the real numbers) if

$$\|f\| = \left(\int \mathrm{d}^n \mathbf{r} (|f(\mathbf{r})|^2 + |\nabla f(\mathbf{r})|^2 \right)^{1/2} < \infty \tag{12}$$

The space of functions $H^1(\mathcal{R}^n)$ is called a Sobolev space. The supindex 1 refers to the fact that the definition of the norm contains only first order derivatives.

We therefore see that finiteness of the kinetic energy implies that Ψ is an element of the function space $H^1(\mathcal{R}^{3N})$. Differentiation of equation (9) and use of the Cauchy–Schwarz inequality then leads to [1]

$$(\nabla_1 n(\mathbf{r}_1))^2 \le 4Nn(\mathbf{r}_1) \sum_{\sigma_1 \cdots \sigma_N} \int \mathrm{d}^3 r_2 \cdots \mathrm{d}^3 r_N |\nabla_1 \Psi|^2 \tag{13}$$

and hence

$$\tfrac{1}{2} \int \mathrm{d}^3\, r(\nabla \sqrt{n(\mathbf{r})})^2 \le T[\Psi] < \infty \tag{14}$$

We see that the finiteness of the kinetic energy puts a constraint on the density. From equation (12) we see that $\sqrt{n}$ belongs to $H^1(\mathcal{R}^3)$. We also see that if we consider systems with a finite kinetic energy, then we only need to consider the following set of densities

$$\mathcal{S} = \left\{ n | n(\mathbf{r}) \ge 0, \sqrt{n} \in H^1(\mathcal{R}^3), \int \mathrm{d}^3 r\, n(\mathbf{r}) = N \right\} \tag{15}$$

This set of densities has a property which will be of importance later, namely $\mathcal{S}$ is convex. With this we mean that if n_1 and n_2 are elements of $\mathcal{S}$, then also $\lambda n_1 + (1-\lambda)n_2$ is an element of $\mathcal{S}$ where $0 \le \lambda \le 1$. This property is easily proven using the Cauchy–Schwarz inequality. Now we will derive constraints on the allowed set of external potentials. In order to do this we introduce some other function spaces. We say that a given function f belongs to the space L^p if

$$\|f\|_p = \left(\int \mathrm{d}^3 r |f(\mathbf{r})|^p \right)^{1/p} < \infty \tag{16}$$

Note that here we only consider functions on the usual three-dimensional coordinate space $\mathcal{R}^3$. The letter L refers to Lebesque integration, a feature that assures that the function spaces are complete (complete normed spaces are also called Banach spaces). We will, however, not go into the detailed mathematics and refer the interested reader to the literature [4]. We just note that for continuous functions the integral is equivalent to the usual (Riemann) integral. Equation (16) defines a norm on the space L^p and we see from equation (10) that the density belongs to L^1. From the condition of finite kinetic energy and the use of a Sobolev inequality one can show that [1]

$$\int \mathrm{d}^3 r\, n^3(\mathbf{r}) \le C \int \mathrm{d}^3 r (\nabla \sqrt{n(\mathbf{r})})^2 < \infty \tag{17}$$

where $C = 3(\pi/2)^{4/3}$. In other words, the finiteness of the kinetic energy implies that the density is also in the space L^3. Since we already know that $n \in L^1$ we find that the density is element of the intersection of both spaces, i.e., $n \in L^1 \cap L^3$.

We also see from the inequality (17) that $\mathcal{S}$ is a subset of $L^1 \cap L^3$. Let us now see what this implies for the allowed set of external potentials when we require the expectation value of the external potential to be finite, i.e., we require

$$\left| \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}) \right| \leq \| n v \|_1 < \infty \tag{18}$$

If the potential is bounded, i.e., $|v(\mathbf{r})| < M$ for some finite number M then

$$\left| \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}) \right| \leq \sup |v(\mathbf{r})| N < \infty \tag{19}$$

The space of bounded functions is called L^∞ and has the norm

$$\| f \|_\infty = \sup |f(\mathbf{r})| \tag{20}$$

The supremum is defined to be the smallest number M such that $|f(\mathbf{r})| \leq M$ almost everywhere. The term 'almost everywhere' has a precise mathematical meaning for which we refer to the literature [4]. We almost never use it in the remainder of this paper. We therefore conclude that if $v \in L^\infty$ then the expectation value of the external potential is finite. To show this we used that $n \in L^1$. But we also know that $n \in L^3$ and if we make use of the Hölder inequality

$$\| f g \|_1 \leq \| f \|_p \| g \|_q \tag{21}$$

with $1/p + 1/q = 1$ we obtain

$$\| n v \|_1 \leq \| n \|_3 \| v \|_{3/2} \tag{22}$$

which is finite if $v \in L^{3/2}$. Therefore the most general set of potentials for which the expectation value $\langle \Psi | \hat{V} | \Psi \rangle$ is finite, is the set

$$L^{3/2} + L^\infty = \{ v | v = u + w, u \in L^{3/2}, w \in L^\infty \} \tag{23}$$

i.e., the set of potentials that can be written as a sum of a function from $L^{3/2}$ and a function from L^∞. This is also a normed function space with norm

$$\| v \| = \inf \{ \| u \|_{3/2} + \| w \|_\infty | v = u + w \} \tag{24}$$

In the remainder of this paper we will always consider the densities to be in the space $L^1 \cap L^3$ and the potentials in the space $L^{3/2} + L^\infty$. It is important to note that the Coulomb potential is in the latter set since we can write

$$\frac{1}{|\mathbf{r}|} = \frac{\theta(1 - |\mathbf{r}|)}{|\mathbf{r}|} + \frac{\theta(|\mathbf{r}| - 1)}{|\mathbf{r}|} \tag{25}$$

where θ is the Heaviside function, $\theta(x) = 0$ if $x \leq 0$ and $\theta(x) = 1$ if $x > 0$. One can readily check that the first and second terms on the right hand side are in $L^{3/2}$ and L^∞, respectively. One can easily extend this result to a finite sum of Coulomb potentials, and therefore every molecule can be described with the potentials in the space $L^{3/2} + L^\infty$. One may finally wonder what the condition of finite Coulombic electron–electron repulsion, i.e., $\langle \Psi | \hat{W} | \Psi \rangle < \infty$, would imply for the density. However, one can show that if the kinetic energy $\langle\Psi|\hat{T}|\Psi\rangle$ is finite then also $\langle\Psi|\hat{W}|\Psi\rangle$ is finite [1], so this does not yield any new constraints on the density.

4. THE HOHENBERG–KOHN THEOREM

The basis of density functional theory is provided by the Hohenberg–Kohn theorem [5]. We will provide a proof of this theorem for nondegenerate ground states. The case of degenerate ground states will be discussed later. The Hohenberg–Kohn theorem states that the density $n(\mathbf{r})$ of a nondegenerate ground state uniquely determines the external potential $v(\mathbf{r})$ up to an arbitrary constant. This means that the external potential is a well-defined functional $v[n](\mathbf{r})$ of the density.

In the proof essential use is made of the fact that the density and the potential are conjugate variables. For the same reason we can, for instance, prove that the two-particle interaction is a unique functional of the diagonal two-particle density matrix. The general mapping between N-particle density matrices and N-body potentials is discussed by De Dominicis and Martin [6].

Let us consider the subset $\mathcal{V} \subset L^{3/2} + L^{\infty}$ of potentials that yields a normalizable nondegenerate ground state. The solution of the Schrödinger equation provides us with a mapping from the external potential to the ground state wavefunction, $v(\mathbf{r}) \rightarrow |\Psi[v]\rangle$. Since we assume that we are dealing with nondegenerate ground states $|\Psi[v]\rangle$ is uniquely determined apart from a trivial phase factor. We have therefore established a map $C : \mathcal{V} \rightarrow \Phi$, where Φ is the set of ground states.

We will first prove that the map C is invertible. Suppose that $|\Psi_1\rangle$ and $|\Psi_2\rangle \in H^1(\mathcal{R}^{3N})$ correspond to external potentials v_1 and $v_2 \in L^{\infty} + L^{3/2}$ where $v_1 \neq v_2 + C$. We have to show that $|\Psi_1\rangle \neq |\Psi_2\rangle$. If we assume that $|\Psi_1\rangle = |\Psi_2\rangle = |\Psi\rangle$ then by subtraction of the Hamiltonian for $|\Psi_1\rangle$ and $|\Psi_2\rangle$ we find that

$$(\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle \tag{26}$$

If $v_1 - v_2$ is not constant in some region then Ψ must vanish in this region for the above equation to be true. However, if $v_1, v_2 \in L^{\infty} + L^{3/2}$ then $|\Psi\rangle$ cannot vanish on an open set (a set with nonzero measure) by the unique continuation theorem [1]. So we obtain a contradiction, and hence we must have made a wrong assumption. Therefore, $|\Psi_1\rangle \neq |\Psi_2\rangle$ and we obtain the result that different potentials (differing more than a constant) give different wavefunctions. Consequently, we find that the map C is invertible.

We now define the set $\mathcal{A}$ as the set of densities which come from a nondegenerate ground state, where we only consider ground state densities from potentials in the set $L^{\infty} + L^{3/2}$. The set $\mathcal{A}$ is obviously a subset of the previously defined set $\mathcal{S}$. From a given wavefunction in the set of ground states Φ we can calculate the density according to equation (9). This provides us with a second map $D : \Phi \rightarrow \mathcal{A}$ from ground state wavefunctions to ground state densities. Also this map is invertible.

To show this we calculate

$$\begin{aligned} E[v_1] &= \langle \Psi[v_1] | \hat{T} + \hat{V}_1 + \hat{W} | \Psi[v_1] \rangle < \langle \Psi[v_2] | \hat{T} + \hat{V}_1 + \hat{W} | \Psi[v_2] \rangle \\ &= \langle \Psi[v_2] | \hat{T} + \hat{V}_2 + \hat{W} | \Psi[v_2] \rangle + \int n_2(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))\, \mathrm{d}\mathbf{r} \\ &= E[v_2] + \int n_2(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))\, \mathrm{d}\mathbf{r} \end{aligned} \tag{27}$$

Likewise we find

$$E[v_2] < E[v_1] + \int n_1(\mathbf{r})(v_2(\mathbf{r}) - v_1(\mathbf{r}))\, \mathrm{d}\mathbf{r} \tag{28}$$

Adding both inequalities then yields the new inequality

$$\int \mathrm{d}^3 r (n_2(\mathbf{r}) - n_1(\mathbf{r}))(v_2(\mathbf{r}) - v_1(\mathbf{r})) < 0 \tag{29}$$

If we assume that $n_1 = n_2$ then we obtain the contradiction $0 < 0$ and we conclude that different ground states must yield different densities. Therefore the map D is also invertible. Consequently, the map $DC : \mathcal{V} \rightarrow \mathcal{A}$ is also invertible and the density therefore uniquely determines the external potential. This proves the Hohenberg–Kohn theorem.

Let us now pick an arbitrary density out of the set $\mathcal{A}$ of densities of nondegenerate ground states. The Hohenberg–Kohn theorem then tells us that there is a unique external potential v (to within a constant) and a unique ground state wavefunction $|\Psi[n]\rangle$ (to within a phase factor) corresponding to this density. This also means that the ground state expectation value of any observable, represented by an operator $\hat{O}$, can be regarded as a density functional

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle \tag{30}$$

In particular we can thus define the Hohenberg–Kohn functional F_{HK} on the set $\mathcal{A}$ as

$$F_{\mathrm{HK}}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle \tag{31}$$

With this functional we can define the energy functional E_v as

$$E_v[n] = \int n(\mathbf{r}) v(\mathbf{r})\, \mathrm{d}\mathbf{r} + F_{\mathrm{HK}}[n] \tag{32}$$

If n_0 is a ground state density corresponding to external potential v_0 and n an arbitrary other ground state density then

$$\begin{aligned} E_{v_0}[n] &= \int n(\mathbf{r}) v_0(\mathbf{r})\, \mathrm{d}\mathbf{r} + F_{\mathrm{HK}}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n] \rangle \\ &\geq \langle \Psi[n_0] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n_0] \rangle = E_{v_0}[n_0] \end{aligned} \tag{33}$$

Therefore

$$E[v] = \inf_{n \in \mathcal{A}} \left\{ \int n(\mathbf{r}) v(\mathbf{r}) \, \mathrm{d}\mathbf{r} + F_{\mathrm{HK}}[n] \right\} \tag{34}$$

and we see that the ground state energy of a many-body system can be obtained by minimization of a density functional. For application of this formula we have to know F_{HK} on the set $\mathcal{A}$. In practice it is, of course, impossible to calculate F_{HK} exactly on this set of densities. Instead one would prefer to make an explicit approximation for F_{HK} as is usually done within the Kohn–Sham scheme. Before we go into that let us first discuss some properties of F_{HK}. The functional F_{HK} is a convex functional, i.e., if $n_1, n_2 \in \mathcal{A}$ and if $\lambda_1 n_1 + \lambda_2 n_2 \in \mathcal{A}$ with $0 \leq \lambda_1, \lambda_2 \leq 1$ and $\lambda_1 + \lambda_2 = 1$ then

$$F_{\mathrm{HK}}[\lambda_1 n_1 + \lambda_2 n_2] \leq \lambda_1 F_{\mathrm{HK}}[n_1] + \lambda_2 F_{\mathrm{HK}}[n_2] \tag{35}$$

This is readily proven. Suppose that the ground state densities $n_1, n_2, \lambda_1 n_1 + \lambda_2 n_2 \in \mathcal{A}$ correspond to the external potentials v_1, v_2 and v. Then

$$\begin{aligned}
F_{\mathrm{HK}}[n] &= \langle \Psi[n] | \hat{T} + \hat{V} + \hat{W} | \Psi[n] \rangle - \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}) \\
&= \lambda_1 \langle \Psi[n] | \hat{H} | \Psi[n] \rangle + \lambda_2 \langle \Psi[n] | \hat{H} | \Psi[n] \rangle - \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}) \\
&\leq \lambda_1 \langle \Psi[n_1] | \hat{T} + \hat{W} | \Psi[n_1] \rangle + \lambda_2 \langle \Psi[n_2] | \hat{T} + \hat{W} | \Psi[n_2] \rangle \\
&\quad + \int (\lambda_1 n_1(\mathbf{r}) + \lambda_2 n_2(\mathbf{r})) v(\mathbf{r}) \, \mathrm{d}^3 r - \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}) \\
&= \lambda_1 F_{\mathrm{HK}}[n_1] + \lambda_2 F_{\mathrm{HK}}[n_2]
\end{aligned} \tag{36}$$

and we obtain the convexity of F_{HK}. Note, however, that the domain $\mathcal{A}$ of F_{HK} does not need to be convex, i.e., if $n_1, n_2 \in \mathcal{A}$ then not necessarily $\lambda_1 n_1 + \lambda_2 n_2 \in \mathcal{A}$ with $0 \leq \lambda_1, \lambda_2 \leq 1$ and $\lambda_1 + \lambda_2 = 1$. We will come back to this point later when we consider the differentiability of F_{HK}. Let us first collect our results in the form a theorem.

Theorem 1 (Hohenberg–Kohn). *The density n corresponding to a nondegenerate ground state specifies the external potential v up to a constant and the ground state wavefunction* $|\Psi[n]\rangle$ *up to a phase factor. Moreover,*

1. *Any ground state expectation value corresponding to an observable* $\hat{O}$ *is a functional of the density according to*

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle$$

2. *The ground state energy of a system with a nondegenerate ground state and an external potential v can be obtained from*

$$E[v] = \inf_{n \in \mathcal{A}} \left\{ \int n(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} + F_{HK}[n] \right\}$$

where $F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$.

3. F_{HK} *is convex.*

We finally discuss an interesting consequence of the Hohenberg–Kohn theorem. Suppose that in equation (29) we take $v_2 = v_1 + \epsilon \, \delta v$ where δv is not a constant. We therefore obtain potential v_2 by a small perturbation from potential v_1. By means of perturbation theory we can then calculate the change in the density which gives

$$n_2(\mathbf{r}) = n_1(\mathbf{r}) + \epsilon \, \delta n(\mathbf{r}) + O(\epsilon^2) \tag{37}$$

where δn can be calculated from the static density response function χ

$$\delta n(\mathbf{r}) = \int d^3 r' \, \chi(\mathbf{r}, \mathbf{r}') \, \delta v(\mathbf{r}') \tag{38}$$

The properties and explicit form of χ are described in more detail in a later section. Therefore

$$(v_2(\mathbf{r}) - v_1(\mathbf{r}))(n_2(\mathbf{r}) - n_1(\mathbf{r})) = \epsilon^2 \, \delta v(\mathbf{r}) \, \delta n(\mathbf{r}) + O(\epsilon^3) \tag{39}$$

If we insert this expression in equation (29) and divide by $\epsilon^2 > 0$ then we obtain:

$$\int d^3 r \, \delta v(\mathbf{r}) \, \delta n(\mathbf{r}) + O(\epsilon) < 0 \tag{40}$$

Now taking the limit $\epsilon \longrightarrow 0$ and expressing δn in terms of the response function we obtain

$$\int d^3 r \, d^3 r' \, \delta v(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') \, \delta v(\mathbf{r}') < 0 \tag{41}$$

This is true for an arbitrary nonconstant potential variation. We therefore see that the eigenvalues of χ, when we regard χ as an integral operator, are negative. Moreover we see that the only potential variation that yields a zero density variation is given by $\delta v = C$ where C is a constant. This implies that χ is invertible. We will go more closely into this matter in a later section where we will prove the same using the explicit form of the density response function.

5. KOHN–SHAM THEORY BY LEGENDRE TRANSFORMS

The method described in this section goes back to the work of De Dominicis and Martin [6]. This work discusses the relations between N-body potentials and N-particle density matrices, of which the density–potential relation to be discussed here is a special case. The ground state energy $E[v]$ and wavefunction $|\Psi[v]\rangle$ are considered to be functionals of the external potential through solving the time-independent Schrödinger equation

$$(\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \tag{42}$$

where the two-particle interaction $\hat{W}$ is kept fixed. From this equation we see that the ground state energy as a functional of the external potential v can also be written as:

$$E[v] = \langle\Psi[v]|\hat{H}_v|\Psi[v]\rangle \tag{43}$$

Our goal is now to go from the potential as our basic variable, to a new variable, which will be the electron density. The deeper reason that this is possible is that the density and the potential are conjugate variables. With this we mean that the contribution of the external potential to the total energy is simply an integral of the potential times the density. We make use of this relation if we take the functional derivative of the energy functional $E[v]$ with respect to the potential v :

$$\begin{aligned}\frac{\delta E}{\delta v(\mathbf{r})} &= \left\langle \frac{\delta \Psi}{\delta v(\mathbf{r})} |\hat{H}_v|\Psi \right\rangle + \left\langle \Psi|\hat{H}_v| \frac{\delta \Psi}{\delta v(\mathbf{r})} \right\rangle + \left\langle \Psi| \frac{\delta \hat{H}_v}{\delta v(\mathbf{r})} |\Psi \right\rangle \\ &= E[v] \frac{\delta}{\delta v(\mathbf{r})} \langle\Psi|\Psi\rangle + \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle = \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle = n(\mathbf{r})\end{aligned} \tag{44}$$

where we used the Schrödinger equation $\hat{H}_v|\Psi\rangle = E[v]|\Psi\rangle$ and the normalization condition $\langle\Psi|\Psi\rangle = 1$. Note that the equation above is nothing but a functional generalization of the well-known Hellmann–Feynman theorem [7]. Now we can go to the density as our basic variable by defining a Legendre transform

$$F[n] = E[v] - \int d^3r\, n(\mathbf{r})v(\mathbf{r}) = \langle\Psi[v]|\hat{T} + \hat{W}|\Psi[v]\rangle \tag{45}$$

where v must now be regarded as a functional of n. The uniqueness of such a mapping is guaranteed by the Hohenberg–Kohn theorem [5]. The set of densities for which the functional $F[n]$ is defined is the set of so-called v-representable densities. These are ground state densities for a Hamiltonian with external potential v. The question which constraints one has to put on a density to make sure that it is v-representable is known as the v-representability problem. We postpone a discussion of these matters to later sections. From $\delta E/\delta v = n$ it follows immediately that:

$$\frac{\delta F}{\delta n(\mathbf{r})} = -v(\mathbf{r}) \tag{46}$$

This is our first basic relation. In order to derive the Kohn–Sham equations we define the following energy functional for a system of noninteracting particles with external potential v_s and with ground state wavefunction $|\Phi[v_s]\rangle$:

$$E_s[v_s] = \langle\Phi[v_s]|\hat{T} + \hat{V}_s|\Phi[v_s]\rangle \tag{47}$$

with Legendre transform

$$F_s[n] = E[v_s] - \int d^3r\, n(\mathbf{r}) v_s(\mathbf{r}) = \langle \Phi[v_s] | \hat{T} | \Phi[v_s] \rangle \tag{48}$$

and derivatives

$$\frac{\delta E_s}{\delta v_s(\mathbf{r})} = n(\mathbf{r}) \tag{49}$$

$$\frac{\delta F_s}{\delta n(\mathbf{r})} = -v_s(\mathbf{r}) \tag{50}$$

We see that $F_s[n]$ in equation (48) is the kinetic energy of a noninteracting system with potential v_s and density n. For this reason the functional F_s is usually denoted by T_s. In the following we will adopt this notation. Finally we define the exchange–correlation functional $E_{\text{xc}}[n]$ by the equation

$$F[n] = T_s[n] + \tfrac{1}{2} \int d^3r\, d^3r'\, n(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + E_{\text{xc}}[n] \tag{51}$$

This equation assumes that the functionals $F[n]$ and $T_s[n]$ are defined on the same domain of densities. We thus assume that for a given ground state density of an interacting system there is a noninteracting system with the same density. In other words, we assume that the interacting density is noninteracting-v-representable. If we differentiate equation (51) with respect to the density n we obtain

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3r'\, n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + v_{\text{xc}}(\mathbf{r}) \tag{52}$$

where

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})} \tag{53}$$

defines the exchange–correlation potential. Now the state $|\Phi[v_s]\rangle$ is a ground state for a system of noninteracting particles, and can therefore be written as an antisymmetrized product of single-particle orbitals $\varphi_i(\mathbf{r})$. If we now collect our results we see that we have converted the ground state problem into the following set of equations:

$$\begin{aligned} E[v] = \sum_{i=1}^{N} -\frac{1}{2} \int d^3r\, \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) + \int d^3r\, n(\mathbf{r}) v(\mathbf{r}) \\ + \frac{1}{2} \int d^3r\, d^3r'\, n(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + E_{\text{xc}}[n] \end{aligned} \tag{54}$$

$$\left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int d^3r'\, n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + v_{\text{xc}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \tag{55}$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 \tag{56}$$

The above equations constitute the ground state Kohn–Sham equations [8]. These equations turn out to be of great practical use. If we can find a good approximation for the exchange–correlation energy, we can calculate the exchange–correlation potential v_{xc} and solve the orbital equations self-consistently. The density we find in this way can then be used to calculate the ground state energy of the system.

The exchange–correlation functional is often split up into an exchange functional E_x and a correlation functional E_c as:

$$E_{\mathrm{xc}}[n] = E_x[n] + E_c[n] \tag{57}$$

in which the exchange and correlation functionals are defined by

$$E_x[n] = \langle \Phi_s[n]|\hat{W}|\Phi_s[n]\rangle - \tfrac{1}{2}\int \mathrm{d}^3r\,\mathrm{d}^3r'\; n(\mathbf{r})n(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|) \tag{58}$$

$$E_c[n] = \langle \Psi[n]|\hat{H}_v|\Psi[n]\rangle - \langle \Phi_s[n]|\hat{H}_v|\Phi_s[n]\rangle \tag{59}$$

In this equation $|\Phi_s[n]\rangle$ is the Kohn–Sham wavefunction and $|\Psi[n]\rangle$ the true ground state wavefunction of the interacting system with density n. Since the Kohn–Sham wavefunction is not a ground state wavefunction of the true system we see immediately from the variational principle that $E_c < 0$. We see also that the form of the exchange functional in terms of the Kohn–Sham orbitals is identical to that of the exchange energy within the well-known Hartree–Fock approximation. However, since the Kohn–Sham and Hartree–Fock orbitals differ, the value of $E_x[n]$ is not equal to the Hartree–Fock exchange. We finally remark that splitting up E_{xc} into an exchange and a correlation part has several disadvantages. First of all, this splitting has only meaning if the ground state of the true or Kohn–Sham system is nondegenerate. We will later see that $E_{\mathrm{xc}}[n]$ is a well-defined functional even for degenerate ground states, but that exchange and correlation separately are ill-defined in that case. Secondly, there are many cases, notably molecular dissociation cases, where the exchange-only theory is a bad starting point for the treatment of correlation effects and for which it is much easier to find good approximations for the combined exchange–correlation functional.

In this section we gave a derivation of the Kohn–Sham equations. However, in this derivation we made a number of assumptions. At first, we assumed that for every ground state density of an interacting system there is a noninteracting system, which has the same density in its ground state. Secondly, we assumed that the density functionals were differentiable. This assumes that the values of the functionals change smoothly with changes in the density. In the following sections we will investigate to which extent these assumptions are justified.

6. DEFINITION OF THE FUNCTIONAL DERIVATIVE

Let us start by defining what we mean with a functional derivative. The derivative we will talk about is what in the mathematical literature [9–14] is refered to as a Gâteaux derivative. Let $G : B \rightarrow \mathcal{R}$ be a functional from a normed function space B to the real numbers $\mathcal{R}$. If for every $h \in B$ there exist a continuous linear functional $\delta G/\delta f : B \rightarrow \mathcal{R}$ defined by:

$$\frac{\delta G}{\delta f}[h] = \lim_{\epsilon \rightarrow 0} \frac{G[f + \epsilon h] - G[f]}{\epsilon} \tag{60}$$

then $\delta G/\delta f$ is called the Gâteaux derivative in $f \in B$. If the limit exists but the resulting functional of h is not linear or continuous then this limit is called a Gâteaux variation. Note that the definition of the Gâteaux derivative is very similar to the definition of the directional derivative in vector calculus where the linear functional corresponds to the inner product of the gradient vector with the vector which specifies the direction of the differentiation. Often the linear functional $\delta G/\delta f$ can be written in the form:

$$\frac{\delta G}{\delta f}[h] = \int \mathrm{d}^3 r \, g(\mathbf{r}) h(\mathbf{r}) \tag{61}$$

If this is the case we write

$$g(\mathbf{r}) = \frac{\delta G}{\delta f(\mathbf{r})} \tag{62}$$

which we will call the functional derivative of G. Note further that although $\delta G/\delta f$ specifies a linear functional when acting on h, the function $g(\mathbf{r})$ depends, in general, on f in a nonlinear way. We also see that the set of functional derivatives on a function space B is equal to the set of continuous linear functionals on that space. This set is called the dual space of B and denoted B^*. For instance, the dual space of $B = L^1 \cap L^3$ is known to be the space $B^* = L^{3/2} + L^\infty$. From this we see that if the derivative of a density functional defined on the set of densities $L^1 \cap L^3$ exists then its derivative is in the set $L^{3/2} + L^\infty$.

Let us now mention a straightforward consequence of the definition of the Gâteaux derivative. Suppose that the functional G which we assume to be Gâteaux differentiable, has a minimum at f_0, i.e., $G[f] \geq G[f_0]$ for all $f \in B$. Then the function

$$g(\epsilon) = G[f_0 + \epsilon h] \geq G[f_0] \tag{63}$$

has a minimum in $\epsilon = 0$ and therefore the derivative of $g(\epsilon)$ in $\epsilon = 0$ vanishes. Thus,

$$0 = \frac{\mathrm{d}g}{\mathrm{d}\epsilon}(0) = \lim_{\epsilon \rightarrow 0} \frac{g(\epsilon) - g(0)}{\epsilon} = \frac{\delta G}{\delta f}(f_0)[h] \tag{64}$$

Therefore, a necessary condition for a differentiable functional for having a minimum at f_0 is that its Gâteaux derivative vanishes at f_0. We further prove one other fact that we will use later. If G is a convex functional, i.e.,

$$G[\lambda f_0 + (1 - \lambda)f_1] \leq \lambda G[f_0] + (1 - \lambda)G[f_1] \tag{65}$$

for $0 \leq \lambda \leq 1$ then the function

$$g(\lambda) = G[f_0 + \lambda(f_1 - f_0)] \tag{66}$$

is a continuous function on the interval [0,1]. To show this we will show that $g(\lambda)$ is convex. Take λ_1, λ_2, and ϵ from the interval [0,1]. Then

$$\begin{aligned} g(\epsilon\lambda_1 + (1 - \epsilon)\lambda_2) &= G[\epsilon(f_0 + \lambda_1(f_1 - f_0)) + (1 - \epsilon)(f_0 + \lambda_2(f_1 - f_0))] \\ &\leq \epsilon g(\lambda_1) + (1 - \epsilon)g(\lambda_2) \end{aligned} \tag{67}$$

Therefore $g(\lambda)$ is a convex real function on the interval [0,1] and hence continuous. The fact that convexity implies continuity is true for functions on the real axis, but this does not extend to infinite-dimensional spaces. Let us finally make some remarks on higher order derivatives. If $g(\epsilon) = G[f_0 + \epsilon h]$ defines a n-fold differentiable function of ϵ then we define the nth Gâteaux variation of G as:

$$\frac{\delta^n G}{\delta f^n}[h, \ldots, h] = \frac{\mathrm{d}^n g}{\mathrm{d}\epsilon^n}(0) \tag{68}$$

where $\delta^n G/\delta f^n$ has now n arguments h. If this expression defines a multilinear continuous functional then we call this the nth-order Gâteaux derivative of G. For more details on this point we refer to Ref. [9]. Again, if this expression can be written in the form:

$$\frac{\delta^n G}{\delta f^n}[h, \ldots, h] = \int \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_n g(\mathbf{r}_1 \cdots \mathbf{r}_n) h(\mathbf{r}_1) \cdots h(\mathbf{r}_n) \tag{69}$$

then we call

$$\frac{\delta^n G}{\delta f(\mathbf{r}_1) \cdots \delta f(\mathbf{r}_n)} = g(\mathbf{r}_1 \cdots \mathbf{r}_n) \tag{70}$$

the nth-order functional derivative of G. So far our discussion has been rather abstract. Let us therefore apply the definition and calculate some functional derivatives.

7. STATIC LINEAR RESPONSE OF THE SCHRÖDINGER EQUATION

We now consider the effect of small changes in the external field on the expectation values of physical observables. This is exactly what is studied in most experimental situations where one switches on and off an external field and studies how the system reacts to this. We will here study a more specific case in which we look at static changes in the external potential and their accompanying changes in the ground state expectation values. By investigating this problem we will learn how to take functional derivatives and how the existence of these derivatives is related to the existence of the linear response function.

Suppose that we have solved the following ground state problem:

$$\hat{H}|\Psi_0\rangle = (\hat{T} + \hat{V} + \hat{W})|\Psi_0\rangle = E_0|\Psi_0\rangle \tag{71}$$

where $|\Psi_0\rangle$ is a nondegenerate ground state $|\Psi[v]\rangle$ of Hamiltonian $\hat{H}$ with external potential $\hat{V}$. From the wavefunction we can then calculate the expectation value of any operator $\hat{O}$ which is a well-defined functional of the external potential

$$O[v] = \langle \Psi[v]|\hat{O}|\Psi[v]\rangle \tag{72}$$

Let us now calculate the functional derivative $\delta O/\delta v$ at a given potential v. According to our definition in the previous section we have to calculate the quantity

$$\frac{\delta O}{\delta v}[\delta v] = \lim_{\epsilon \to 0} \frac{O[v + \epsilon\, \delta v] - O[v]}{\epsilon} \tag{73}$$

To evaluate this limit we have to calculate $O[v + \epsilon\, \delta v]$ which we will do using static perturbation theory. We therefore make a slight change

$$\epsilon\, \delta\hat{V} = \epsilon \int d^3r\, \hat{n}(\mathbf{r})\, \delta v(\mathbf{r}) \tag{74}$$

in the external potential of Hamiltonian $\hat{H}$, i.e., we change the potential to $\hat{V} + \epsilon\, \delta\hat{V}$. The new ground state wavefunction which we will denote by $|\Psi(\epsilon)\rangle$ satisfies

$$(\hat{H} + \epsilon\, \delta\hat{V})|\Psi(\epsilon)\rangle = E(\epsilon)|\Psi(\epsilon)\rangle \tag{75}$$

We will solve this equation to first order in ϵ with the condition $|\Psi(0)\rangle = |\Psi_0\rangle$. We note that the solution of equation (75) is not unique, because if $|\Psi(\epsilon)\rangle$ is a solution then also $|\Phi(\epsilon)\rangle = e^{i\theta(\epsilon)}|\Psi(\epsilon)\rangle$ is a solution, where $\theta(\epsilon)$ is an arbitrary function of ϵ. If we choose $\theta(0) = 0$ then $|\Phi(\epsilon)\rangle$ also satisfies the condition $|\Phi(0)\rangle = |\Psi_0\rangle$. The arbitrariness of the phase factor obviously does not affect the value of any expectation value, i.e.,

$$O(\epsilon) = \langle \Psi(\epsilon)|\hat{O}|\Psi(\epsilon)\rangle = \langle \Phi(\epsilon)|\hat{O}|\Phi(\epsilon)\rangle \tag{76}$$

which is a unique function of ϵ. However, it affects the appearance of our first order expansion, which for both functions looks like

$$|\Psi(\epsilon)\rangle = |\Psi_0\rangle + \epsilon|\Psi'(0)\rangle + O(\epsilon^2) \tag{77}$$

$$|\Phi(\epsilon)\rangle = |\Psi_0\rangle + \epsilon(|\Psi'(0)\rangle + i\theta'(0)|\Psi_0\rangle) + O(\epsilon^2) \tag{78}$$

where $|\Psi'(0)\rangle$ and $\theta'(0)$ are the first order derivatives of $|\Psi(\epsilon)\rangle$ and $\theta(\epsilon)$ in $\epsilon = 0$. We see that $|\Psi(\epsilon)\rangle$ and $|\Phi(\epsilon)\rangle$ differ in first order by the amount $i\epsilon\theta'(0)|\Psi_0\rangle$, i.e., by an imaginary number times the unperturbed ground state. This is exactly the freedom we will find in our expansion when we try to obtain the first order change in the wavefunction.

Let us expand the wavefunction and energy in equation (75) to first order in ϵ. We then obtain

$$(\hat{H} - E_0)|\Psi'(0)\rangle = (E'(0) - \delta\hat{V})|\Psi_0\rangle \tag{79}$$

where $E'(0)$ is the first order derivative of $E(\epsilon)$ in $\epsilon = 0$. To solve this equation we expand $|\Psi'(0)\rangle$ in an orthonormal set of eigenstates of the unperturbed Hamiltonian $\hat{H}$ as:

$$|\Psi'(0)\rangle = \sum_{i=0}^{\infty} c_i |\Psi_i\rangle \tag{80}$$

If the unperturbed Hamiltonian has a continuous spectrum then for the corresponding energy eigenstates the summation in this equation has to be replaced by integration. If we insert the expansion (80) into equation (79) for $|\Psi'(0)\rangle$ we find the equation

$$\sum_{i=0}^{\infty} c_i (E_i - E_0)|\Psi_i\rangle = (E'(0) - \delta\hat{V})|\Psi_0\rangle \tag{81}$$

where the energies E_i for $i > 0$ are the eigenenergies of the excited states of the unperturbed Hamiltonian. If we multiply this equation from the left with $\langle\Psi_0|$ we obtain for the change in energy

$$E'(0) = \langle\Psi_0|\delta\hat{V}|\Psi_0\rangle = \int \mathrm{d}^3 r\, n_0(\mathbf{r})\, \delta v(\mathbf{r}) \tag{82}$$

where n_0 is the density of the unperturbed system. We have therefore shown that

$$E'(0) = \lim_{\epsilon \to 0} \frac{E[v + \epsilon\, \delta v] - E[v]}{\epsilon} = \int \mathrm{d}^3 r\, n_0(\mathbf{r})\, \delta v(\mathbf{r}) \tag{83}$$

As has been derived before we find $\delta E / \delta v(\mathbf{r}) = n_0(\mathbf{r})$. If we now multiply equation (81) from the left with $\langle\Psi_k|$ for $k > 0$ we find

$$c_k = -\frac{\langle\Psi_k|\delta\hat{V}|\Psi_0\rangle}{E_k - E_0} \qquad (\text{for } k > 0) \tag{84}$$

Note that these coefficients are well-defined because $E_k > E_0$, since we are dealing with an isolated nondegenerate ground state. We therefore find for the first order change in the wavefunction

$$|\Psi'(0)\rangle = c_0|\Psi_0\rangle - \sum_{k=1}^{\infty} \frac{|\Psi_k\rangle\langle\Psi_k|\delta\hat{V}|\Psi_0\rangle}{E_k - E_0} \tag{85}$$

The coefficient c_0 remains undetermined by these equations. However, from the requirement that the perturbed system remains normalized we find

$$0 = \frac{\mathrm{d}\langle\Psi|\Psi\rangle}{\mathrm{d}\epsilon}(0) = \langle\Psi'(0)|\Psi_0\rangle + \langle\Psi_0|\Psi'(0)\rangle = c_0^* + c_0 \tag{86}$$

and hence c_0 must be purely imaginary. This is exactly the kind of freedom in the first order wavefunction that we noted before. However, as we have seen this is related to choice of phase and does not affect the expectation values. We now want to calculate the first order change in an arbitrary expectation value due to a change $\epsilon\, \delta v$ of the external potential. This change is given by

$$O'(0) = \lim_{\epsilon \to 0} \frac{O[v + \epsilon\, \delta v] - O[v]}{\epsilon} = \langle \Psi'(0) | \hat{O} | \Psi_0 \rangle + \langle \Psi_0 | \hat{O} | \Psi'(0) \rangle \tag{87}$$

where $O'(0)$ is the derivative of $O(\epsilon)$ in $\epsilon = 0$ and where we assumed that the operator $\hat{O}$ does not depend on $\hat{V}$ (as for instance the Hamiltonian does). From equation (85) we obtain

$$\begin{aligned} O'(0) &= (c_0^* + c_0) \langle \Psi_0 | \hat{O} | \Psi_0 \rangle \\ &\quad - \sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \delta \hat{V} | \Psi_k \rangle \langle \Psi_k | \hat{O} | \Psi_0 \rangle + \langle \Psi_0 | \hat{O} | \Psi_k \rangle \langle \Psi_k | \delta \hat{V} | \Psi_0 \rangle}{E_k - E_0} \end{aligned} \tag{88}$$

From the normalization condition equation (86) we see that the first term on the right hand side vanishes and we can rewrite the equation as:

$$O'(0) = \frac{\delta O}{\delta v}[\delta v] = \int \mathrm{d}^3 r \frac{\delta O}{\delta v(\mathbf{r})} \delta v(\mathbf{r}) \tag{89}$$

where

$$\frac{\delta O}{\delta v(\mathbf{r})} = -\sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \hat{O} | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{E_k - E_0} + \text{c.c.} \tag{90}$$

For a system with a nondegenerate ground state we therefore have obtained an explicit expression for the functional derivative $\delta O / \delta v$ of the expectation value $O[v]$, evaluated at potential $v(\mathbf{r})$. We will use this formula later when we are studying functional derivatives with respect to the density.

8. INVERTABILITY OF THE DENSITY RESPONSE FUNCTION

In the previous section we obtained an expression for the functional derivative of an arbitrary expectation value. We now make a special choice for the operator $\hat{O}$ and we choose $\hat{O} = \hat{n}(\mathbf{r}')$. In that case we obtain from equation (90):

$$\chi(\mathbf{r}', \mathbf{r}) = \frac{\delta n(\mathbf{r}')}{\delta v(\mathbf{r})} = -\sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}') | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{E_k - E_0} + \text{c.c.} \tag{91}$$

where $\chi(\mathbf{r}', \mathbf{r})$ is the static density response function. From this expression we see immediately that χ is real and symmetric, i.e., $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}', \mathbf{r})$. The density response function relates first order changes in the potential to first order changes in the density according to

$$\delta n(\mathbf{r}) = \int \mathrm{d}^3 r' \; \chi(\mathbf{r}, \mathbf{r}') \, \delta v(\mathbf{r}') \tag{92}$$

If we change the potential by a constant then the density does not change. We therefore must have

$$\int \mathrm{d}^3 r' \; \chi(\mathbf{r}, \mathbf{r}') = 0 \tag{93}$$

which can also be checked immediately from equation (91). Because of this property we also see that the induced density $\delta n(\mathbf{r})$ automatically integrates to zero. The density response function has therefore indeed the physical properties that we expect. On the basis of the Hohenberg–Kohn theorem we may further expect that the only potential variation that yields a zero density variation is the constant potential, i.e., if

$$0 = \int \mathrm{d}^3 r' \; \chi(\mathbf{r}, \mathbf{r}') \, \delta v(\mathbf{r}') \tag{94}$$

then $\delta v(\mathbf{r}) = C$. This readily proven from the properties of the response function. Suppose equation (94) is true for some $\delta v(\mathbf{r}')$. Then we obtain by integration with $\delta v(\mathbf{r})$:

$$0 = \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \; \delta v(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') \, \delta v(\mathbf{r}') = -2 \sum_{k=1}^{\infty} \frac{|a_k|^2}{E_k - E_0} \tag{95}$$

where we defined a_k by

$$a_k = \int \mathrm{d}^3 r \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \, \delta v(\mathbf{r}) \tag{96}$$

Since $E_k - E_0 > 0$ equation (95) can only be true if $a_k = 0$ for all $k \geq 1$. But this implies that

$$\begin{aligned} 0 = \sum_{k=1}^{\infty} a_k | \Psi_k \rangle &= \sum_{k=1}^{\infty} \int \mathrm{d}^3 r | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \, \delta v(\mathbf{r}) \\ &= \int \mathrm{d}^3 r \; \delta v(\mathbf{r}) (1 - | \Psi_0 \rangle \langle \Psi_0 |) \hat{n}(\mathbf{r}) | \Psi_0 \rangle \\ &= \int \mathrm{d}^3 r \; \delta v(\mathbf{r}) (\hat{n}(\mathbf{r}) - n_0(\mathbf{r})) | \Psi_0 \rangle \end{aligned} \tag{97}$$

where $n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle$ is the ground state density. Thus, written in first quantization this implies that

$$\sum_{i=1}^{N} \Delta v(\mathbf{r}_i) | \Psi_0 \rangle = 0 \tag{98}$$

where N is the number of electrons and Δv the potential

$$\Delta v(\mathbf{r}) = \delta v(\mathbf{r}) - \frac{1}{N} \int d^3 r \, n_0(\mathbf{r}) \, \delta v(\mathbf{r}) \tag{99}$$

Now equation (98) implies that $\Delta v(\mathbf{r}) = 0$ which together with equation (99) implies that $\delta v(\mathbf{r}) = C$. We have therefore shown that only constant potentials yield a zero-density variation, and therefore the density response function is invertible up to a constant. One should, however, be careful with what one means with the inverse response function. The response function defines a mapping $\chi : \delta\mathcal{V} \rightarrow \delta\mathcal{A}$ from the set of potential variations from a nondegenerate ground state, which we call $\delta\mathcal{V}$ and is a subset of $L^{3/2} + L^{\infty}$, to the set of first order densities variations, which we call $\delta\mathcal{A}$, that are produced by it. We have just shown that the inverse $\chi^{-1} : \delta\mathcal{A} \rightarrow \delta\mathcal{V}$ is well-defined modulo a constant function. However, there are density variations that can never be produced by a potential variation and which are therefore not in the set $\delta\mathcal{A}$. An example of such a density variation is one which is identically zero on some finite volume.

From our analysis we can further derive another property of the static response function. Since $\chi(\mathbf{r}, \mathbf{r}')$ is a real Hermitian integral kernel it has an orthonormal set of eigenfunctions which can be chosen to be real. Let $f(\mathbf{r})$ be such an eigenfunction, i.e.,

$$\int d^3 r' \, \chi(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') = \lambda f(\mathbf{r}) \tag{100}$$

Multiplication from the right with $f(\mathbf{r})$ and subsequent integration yields

$$\lambda \int d^3 r \, f^2(\mathbf{r}) = \int d^3 r \, d^3 r' \, f(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') = -2 \sum_{k=1}^{\infty} \frac{|b_k|^2}{E_k - E_0} \leq 0 \tag{101}$$

where

$$b_k = \int d^3 r \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle f(\mathbf{r}) \tag{102}$$

We therefore find that $\lambda \leq 0$. However, we already know that $\lambda = 0$ is only possible if $f(\mathbf{r})$ is constant. We have therefore obtained the result that if a nonzero density variation is proportional to the potential that generates it, i.e., $\delta n = \lambda \, \delta v$, then the constant of proportionality λ is negative. This is exactly what one would expect on the basis of physical considerations. In actual calculations one indeed finds that the eigenvalues of χ are negative. Moreover, it is found that there is a infinite number of negative eigenvalues arbitrarily close to zero, which causes considerable numerical difficulties when one tries to obtain the potential variation that is responsible for a given density variation. We finally note the invertability proof for the static response function can be extended to the time-dependent case. For a recent review we refer to Ref. [15].

9. FUNCTIONAL DERIVATIVES AND v-REPRESENTABILITY

We are now ready to tackle the question of how to calculate functional derivatives with respect to the density. By the Hohenberg–Kohn theorem every density associated with a nondegenerate ground state uniquely determines that ground state and the external potential that produced it. Because the density n determines the external potential v and *vice versa* we can parametrize the ground state either by the density or the external potential. The same is, of course, true for the expectation value of any operator $\hat{O}$ that we calculate from the ground state. We will therefore write

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle = \langle \Psi[v] | \hat{O} | \Psi[v] \rangle = O[v] \tag{103}$$

Since we know how to calculate the functional derivative with respect to v the functional derivative with respect to n seems rather straightforward. By the chain rule for differentiation we obtain

$$\frac{\delta O}{\delta n(\mathbf{r})} = \int \mathrm{d}^3 r' \, \frac{\delta O}{\delta v(\mathbf{r}')} \frac{\delta v(\mathbf{r}')}{\delta n(\mathbf{r})} = \int \mathrm{d}^3 r' \, \frac{\delta O}{\delta v(\mathbf{r}')} \chi^{-1}(\mathbf{r}', \mathbf{r}) \tag{104}$$

where we used that the density response function has an inverse (modulo a constant). However, great care must be taken when deriving this equation. One needs to consider under which conditions the use of this chain rule is applicable. Let us therefore start with the definition of the functional derivative and try to calculate

$$\frac{\delta O}{\delta n}[\delta n] = \lim_{\epsilon \to 0} \frac{O[n_0 + \epsilon \, \delta n] - O[n_0]}{\epsilon} \tag{105}$$

where n_0 is the density of a given nondegenerate ground state with external potential v_0. Now we run into the following problem. In order to make the value of $O[n_0 + \epsilon \times \delta n]$ well defined we have to make sure that $n_0 + \epsilon \, \delta n \in \mathcal{A}$, i.e., we have to make sure that this perturbed density belongs to a nondegenerate ground state. Whether or not this is true obviously depends on the choice we make for δn. A natural choice would be to take $\delta n \in \delta \mathcal{A}$, i.e., we take a δn from the set of first order density variations produced by some potential variations $\delta v \in \delta \mathcal{V}$. In this way we know that for every such δn there is a potential $v_0 + \epsilon \, \delta v$ that generates, to first order in ϵ, the required density. However, this still does not imply that $n_0 + \epsilon \, \delta n \in \mathcal{A}$. This will only be so if we can find an additional potential that would make the higher order terms in ϵ disappear and it is not clear how to prove the existence of such a potential.

Nevertheless, this idea is sufficient to make a useful statement about the functional derivative. Let us therefore take some $\delta n \in \delta \mathcal{A}$. Then, by the invertability of the density response function, there is a unique δv modulo a constant, such that

$$\delta n(\mathbf{r}) = \int \mathrm{d}^3 r' \, \chi_0(\mathbf{r}, \mathbf{r}') \, \delta v(\mathbf{r}') \tag{106}$$

where χ_0 is the static density response function belonging to the nondegenerate ground state $|\Psi_0\rangle$ with density n_0. Consider now the set of external potentials

$v_0 + \epsilon\,\delta v$. For each ϵ we can solve the Schrödinger equation and obtain a ground state density $n_\epsilon(\mathbf{r})$, which for ϵ small enough will correspond to a nondegenerate ground state, i.e., $n_\epsilon(\mathbf{r}) \in \mathcal{A}$. By construction $n_\epsilon - n_0$ will, to first order in ϵ, be equal to the chosen δn we started with, i.e., n_ϵ can be written as:

$$n_\epsilon(\mathbf{r}) = n_0(\mathbf{r}) + \epsilon\,\delta n(\mathbf{r}) + m_\epsilon(\mathbf{r}) \in \mathcal{A} \tag{107}$$

where the term $m_\epsilon(\mathbf{r})$ satisfies

$$\lim_{\epsilon \longrightarrow 0} \frac{m_\epsilon(\mathbf{r})}{\epsilon} = 0 \tag{108}$$

Since n_ϵ is the density of a nondegenerate ground state the expectation value $O[n_\epsilon]$ is now well-defined and we can calculate

$$\lim_{\epsilon \longrightarrow 0} \frac{O[n_\epsilon] - O[n_0]}{\epsilon} = \lim_{\epsilon \longrightarrow 0} \frac{O[v_0 + \epsilon\,\delta v] - O[v_0]}{\epsilon} = \int d^3r \frac{\delta O}{\delta v(\mathbf{r})} \delta v(\mathbf{r}) \tag{109}$$

We have therefore found a parametrized set of densities $n_\epsilon \in \mathcal{A}$ for which the limit above is well-defined. Moreover, in this equation δv is uniquely defined by the $\delta n \in \delta\mathcal{A}$ we started with by $\delta v = \chi_0^{-1} \delta n$, so that we can write

$$\lim_{\epsilon \longrightarrow 0} \frac{O[n_0 + \epsilon\,\delta n + m_\epsilon] - O[n_0]}{\epsilon} = \int d^3r \frac{\delta O}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) \tag{110}$$

where the functional derivative $\delta O/\delta n(\mathbf{r})$ is given (modulo a constant) by

$$\frac{\delta O}{\delta n(\mathbf{r})} = -\int d^3r' \left(\sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \hat{O} | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}') | \Psi_0 \rangle}{E_k - E_0} + \text{c.c.} \right) \chi_0^{-1}(\mathbf{r}', \mathbf{r}) \tag{111}$$

Note that this derivative is defined up to a constant, since $\delta n(\mathbf{r})$ integrates to zero. The functional derivative $\delta O/\delta n[\delta n]$ in equation (110), regarded as a linear functional acting on δn, is of course independent of this constant. We have therefore a result that is in accordance with our naive expectation of equation (104). The functional derivative in equation (111) is well defined in terms of the properties of the unperturbed system and independent of the choice for δn, and therefore independent of the parametrized path $n_\epsilon \in \mathcal{A}$ that we used to approach n_0. Moreover, n_ϵ approaches the straight path $n_0 + \epsilon\,\delta n$ arbitrarily closely for $\epsilon \longrightarrow 0$ and this is exactly the limit that we are interested in. We will therefore call the $\delta O/\delta n$ of equation (111) the functional derivative of $O[n]$. Let us check that equation (111) gives us back some known results. Let us take $\hat{O} = \hat{T} + \hat{W}$ so that $O[n] = F_{\text{HK}}[n]$. If we insert this operator in equation (111) we see that we have to calculate

$$\begin{aligned} \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_k \rangle &= \langle \Psi_0 | \hat{H}_0 - \hat{V}_0 | \Psi_k \rangle \\ &= E_k \delta_{k0} - \int d^3r\, v_0(\mathbf{r}) \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_k \rangle \end{aligned} \tag{112}$$

where $\hat{H}_0 = \hat{T} + \hat{V}_0 + \hat{W}$. If we insert this matrix element into equation (111) we obtain:

$$\frac{\delta F_{\text{HK}}[n]}{\delta n(\mathbf{r})} = -\int \mathrm{d}^3r'\, \mathrm{d}^3r''\, v_0(\mathbf{r}'')\chi_0(\mathbf{r}'',\mathbf{r}')\chi_0^{-1}(\mathbf{r}',\mathbf{r}) = -v_0(\mathbf{r}) \qquad (113)$$

This is exactly the result that we derived earlier using Legendre transforms. We can, of course, also do this derivation for a noninteracting system where $\hat{W} = 0$ and therefore $\hat{O} = \hat{T}$, in which case we obtain

$$\frac{\delta T_s}{\delta n(\mathbf{r})} = -v_s[n_0](\mathbf{r}) \qquad (114)$$

where $v_s[n_0]$ is the potential that in a noninteracting system generates density n_0, i.e., the Kohn–Sham potential corresponding to density n_0.

10. THE HOHENBERG–KOHN THEOREM FOR DEGENERATE GROUND STATES

Until now we considered only nondegenerate ground states. These ground states have the simplifying feature that they are determined uniquely (up to a phase factor) by the external potential and therefore any expectation value calculated from the ground state wavefunction is a well-defined functional of the external potential v. However, degenerate ground states do occur (for instance, in open shell atoms) and in that case the external potential does not generate a unique ground state but a linearly independent set of q different ground states. The expectation value of any operator (except the total energy) will then depend on which ground state out of the ground state manifold we choose to compute the expectation value from. This is in particular true for the density operator, and therefore different ground states $|\Psi_i\rangle$ out of the ground state multiplet will yield different densities n_i. If we want to consider degenerate ground states, then the density is no longer a unique functional of the external potential. However, we will show that the inverse mapping $n \rightarrow v$ is well defined, i.e., every ground state density determines uniquely the external potential that generated it. We will first generalize this statement somewhat. Instead of pure-state densities, which come from an eigenstate of the Hamiltonian $\hat{H}$, we will consider ensemble densities. To define this concept we first introduce for a q-fold degenerate ground state $\{|\Psi_i\rangle,\ i = 1\cdots q\}$ the density matrix

$$\hat{D} = \sum_{i=1}^{q} \lambda_i |\Psi_i\rangle\langle\Psi_i| \qquad \sum_{i}^{q} \lambda_i = 1 \qquad (0 \leq \lambda_i \leq 1) \qquad (115)$$

where the ground state wavefunctions $|\Psi_i\rangle$ are chosen to be orthonormal. We then define the ground state expectation value of operator $\hat{O}$ as:

$$\langle O \rangle = \mathrm{Tr}\hat{D}\hat{O} \qquad (116)$$

where the trace operation for an arbitrary operator is defined as:

$$\mathrm{Tr}\hat{A} = \sum_{i=1}^{\infty} \langle \Phi_i | \hat{A} | \Phi_i \rangle \tag{117}$$

where $\{|\Phi_i\rangle\}$ is an arbitrary complete set of states. The trace is independent of the complete set that we choose, as follows simply by insertion of a different complete set $\{|\Psi_i\rangle\}$:

$$\begin{aligned}\mathrm{Tr}\hat{A} &= \sum_{i=1}^{\infty} \langle \Phi_i | \hat{A} | \Phi_i \rangle = \sum_{i,j=1}^{\infty} \langle \Phi_i | \hat{A} | \Psi_j \rangle \langle \Psi_j | \Phi_i \rangle \\ &= \sum_{i,j=1}^{\infty} \langle \Psi_j | \Phi_i \rangle \langle \Phi_i | \hat{A} | \Psi_j \rangle = \sum_{j=1}^{\infty} \langle \Psi_j | \hat{A} | \Psi_j \rangle\end{aligned} \tag{118}$$

If we choose the complete set to be the set of eigenstates of Hamiltonian $\hat{H}$ then we find

$$\mathrm{Tr}\hat{D}\hat{O} = \sum_{i=1}^{\infty} \langle \Psi_i | \hat{D}\hat{O} | \Psi_i \rangle = \sum_{i=1}^{q} \lambda_i \langle \Psi_i | \hat{O} | \Psi_i \rangle \tag{119}$$

This defines the expectation value of an observable $\hat{O}$ in an ensemble described by density matrix $\hat{D}$. For the particular case of the density operator we have

$$n(\mathbf{r}) = \mathrm{Tr}\hat{D}\hat{n}(\mathbf{r}) = \sum_{i=1}^{q} \lambda_i \langle \Psi_i | \hat{n}(\mathbf{r}) | \Psi_i \rangle = \sum_{i=1}^{q} \lambda_i n_i(\mathbf{r}) \tag{120}$$

We will denote densities $n(\mathbf{r})$ of this type, which are obtained from an orthonormal set of ground states $\{|\Psi_i\rangle,\ i = 1\cdots q\}$ corresponding to a potential v, as ensemble v-representable densities, or for short E-V-densities. We further denote the set of all E-V-densities generated by potentials in $L^{3/2} + L^{\infty}$ as $\mathcal{B}$. A density will be called a pure state v-representable density or for short PS-V-density if it can be written as $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$, where $|\Psi\rangle$ is a ground state. Obviously PS-V-densities are special cases of E-V-densities and the set of PS-V-densities is therefore a subset of the set of E-V-densities.

We are now ready to formulate the Hohenberg–Kohn theorem for degenerate ground states: Every E-V-density determines the external potential that generated it up to an arbitrary constant. Let us make this statement a bit more specific. Suppose that $\hat{D}_1$ and $\hat{D}_2$ are density matrices belonging to ground state ensembles for potentials v_1 and v_2, respectively, with corresponding ensemble densities n_1 and n_2. If $v_1 \neq v_2 + C$ with C a constant, then $n_1 \neq n_2$. The proof is analogous to the proof of the nondegenerate case.

Suppose v_1 generates the ground state multiplet $A_1 = \{|\Phi_i\rangle,\ i = 1\cdots q_1\}$ and v_2 generates the ground state multiplet $A_2 = \{|\Psi_i\rangle,\ i = 1\cdots q_2\}$. All the wavefunctions within these multiplets may, without loss of generality, be chosen orthonormal. Then none of the wavefunctions in the sets A_1 and A_2 are equal. This follows from the same argument as used in the proof of the Hohenberg–Kohn theorem for the nondegenerate case. In particular, as the sets A_1 and A_2 are only defined to within a unitary transformation no $|\Psi_i\rangle$ in A_2 is a linear combination of the $|\Phi_i\rangle$ in A_1. This then implies that two ground state ensemble density matrices constructed from the ground states in A_1 and A_2 are different

$$\hat{D}_1 = \sum_{i=1}^{q_1} \lambda_i |\Phi_i\rangle\langle\Phi_i| \neq \sum_{i=1}^{q_2} \mu_i |\Psi_i\rangle\langle\Psi_i| = \hat{D}_2 \tag{121}$$

where $\sum \lambda_i = \sum \mu_i = 1$. This follows, for instance, by taking the inner product on both sides with $|\Psi_m\rangle$ as the $|\Psi_i\rangle$ are not linear combinations of the $|\Phi_i\rangle$. We have thus established that the sets of ground state density matrices for the two different potentials v_1 and v_2 are disjoint. We now have to prove that the density matrices in these sets yield different densities. If $\hat{H}_1 = \hat{T} + \hat{V}_1 + \hat{W}$ and $\hat{H}_2 = \hat{T} + \hat{V}_2 + \hat{W}$ then

$$\mathrm{Tr}\hat{D}_1\hat{H}_2 > \mathrm{Tr}\hat{D}_2\hat{H}_2 \tag{122}$$

This follows directly from

$$\begin{aligned}\mathrm{Tr}\hat{D}_1\hat{H}_2 &= \sum_{i=1}^{q_1} \lambda_i \langle\Phi_i|\hat{H}_2|\Phi_i\rangle > \sum_{i=1}^{q_1} \lambda_i \langle\Psi_i|\hat{H}_2|\Psi_i\rangle = \sum_{i=1}^{q_1} \lambda_i E[v_2] = E[v_2] \\ &= \sum_{i=1}^{q_2} \mu_i \langle\Psi_i|\hat{H}_2|\Psi_i\rangle = \mathrm{Tr}\hat{D}_2\hat{H}_2\end{aligned} \tag{123}$$

We can now show that $\hat{D}_1$ and $\hat{D}_2$ yield different densities. We proceed again by *reductio ad absurdum*. We have

$$\begin{aligned}E[v_1] &= \mathrm{Tr}\hat{D}_1\hat{H}_1 = \mathrm{Tr}\hat{D}_1(\hat{H}_2 + \hat{V}_1 - \hat{V}_2) \\ &= \mathrm{Tr}\hat{D}_1\hat{H}_2 + \int n_1(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))\mathrm{d}\mathbf{r} \\ &> \mathrm{Tr}\hat{D}_2\hat{H}_2 + \int n_1(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))\mathrm{d}\mathbf{r} \\ &= E[v_2] + \int n_1(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))\mathrm{d}\mathbf{r}\end{aligned} \tag{124}$$

Likewise we have

$$E[v_2] > E[v_1] + \int n_2(\mathbf{r})(v_2(\mathbf{r}) - v_1(\mathbf{r}))\mathrm{d}\mathbf{r} \tag{125}$$

which added to the last inequality leads to

$$\int \mathrm{d}^3r(n_2(\mathbf{r}) - n_1(\mathbf{r}))(v_2(\mathbf{r}) - v_1(\mathbf{r})) < 0 \tag{126}$$

This leads again to the contradiction $0 < 0$ if we assume that $n_1 = n_2$. Therefore $\hat{D}_1$ and $\hat{D}_2$ must give different densities, which proves the theorem.

Within the set of ensemble ground state density matrices corresponding to the *same* potential however, two different density matrices can yield the same density. The simplest example is the hydrogen atom with the degenerate ground state wavefunctions for an electron with spin up and spin down, i.e., $\Psi_\uparrow = (1\mathrm{s})\alpha$ and $\Psi_\downarrow = (1\mathrm{s})\beta$ where α and β are the spin wavefunctions. Both wavefunctions obviously have the same total density. Another example is provided by the the two degenerate ground state wavefunctions $(1\mathrm{s})^2 2\mathrm{p}^+$ and $(1\mathrm{s})^2 2\mathrm{p}^-$ of the noninteracting lithium atom, where $2\mathrm{p}^\pm$ are p-orbitals with angular momentum quantum numbers $l = \pm 1$. Both wavefunctions lead to the same density

$$n(\mathbf{r}) = 2|\varphi_{1\mathrm{s}}(\mathbf{r})|^2 + |\varphi_{2\mathrm{p}^+}(\mathbf{r})|^2 = 2|\varphi_{1\mathrm{s}}(\mathbf{r})|^2 + |\varphi_{2\mathrm{p}^-}(\mathbf{r})|^2 \tag{127}$$

We have therefore constructed two degenerate ground states with the same density. As a consequence the ground state expectation value of a given operator may no longer be considered as a functional of the density (take, for instance, the expectation values of the spin and angular momentum in our examples). However, if two different ground state density matrices have the same density then also the energy $\mathrm{Tr}\,\hat{D}\hat{H}$ for those different density matrices is the same. For every E-V-density n we can therefore unambiguously define the ensemble version of the F_{HK} functional as [16]

$$F_{\mathrm{EHK}}[n] = \mathrm{Tr}\hat{D}[n](\hat{T} + \hat{W}) \tag{128}$$

where $\hat{D}[n]$ is any of the ground state ensemble density matrices corresponding to n. We can now define an extension of the energy functional E_v to the set of E-V-densities

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + F_{\mathrm{EHK}}[n] = \mathrm{Tr}\hat{D}[n]\hat{H} \tag{129}$$

Similarly as for F_{HK} we easily can prove

$$E[v] = \inf_{n \in \mathcal{B}} \left\{ \int n(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + F_{\mathrm{EHK}}[n] \right\} \tag{130}$$

The functional F_{EHK} is an extension of F_{HK} since

$$F_{\mathrm{EHK}}[n] = F_{\mathrm{HK}}[n] \qquad \text{if } n \in \mathcal{A} \tag{131}$$

This follows directly from the fact that for a nondegenerate ground state $|\Psi[n]\rangle$ corresponding to n we have $\hat{D}[n] = |\Psi[n]\rangle\langle\Psi[n]|$, so

$$F_{\mathrm{EHK}}[n] = \mathrm{Tr}\hat{D}[n](\hat{T} + \hat{W}) = \langle\Psi[n]|\hat{T} + \hat{W}|\Psi[n]\rangle = F_{\mathrm{HK}}[n] \tag{132}$$

We can furthermore prove that F_{EHK} is convex by the same proof as for F_{HK}. Nothing is however known about the convexity of the set of E-V-densities $\mathcal{B}$ itself which constitute the domain of F_{EHK}. Let us collect our results in the form of a theorem.

Theorem 2 (Hohenberg–Kohn). *The E-V-density n specifies the external potential up to a constant. Moreover,*

1. *The ground state energy of a system with external potential v can be obtained from*

$$E[v] = \inf_{n \in \mathcal{B}} \left\{ \int n(\boldsymbol{r}) v(\boldsymbol{r})\, d\boldsymbol{r} + F_{\mathrm{EHK}}[n] \right\}$$

where $F_{\mathrm{EHK}}[n] = Tr\hat{D}[n](\hat{T} + \hat{W})$ and $\hat{D}[n]$ is a ground state density matrix with $Tr\hat{D}[n]\hat{n}(\boldsymbol{r}) = n(\boldsymbol{r})$.

2. *F_{EHK} is convex.*

As we will now demonstrate the subset of PS-V-densities of $\mathcal{B}$ is not convex. More precisely, we will now show that there are E-V-densities which are not PS-V-densities [1,17]. As any E-V-density is a convex combination of PS-V-densities, this then demonstrates the nonconvexity of the set of PS-V-densities.

Consider an atom with total angular momentum quantum number $L > 0$ which has a $2L + 1$-degenerate ground state. The external potential v is the spherically symmetric Coulomb potential of the atomic nucleus and the degeneracy is a result of rotational invariance of the Hamiltonian of the system. The ground state wavefunctions then transform among one another according to a $2L+1$-dimensional unitary representation of the rotation group. We assume that there is no accidental degeneracy. If we denote the ground state wavefunctions by $\{|\Psi[n_i]\rangle = |\Psi_i\rangle,\ i = 1 \cdots 2L + 1\}$ and the corresponding electron densities by n_i then the following convex combination:

$$\bar{n} = \frac{1}{2L+1} \sum_{i=1}^{2L+1} n_i \tag{133}$$

is invariant under all rotations and therefore spherically symmetric. However, the densities n_i are not spherical. In fact, there is no linear combination of the ground states $|\Psi_i\rangle$ that leads to a spherically symmetric density. As the n_j is obtained from $|\Psi_j\rangle$, which by a unitary transformation can be obtained from any other $|\Psi_i\rangle$, and the external potential is invariant under rotations we find that

$$\int n_i(\mathbf{r}) v(\mathbf{r})\, \mathrm{d}\mathbf{r} = \int n_j(\mathbf{r}) v(\mathbf{r})\, \mathrm{d}\mathbf{r} = \int \bar{n}(\mathbf{r}) v(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{134}$$

for all $0 \leq i, j \leq 2L + 1$. Let us now suppose that $\bar{n}$ is a ground state density obtained from a pure state wavefunction $|\Psi[\bar{n}]\rangle$. This wavefunction is not a linear combination of the $|\Psi_i\rangle$ otherwise $\bar{n}$ would not be spherically symmetric. We then find

$$\begin{aligned} F_{\mathrm{EHK}}[\bar{n}] &= \langle \Psi[\bar{n}]|\hat{H}_v|\Psi[\bar{n}]\rangle - \int \bar{n}(\mathbf{r})v(\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &> \sum_{i=1}^{2L+1} \frac{1}{2L+1}\langle \Psi[n_i]|\hat{H}|\Psi[n_i]\rangle - \int \bar{n}(\mathbf{r})v(\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &= \sum_{i=1}^{2L+1} \frac{1}{2L+1} F_{\mathrm{EHK}}[n_i] \end{aligned} \tag{135}$$

This then gives

$$F_{\mathrm{EHK}}[\bar{n}] > \sum_{i=1}^{2L+1} \frac{1}{2L+1} F_{\mathrm{EHK}}[n_i] \tag{136}$$

But we also know that F_{EHK} is convex on the set of E-V-densities. This leads to a contradiction and hence we must conclude that $\bar{n}$ cannot be a pure state density of any potential. The density $\bar{n}$ is, however, a convex combination of ground state densities corresponding to the same external potential and therefore, by definition, an ensemble v-representable density. We therefore have constructed an E-V-density, which is not a PS-V-density. For an explicit numerical example of such a density we refer to the work of Aryasetiawan and Stott [18].

11. LINEAR RESPONSE FOR DEGENERATE GROUND STATES AND THE DIFFERENTIABILITY OF F_{EHK}

In the previous sections we learned to take functional derivatives on the basis of linear response theory. We concentrated on nondegenerate ground states for which the response functions are well defined. We will now use response theory for degenerate ground states to study the differentiability of the functional F_{EHK}.

It is clear that in the case of degeneracy the expectation value of all observables, except the energy, depends on which particular ground state we choose to calculate the expectation value from. This poses a clear difficulty for the definition of general density functionals and their functional derivatives. One may, however, argue that if a potential v_0 leads to a degenerate ground state then we can always find an arbitrarily small perturbation of the potential $\epsilon\,\delta v$ that lifts the degeneracy and therefore the expectation value

$$O[v_0 + \epsilon\,\delta v] = \langle \Psi[v_0 + \epsilon\,\delta v]|\hat{O}|\Psi[v_0 + \epsilon\,\delta v]\rangle \tag{137}$$

of an observable described by an operator $\hat{O}$ does exist for any $\epsilon > 0$, where $|\Psi[v_0 + \epsilon\,\delta v]\rangle$ is the ground state wavefunction of the perturbed system. Therefore also the limit

$$\bar{O}[v_0, \delta v] = \lim_{\epsilon \to 0} O[v_0 + \epsilon\,\delta v] \tag{138}$$

is defined, although it will in general depend on the potential variation δv. One can therefore define the functional derivative as follows:

$$O'[\delta v] = \lim_{\epsilon \to 0} \frac{O[v_0 + \epsilon\, \delta v] - \bar{O}[v_0, \delta v]}{\epsilon} \tag{139}$$

However, we will see that these derivatives depend in a nonlinear way on δv and are therefore only defined as Gâteaux variations rather than Gâteaux derivatives. We shall especially be interested in the case where $\hat{O}$ is the density operator. For the energy the limit in equation (138) is independent of δv and we may wonder if a Gâteaux derivative still exists. Let us investigate this in more detail. Suppose we have an Hamiltonian $\hat{H}_0$ with external potential v_0 which has a q-fold degenerate ground state. Let us now apply a perturbation $\epsilon\, \delta v$ which lifts the degeneracy. Then there are q eigenstates $\{|\Psi_k(\epsilon)\rangle,\ k = 1 \cdots q\}$ with energies $E_k(\epsilon)$ of the perturbed Hamiltonian that are continuously connected to degenerate ground states $|\Psi_k(0)\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$, i.e.,

$$\lim_{\epsilon \to 0} |\Psi_k(\epsilon)\rangle = |\Psi_k(0)\rangle \tag{140}$$

with

$$E_k(0) = \langle \Psi_k(0)|\hat{H}_0|\Psi_k(0)\rangle = E_0 \tag{141}$$

Note that since the states $|\Psi_k(\epsilon)\rangle$ are orthonormal, also the limiting states $|\Psi_k(0)\rangle$ in the degenerate ground state multiplet are orthonormal. Which particular ground states of the ground state manifold are reached by the $\epsilon \to 0$ limit depends obviously on the form of the perturbation δv. In which way it depends on δv we will investigate now. The ground state wavefunctions $|\Psi_k(\epsilon)\rangle$ satisfy the equation

$$(\hat{H}_0 + \epsilon\, \delta\hat{V} + \frac{\epsilon^2}{2} \delta\hat{U})|\Psi_k(\epsilon)\rangle = E_k(\epsilon)|\Psi_k(\epsilon)\rangle \tag{142}$$

where, for the latter discussion, we also added a one-body potential $\delta\hat{U}$ which is of second order in ϵ. It turns out that this term influences the first order density response. We note, like in the nondegenerate case, that if $|\Psi_k(\epsilon)\rangle$ is a solution to this equation then also $|\Phi_k(\epsilon)\rangle = e^{i\theta_k(\epsilon)}|\Psi_k(\epsilon)\rangle$ is a solution, where $\theta_k(\epsilon)$ is an arbitrary function of ϵ. This freedom will, as in the nondegenerate case, not affect any of the expectation values. If we expand the Schrödinger equation (142) to first order in ϵ we obtain

$$(\hat{H}_0 - E_0)|\Psi_k'(0)\rangle = (E_k'(0) - \delta\hat{V})|\Psi_k(0)\rangle \tag{143}$$

where $E_k'(0)$ and $|\Psi_k'(0)\rangle$ are the first order derivatives of $E_k(\epsilon)$ and $|\Psi_k(\epsilon)\rangle$ with respect to ϵ in $\epsilon = 0$. In order to solve this equation for $|\Psi_k'(0)\rangle$ we expand this quantity in the q ϵ-connected ground states and all the other eigenstates of $\hat{H}_0$, i.e.,

$$|\Psi_k'(0)\rangle = \sum_{i=1}^{\infty} c_i^k |\Psi_i\rangle \tag{144}$$

where $|\Psi_i\rangle = |\Psi_i(0)\rangle$ for $i = 1 \cdots q$ and the states $\{|\Psi_i\rangle, i > q\}$ are eigenstates of $\hat{H}_0$ with eigenenergies $E_i > E_0$. If we insert this expansion into the first order Schrödinger equation (143) we obtain the equation

$$\sum_{i=1}^{\infty} c_i^k (E_i - E_0) |\Psi_i\rangle = (E_k'(0) - \delta\hat{V}) |\Psi_k(0)\rangle \tag{145}$$

If we multiply this equation from the left with $\langle \Psi_j|$ where $1 \leq j \leq q$ we obtain

$$0 = E_k{}'(0)\delta_{jk} - \langle \Psi_j(0)|\delta\hat{V}|\Psi_k(0)\rangle \tag{146}$$

This is the equation that tells us exactly how δv picks out the ground states in the degenerate multiplet. They are exactly the ones that diagonalize $\delta\hat{V}$ within the q-dimensional space of degenerate ground state functions. This equation also tells us that

$$E_k'(0) = \langle \Psi_k(0)|\delta\hat{V}|\Psi_k(0)\rangle = \int \mathrm{d}^3 r \, n_k(\mathbf{r}) \, \delta v(\mathbf{r}) \tag{147}$$

If the perturbed state with the lowest energy has label $k = 1$ then we see that the functional derivative of the ground state energy is given as:

$$\frac{\delta E}{\delta v(\mathbf{r})} = n_1(\mathbf{r}) \tag{148}$$

However, since n_1 implicitly depends on the perturbation δv which picked out a particular ground state, this is not a proper Gâteaux derivative but only a Gâteaux variation. So even the energy functional has no functional derivative in the proper sense. Let us investigate the consequences for different expectation values. We therefore first have to determine the first order wavefunction. If we multiply equation (145) from the right with $\langle \Psi_i|$ where $i > q$ we obtain the coefficient c_i^k for $i > q$ and the following expression for $|\Psi_k'(0)\rangle$:

$$|\Psi_k'(0)\rangle = \sum_{i=1}^{q} c_i^k |\Psi_i\rangle - \sum_{i=q+1}^{\infty} \frac{|\Psi_i\rangle\langle \Psi_i|\delta\hat{V}|\Psi_k(0)\rangle}{E_i - E_0} \tag{149}$$

However, the coefficients c_i^k for $1 \leq i \leq q$ are not determined by equation (143). We know from the orthonormality of the states $|\Psi_k(\epsilon)\rangle$ that

$$0 = \frac{\mathrm{d}\langle \Psi_i|\Psi_k\rangle}{\mathrm{d}\epsilon}(0) = \langle \Psi_i'(0)|\Psi_k(0)\rangle + \langle \Psi_i(0)|\Psi_k'(0)\rangle = c_k^{i*} + c_i^k \tag{150}$$

i.e., the coefficients c_i^k form an anti-Hermitian matrix. In particular, we find that the coefficients c_k^k are purely imaginary. The value of these diagonal elements is undetermined by the Schrödinger equation as they are related to the arbitrary phase $\theta_k(\epsilon)$ which we can choose for each $|\Psi_k(\epsilon)\rangle$. As in the nondegenerate case the value of any expectation value does not depend on the coefficients c_k^k. This leaves us with the determination of the off-diagonal terms c_i^k for $i \neq k$. These coefficients can be found by expanding equation (142) to second order in ϵ^2. This yields

$$(\hat{H}_0 - E_0)|\Psi_k''(0)\rangle = 2(E_k'(0) - \delta\hat{V})|\Psi_k'(0)\rangle + (E_k''(0) - \delta\hat{U})|\Psi_k(0)\rangle \qquad (151)$$

where $|\Psi_k''(0)\rangle$ and $E_k'(0)$ are the second order derivatives of $|\Psi_k(\epsilon)\rangle$ and $E_k(\epsilon)$ in $\epsilon = 0$. If we multiply this equation from the left with $\langle\Psi_l(0)|$ where $1 \leq l \leq q$ and use equations (146) and (149) we obtain

$$\begin{aligned} 0 = {} & 2(E_k'(0) - E_l'(0))c_l^k + E_k''(0)\delta_{lk} - \langle\Psi_l(0)|\delta\hat{U}|\Psi_k(0)\rangle \\ & + 2\sum_{i=q+1}^{\infty} \frac{\langle\Psi_l(0)|\delta\hat{V}|\Psi_i\rangle\langle\Psi_i|\delta\hat{V}|\Psi_k(0)\rangle}{E_i - E_0} \end{aligned} \qquad (152)$$

If we in this equation take $k = l$ we obtain an expression for the energy to second order in ϵ :

$$E_k''(0) = 2\int \mathrm{d}^3r\,\mathrm{d}^3r'\,\delta v(\mathbf{r})\chi_k(\mathbf{r},\mathbf{r}')\,\delta v(\mathbf{r}') + \int \mathrm{d}^3r\,n_k(\mathbf{r})\,\delta u(\mathbf{r}) \qquad (153)$$

where n_k is the density corresponding to $|\Psi_k(0)\rangle$ and χ_k the following function:

$$\chi_k(\mathbf{r},\mathbf{r}') = \sum_{i=q+1}^{\infty} \frac{\langle\Psi_k(0)|\hat{n}(\mathbf{r})|\Psi_i\rangle\langle\Psi_i|\hat{n}(\mathbf{r}')|\Psi_k(0)\rangle}{E_i - E_0} + \text{c.c.} \qquad (154)$$

If, on the other hand, we take $l \neq k$ we obtain our desired equation for the coefficients c_i^k :

$$\begin{aligned} c_l^k = {} & \frac{1}{2}\frac{\langle\Psi_l(0)|\delta\hat{U}|\Psi_k(0)\rangle}{E_k'(0) - E_l'(0)} \\ & + \frac{1}{E_k'(0) - E_l'(0)}\sum_{i=q+1}^{\infty} \frac{\langle\Psi_l(0)|\delta\hat{V}|\Psi_i\rangle\langle\Psi_i|\delta\hat{V}|\Psi_k(0)\rangle}{E_i - E_0} \end{aligned} \qquad (155)$$

We see that indeed $c_l^{k*} = -c_k^l$ as expected. We have therefore completely determined the first order change in the wavefunction. Let us see what this implies for the observables. The first order change in the expectation value of an observable $\hat{O}$ is given by

$$O'(0) = \langle\Psi_k(0)|\hat{O}|\Psi_k'(0)\rangle + \text{c.c.} \qquad (156)$$

If we insert our expression for the first order change in the wavefunction we obtain

$$\begin{aligned} O'(0) = {} & \int \mathrm{d}^3r\,\zeta_k(\mathbf{r})\,\delta v(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}^3r\,\eta_k(\mathbf{r})\,\delta u(\mathbf{r}) \\ & + \int \mathrm{d}^3r\,\mathrm{d}^3r'\,\xi_k(\mathbf{r},\mathbf{r}')\,\delta v(\mathbf{r})\,\delta v(\mathbf{r}') \end{aligned} \qquad (157)$$

where we defined the following functions:

$$\zeta_k(\mathbf{r}) = \sum_{i=q+1}^{\infty} \frac{\langle \Psi_k(0)|\hat{O}|\Psi_i\rangle\langle \Psi_i|\hat{n}(\mathbf{r})|\Psi_k(0)\rangle}{E_i - E_0} + \text{c.c.} \tag{158}$$

$$\eta_k(\mathbf{r}) = \sum_{l=1(l\neq k)}^{q} \frac{\langle \Psi_k(0)|\hat{O}|\Psi_l\rangle\langle \Psi_l|\hat{n}(\mathbf{r})|\Psi_k(0)\rangle}{E_k'(0) - E_l'(0)} + \text{c.c.} \tag{159}$$

$$\xi_k(\mathbf{r},\mathbf{r}') = \sum_{l=1}^{q}\sum_{i=q+1}^{\infty} \frac{\langle \Psi_k(0)|\hat{O}|\Psi_l\rangle\langle \Psi_l|\hat{n}(\mathbf{r})|\Psi_i\rangle\langle \Psi_i|\hat{n}(\mathbf{r}')|\Psi_k(0)\rangle}{(E_k'(0) - E_l'(0))(E_i - E_0)} \tag{160}$$

If we choose $\hat{O} = \hat{n}(\mathbf{r}'')$ then we obtain an expression for the first order change in the density

$$\begin{aligned}\delta n_k(\mathbf{r}'') = &\int \mathrm{d}^3r\, \chi_k(\mathbf{r}'',\mathbf{r})\,\delta v(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}^3r\, \eta_k(\mathbf{r}'',\mathbf{r})\,\delta u(\mathbf{r}) \\ &+ \int \mathrm{d}^3r\,\mathrm{d}^3r'\, \xi_k(\mathbf{r}'',\mathbf{r},\mathbf{r}')\,\delta v(\mathbf{r})\,\delta v(\mathbf{r}')\end{aligned} \tag{161}$$

where the functions χ_k, η_k, and ξ_k are obtained by inserting $\hat{n}(\mathbf{r}'')$ for $\hat{O}$ in equations (158)–(160). If we denote the perturbed state with label $k = 1$ as the one with the lowest energy then δn_1 represents the change in ground state density. We see that this density change does not depend linearly on the first order change δv in the potential and even the second order change δu of the potential contributes to its value. Let us now take $\delta u = 0$ and write

$$\delta n_1(\mathbf{r}'') = \int \mathrm{d}^3r\, \chi_1(\mathbf{r}'',\mathbf{r})\,\delta v(\mathbf{r}) + \int \mathrm{d}^3r\,\mathrm{d}^3r'\, \xi_1(\mathbf{r}'',\mathbf{r},\mathbf{r}')\,\delta v(\mathbf{r})\,\delta v(\mathbf{r}') \tag{162}$$

We can ask ourselves the question whether a given first order variation δn_1 uniquely determines the first order density change δv. One can show from the Hohenberg–Kohn theorem for degenerate states that this is indeed the case. If we in equation (126) take $v_2 = v_1 + \epsilon\, \delta v(\mathbf{r})$ where δv is not a constant function we obtain

$$\epsilon^2 \int \mathrm{d}^3r\, \delta n_1(\mathbf{r})\,\delta v(\mathbf{r}) + O(\epsilon^3) < 0 \tag{163}$$

Dividing by ϵ^2 and taking the limit $\epsilon \longrightarrow 0$ then yields

$$\int \mathrm{d}^3r\, \delta n_1(\mathbf{r})\,\delta v(\mathbf{r}) < 0 \tag{164}$$

We see that the first order density change δn_1 cannot be zero if δv is not a constant. In contrast to the nondegenerate case equation (164) does not imply that the function χ_1 is invertible, only the relation in equation (162) is invertible where the inverse only exists on the set of v-representable density variations within the set $\mathcal{B}$.

Let us now see what the linear response theory can tell us about the differentiability of F_{EHK}. We consider again a system with a degenerate ground state and external potential v_0. Let us take out of the set of ground state ensemble densities for this system a particular density n_0. We may then wonder whether the following limit

$$\frac{\delta F_{\mathrm{EHK}}}{\delta n}[\delta n] = \lim_{\epsilon \to 0} \frac{F_{\mathrm{EHK}}[n_0 + \epsilon\, \delta n] - F_{\mathrm{EHK}}[n_0]}{\epsilon} \tag{165}$$

exists. For this limit to be well-defined we have to make sure that $n_0 + \epsilon\, \delta n \in \mathcal{B}$ and we run into the same problem as for the nondegenerate case. However, in the nondegenerate case we could solve this difficulty using response theory. We will do the same for the degenerate case, but we will see that some difficulties remain. Suppose we look at the perturbed system with potential $v_0 + \epsilon\, \delta v$ in which the degeneracy is lifted. For this system there is a well-defined ground state density $n_\epsilon = n[v_0 + \epsilon\, \delta v]$. From response theory we known that we can write n_ϵ as:

$$n_\epsilon(\mathbf{r}) = n_1(\mathbf{r}) + \epsilon\, \delta n_1(\mathbf{r}) + m_\epsilon(\mathbf{r}) \tag{166}$$

where

$$n_1(\mathbf{r}) = \lim_{\epsilon \to 0} n[v_0 + \epsilon\, \delta v] \tag{167}$$

$$0 = \lim_{\epsilon \to 0} \frac{m_\epsilon(\mathbf{r})}{\epsilon} \tag{168}$$

and where δn_1 is explicitly given in equation (162). Now by construction the density n_ϵ is in $\mathcal{B}$ for all values of ϵ. We can now consider the limit

$$\begin{aligned} \frac{\delta F_{\mathrm{EHK}}}{\delta n}[\delta n_1] &= \lim_{\epsilon \to 0} \frac{F_{\mathrm{EHK}}[n_1 + \epsilon\, \delta n_1 + m_\epsilon] - F_{\mathrm{EHK}}[n_1]}{\epsilon} \\ &= \lim_{\epsilon \to 0} \frac{F_{\mathrm{EHK}}[v_0 + \epsilon\, \delta v] - \bar{F}_{\mathrm{EHK}}[v_0, \delta v]}{\epsilon} \end{aligned} \tag{169}$$

where $\bar{F}_{\mathrm{EHK}}[v_0, \delta v]$ is defined as in equation (138). The latter limit is readily calculated by inserting $\hat{T} + \hat{W} = \hat{H}_0 - \hat{V}_0$ for the operator $\hat{O}$ in equations (158) and (160). We obtain for the first order change of F_{EHK}

$$\begin{aligned} \delta F_{\mathrm{EHK}} = &- \int \mathrm{d}^3 r\, \mathrm{d}^3 r''\, v_0(\mathbf{r}'') \chi_1(\mathbf{r}'', \mathbf{r})\, \delta v(\mathbf{r}) \\ &- \int \mathrm{d}^3 r\, \mathrm{d}^3 r'\, \mathrm{d}^3 r''\, v_0(\mathbf{r}'') \xi_1(\mathbf{r}'', \mathbf{r}, \mathbf{r}')\, \delta v(\mathbf{r})\, \delta v(\mathbf{r}') \\ = &- \int \mathrm{d}^3 r\, v_0(\mathbf{r})\, \delta n_1(\mathbf{r}) \end{aligned} \tag{170}$$

and we thus obtain

$$\lim_{\epsilon \to 0} \frac{F_{\mathrm{EHK}}[n_1 + \epsilon\, \delta n_1 + m_\epsilon] - F_{\mathrm{EHK}}[n_1]}{\epsilon} = - \int \mathrm{d}^3 r\, v_0(\mathbf{r})\, \delta n_1(\mathbf{r}) \tag{171}$$

We see that this limit is linear in δn_1 and that furthermore v_0 is independent of δn_1.

Therefore, we can write for the functional derivative of F_{EHK} in n_1 :

$$\frac{\delta F_{\mathrm{EHK}}}{\delta n(\mathbf{r})}(n_1) = -v_0(\mathbf{r}) \tag{172}$$

up to an arbitrary constant. However, we see that this derivative only exists for some special set of ground state densities corresponding to potential v_0. The derivative exists for those ground state densities that correspond to pure states that can be obtained in the $\epsilon \rightarrow 0$ limit for a perturbed system with potential $v_0 + \epsilon\, \delta v$. It is not clear how to take the functional derivative at an arbitrary ensemble density n_0 for potential v_0. We saw that there exist E-V-densities that are not PS-V-densities. If we consider an ensemble corresponding to such a density and change the external potential to $v_0 + \epsilon\, \delta v$ where δv lifts the degeneracy then for $\epsilon > 0$ the ensemble will change into a pure state and the density will change abruptly. We must therefore conclude that for general E-V-densities the functional derivative of F_{EHK} does not exist. This poses not only a theoretical problem but also a practical one. As we will discuss later, it is known from numerical investigations that there are ground state densities of interacting systems that are not pure state densities for a noninteracting system, and therefore there is a clear need for establishing a Kohn–Sham scheme for arbitrary E-V-densities. Fortunately, it turns out that one can define an extension of the functional F_{EHK} to a larger domain of densities which can be shown to be differentiable at the set of all E-V-densities. This functional is the Lieb functional F_{L} and will be studied in the next section.

12. THE LEVY AND LIEB FUNCTIONALS $F_{\mathrm{LL}}[n]$ AND $F_{\mathrm{L}}[n]$

The functionals F_{HK} and F_{EHK} have the unfortunate mathematical difficulty that their domains of definition $\mathcal{A}$ and $\mathcal{B}$, although they are well defined, are difficult to characterize, i.e., it is difficult to know if a given density n belongs to $\mathcal{A}$ or $\mathcal{B}$. It is therefore desirable to extend the domains of definition of F_{HK} and F_{EHK} to an easily characterizable (preferably convex) set of densities. This can be achieved using the constrained search procedure introduced by Levy [19]. We define the Levy–Lieb functional F_{LL} as:

$$F_{\mathrm{LL}}[n] = \inf_{\Psi} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \tag{173}$$

where the infimum is searched over all normalized antisymmetric N-particle wavefunctions in $H^1(\mathcal{R}^{3N})$ yielding density n. As shown earlier such a density is always in the convex set S which is again a subspace of $L^1 \cap L^3$. One can furthermore show, as has been done by Simon [1], that the infimum is always a minimum, i.e., there is always a minimizing wavefunction. As this is the first important result that we obtain for F_{LL} we put it in the form of a theorem.

Theorem 3. *For any* $n \in \mathcal{S}$ *there is a* $|\Psi[n]\rangle \in H^1(\mathcal{R}^{3N})$ *such that*

$$F_{\mathrm{LL}}[n] = \langle \Psi[n]|\hat{T} + \hat{W}|\Psi[n]\rangle$$

Let us discuss some properties of F_{LL}. The functional F_{LL} is an extension of the Hohenberg–Kohn functional F_{HK}, which is defined on $\mathcal{A}$, to the larger set $\mathcal{S}$, i.e.,

$$F_{\mathrm{LL}}[n] = F_{\mathrm{HK}}[n] \qquad \text{if } n \in \mathcal{A} \tag{174}$$

This is readily derived. Suppose n is some ground state density corresponding to some external potential v and ground state $|\Psi[n]\rangle$ then

$$\begin{aligned} \int n(\mathbf{r})v(\mathbf{r})\, \mathrm{d}\mathbf{r} + F_{\mathrm{HK}}[n] &= \langle \Psi[n]|\hat{H}|\Psi[n]\rangle = \inf_{\Psi \to n} \langle \Psi|\hat{H}|\Psi\rangle \\ &= \int n(\mathbf{r})v(\mathbf{r})\, \mathrm{d}\mathbf{r} + \inf_{\Psi \to n} \langle \Psi|\hat{T} + \hat{W}|\Psi\rangle = \int n(\mathbf{r})v(\mathbf{r})\, \mathrm{d}\mathbf{r} + F_{\mathrm{LL}}[n] \end{aligned} \tag{175}$$

We define a corresponding energy functional

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})\, \mathrm{d}\mathbf{r} + F_{\mathrm{LL}}[n] \tag{176}$$

If n_0 is the ground state density for potential v with corresponding ground state wavefunction $\Psi[n_0]$ then

$$E_v[n] = \inf_{\Psi \to n} \langle \Psi|\hat{H}|\Psi\rangle \geq \langle \Psi[n_0]|\hat{H}|\Psi[n_0]\rangle = E_v[n_0] \tag{177}$$

Minimizing E_v over the set $\mathcal{S}$ therefore yields the ground state density n_0 corresponding to external potential v. The functional F_{LL} has however the inconvenient property that it is not convex.

Theorem 4. *The functional* F_{LL} *is not convex.*

To show this we take the example of a previous section where we presented a density $\bar{n}$ which did not correspond to a ground state wavefunction. It was a convex combination of $2L+1$ degenerate ground state densities n_i with corresponding ground states $|\Psi[n_i]\rangle$ for an external potential v. Then we find

$$\begin{aligned} \int \bar{n}(\mathbf{r})v(\mathbf{r})\, \mathrm{d}\mathbf{r} + F_{\mathrm{LL}}[\bar{n}] &= \inf_{\Psi \to \bar{n}} \langle \Psi|\hat{H}|\Psi\rangle > \frac{1}{2L+1} \sum_{i=1}^{2L+1} \langle \Psi[n_i]|\hat{H}|\Psi[n_i]\rangle \\ &= \frac{1}{2L+1} \sum_{i=1}^{2L+1} F_{\mathrm{LL}}[n_i] + \int \bar{n}(\mathbf{r})v(\mathbf{r})\, \mathrm{d}\mathbf{r} \end{aligned} \tag{178}$$

and we find

$$F_{\mathrm{LL}}[\bar{n}] > \frac{1}{2L+1} \sum_{i=1}^{N} F_{\mathrm{LL}}[n_i] \tag{179}$$

which proves the nonconvexity of F_{LL}. This is somewhat unfortunate as convexity is an important property which can be used to derive differentiability of functionals. We will therefore now define a different but related convex functional with the same domain $\mathcal{S}$. This is the Lieb functional F_{L} defined as:

$$F_{\mathrm{L}}[n] = \inf_{\hat{D} \to n} \mathrm{Tr}\hat{D}(\hat{T} + \hat{W}) \tag{180}$$

where the infimum is searched over all N-particle density matrices

$$\hat{D} = \sum_{i=1} \lambda_i |\Psi_i\rangle\langle\Psi_i| \qquad \sum_{i=1} \lambda_i = 1 \qquad |\Psi_i\rangle \in H^1(\mathcal{R}^{3N}) \tag{181}$$

which yield the given density $n(\mathbf{r}) = \mathrm{Tr}\hat{D}\hat{n}(\mathbf{r})$ where $\{|\Psi_i\rangle\}$ is an orthonormal set. Also for this case one can prove the infimum to be a minimum, i.e., there is a minimizing density matrix. We put the result again in the form of a theorem.

Theorem 5. *For every $n \in \mathcal{S}$ there is a density matrix $\hat{D}[n]$ such that*

$$F_L[n] = \mathrm{Tr}\hat{D}[n](\hat{T} + \hat{W})$$

For the proof of this theorem we again refer to Lieb [1]. The functional F_{L} is an extension of F_{EHK} to the larger set $\mathcal{S}$, i.e.,

$$F_{\mathrm{L}}[n] = F_{\mathrm{EHK}}[n] \quad \text{if } n \in \mathcal{B} \tag{182}$$

This follows directly from the fact that if $n \in \mathcal{B}$ then there is a potential v which generates a ground state ensemble density matrix $\hat{D}[n]$ which yields n. So

$$\begin{aligned} \int n(\mathbf{r})v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{EHK}}[n] &= \int n(\mathbf{r})v(\mathbf{r})\, d\mathbf{r} + \mathrm{Tr}\hat{D}[n](\hat{T} + \hat{W}) = \mathrm{Tr}\hat{D}[n]\hat{H} \\ &= \inf_{\hat{D} \to n} \mathrm{Tr}\hat{D}\hat{H} = \int n(\mathbf{r})v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{L}}[n] \end{aligned} \tag{183}$$

We can again define energy functional

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{L}}[n] \tag{184}$$

which by a similar proof as for F_{LL} assumes its minimum at the ground state density corresponding to potential v. We further have the following relations:

$$F_{\mathrm{L}}[n] = F_{\mathrm{LL}}[n] \quad \text{if } n \in \mathcal{A} \tag{185}$$

and

$$F_{\mathrm{L}}[n] < F_{\mathrm{LL}}[n] \quad \text{if } n \in \mathcal{B} \text{ and } n \notin \mathcal{A} \tag{186}$$

The first relation follows from the fact that if the density n is a pure state v-representable density then the minimizing density matrix for F_{L} is a pure state density matrix. The second relation also easily follows. We take n to be an E-V-density which is not a PS-V-density. There is a ground state ensemble density matrix $\hat{D}[n]$ for which we have

$$\int n(\mathbf{r})v(\mathbf{r})\,\mathrm{d}\mathbf{r} + F_{\mathrm{L}}[n] = \int n(\mathbf{r})v(\mathbf{r})\,\mathrm{d}\mathbf{r} + \mathrm{Tr}\hat{D}[n](\hat{T} + \hat{W}) = \langle \Psi_i | \hat{H} | \Psi_i \rangle \tag{187}$$

where $|\Psi_i\rangle$ is any of the ground states in the degenerate ground state multiplet. Any wavefunction yielding density n cannot be a linear combination of these ground state wavefunctions otherwise n would be pure state v-representable. Therefore its expectation value with the Hamiltonian must be larger, i.e.,

$$\langle \Psi_i | \hat{H} | \Psi_i \rangle < \inf_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle = \int n(\mathbf{r})v(\mathbf{r})\,\mathrm{d}\mathbf{r} + F_{\mathrm{LL}}[n] \tag{188}$$

which proves our statement.

We will now demonstrate another important property of F_{L}, which is its convexity.

Theorem 6. *The functional* F_{L} *is convex.*

This is easily shown. If $n = \lambda_1 n_1 + \lambda_2 n_2$ with $\lambda_1 + \lambda_2 = 1$ and $0 \leq \lambda_1, \lambda_2 \leq 1$ then we have

$$\begin{aligned} \lambda_1 F_{\mathrm{L}}[n_1] + \lambda_2 F_{\mathrm{L}}[n_2] &= \lambda_1 \inf_{\hat{D}_1 \to n_1} \mathrm{Tr}\hat{D}_1(\hat{T} + \hat{W}) + \lambda_2 \inf_{\hat{D}_2 \to n_2} \mathrm{Tr}\hat{D}_2(\hat{T} + \hat{W}) \\ &= \inf_{\hat{D}_1, \hat{D}_2 \to n_1, n_2} \mathrm{Tr}(\lambda_1 \hat{D}_1 + \lambda_2 \hat{D}_2)(\hat{T} + \hat{W}) \\ &\geq \inf_{\hat{D} \to n} \mathrm{Tr}\hat{D}(\hat{T} + \hat{W}) = F_{\mathrm{L}}[n] \end{aligned} \tag{189}$$

We therefore now have established that F_{L} is a convex functional on a convex space. This is important information which enables us to derive the Gâteaux differentiability of the functional F_{L} at the set $\mathcal{B}$ of ensemble v-representable densities. We will discuss this feature of F_{L} in the next section.

Having obtained some desirable convexity properties of F_{L} we try to obtain some analytic properties of this functional. An obvious question to ask is whether this functional is continuous. To be more precise, suppose that a series of densities n_k approaches a given density n in some sense, for instance $\|n - n_k\|_1 \to 0$ and $\|n - n_k\|_3 \to 0$ for $k \to \infty$ in $L^1 \cap L^3$. Does this imply that $|F_{\mathrm{L}}[n_k] - F_{\mathrm{L}}[n]| \to 0$? It turns out that this question is not easily answered. However, one can prove a weaker statement. Suppose n is an E-V-density corresponding to potential v of

Hamiltonian $\hat{H}_v$. Then

$$F_{\mathrm{L}}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v(\mathbf{r}) = \mathrm{Tr}\hat{D}[n]\hat{H}_v \leq \mathrm{Tr}\hat{D}[n_k]\hat{H}_v$$

$$= F_{\mathrm{L}}[n_k] + \int \mathrm{d}^3r\, n_k(\mathbf{r})v(\mathbf{r}) \tag{190}$$

and therefore

$$F_{\mathrm{L}}[n] \leq F_{\mathrm{L}}[n_k] + \int \mathrm{d}^3r\, v(\mathbf{r})(n_k(\mathbf{r}) - n(\mathbf{r})) \tag{191}$$

Further, since $n_k \rightarrow n$ in the norms on $L^1 \cap L^3$ for each $\epsilon > 0$ there is an integer M such that $\|n - n_k\|_1 \leq \epsilon$ and $\|n - n_k\|_3 \leq \epsilon$ for $k > M$. Now we can split $v \in L^{3/2} + L^\infty$ as $v = u + w$ where $u \in L^{3/2}$ and $w \in L^\infty$ and we have

$$\left|\int \mathrm{d}^3r\, v(\mathbf{r})(n_k(\mathbf{r}) - n(\mathbf{r}))\right| \leq \|u\|_{3/2}\|n - n_k\|_3 + \|w\|_\infty \|n - n_k\|_1 \tag{192}$$

So if $\|n - n_k]\|_1 \leq \epsilon/C$ and $\|n - n_k]\|_3 \leq \epsilon/C$, where $C = \|u\|_{3/2} + \|w\|_\infty$ then

$$F_{\mathrm{L}}[n] \leq F_{\mathrm{L}}[n_k] + \epsilon \tag{193}$$

for k sufficiently large. We therefore see that if we take $\epsilon \rightarrow 0$ from above then $F_{\mathrm{L}}[n_k]$ approaches $F_{\mathrm{L}}[n]$ from above and $n_k \rightarrow n$ in the norms on $L^1 \cap L^3$. This, of course, does not imply that $F_{\mathrm{L}}[n]$ is continuous in n. For that we would have to prove that $|F_{\mathrm{L}}[n] - F_{\mathrm{L}}[n_k]| \leq \epsilon$ rather than $F_{\mathrm{L}}[n] - F_{\mathrm{L}}[n_k] \leq \epsilon$. What we have proven is a weaker form of continuity, known as semicontinuity. Because the limit point is a lower bound, the functional with the property in equation (193) is called lower semicontinuous. This can also be characterized differently. If we define $\inf F[n_m]$ by $\inf F_{\mathrm{L}}[n_m] = \inf\{F_{\mathrm{L}}[n_k] | k \geq m\}$ then lower semicontinuity implies

$$F_{\mathrm{L}}[n] \leq \lim_{m \rightarrow \infty} \inf F_{\mathrm{L}}[n_m] \tag{194}$$

Since we required that n is an E-V-density we have proven that F_{L} is lower semicontinuous on the set of E-V-densities. It turns out that one can prove that F_{L} is lower semicontinuous on all densities in $\mathcal{S}$ (see Theorem 4.4 of Lieb [1]). However, the proof of this is not simple and we will therefore not try to reproduce it here. Since the result is important we present it here in the form of a theorem.

Theorem 7. *Suppose n_k and $n \in \mathcal{S}$ and $n_k \rightarrow n$ for $k \rightarrow \infty$ in the norms on $L^1 \cap L^3$. Then*

$$F_L[n] \leq \lim_{k \rightarrow \infty} \inf F_L[n_k]$$

In other words F_L is lower semicontinuous on the set $\mathcal{S}$.

One can prove an even stronger theorem in which we only need weak convergence of the series n_k. We will, however, not need that property in the remainder of this review. The notion of lower semicontinuity is an important property for convex functionals which will allow us to make several other useful statements about other properties of F_{L}. One particular consequence of lower semicontinuity that we will use, is that for a lower semicontinuous convex functional $G : B \rightarrow \mathcal{R}$ the following set of points

$$\mathrm{epi}(G) = \{(n, r) \in B \times \mathcal{R} | G[n] \leq r\} \tag{195}$$

is closed and convex [11]. This set is called the epigraph of G and is simply the set of points that lie above the graph of G. The closedness property means that if a series of points (n_k, r_k) in the epigraph of G converges to a point (n, r) then this point also lies in the epigraph. This also implies that the set of interior points of epi(G), i.e., the set of points that lie strictly above G, is an open convex set (this means that for every point in this set there is a neighborhood that contains it). We will need this property in the next section.

13. DIFFERENTIABILITY OF F_{L}

In this section we will prove that the Lieb functional is differentiable on the set of E-V-densities and nowhere else. The functional derivative at a given E-V-density is equal to $-v$ where v is the external potential that generates the E-V-density at which we take the derivative. To prove existence of the derivative we use the geometric idea that if a derivative of a functional $G[n]$ in a point n_0 exists, then there is a unique tangent line that touches the graph of G in a point $(n_0, G[n_0])$. To discuss this in more detail we have to define what we mean with a tangent. The discussion is simplified by the fact that we are dealing with convex functionals. If $G : B \rightarrow \mathcal{R}$ is a differentiable and convex functional from a normed linear space B to the real numbers then from the convexity property it follows that for $n_0, n_1 \in B$ and $0 \leq \lambda \leq 1$ that

$$G[n_0 + \lambda(n_1 - n_0)] - G[n_0] \leq \lambda(G[n_1] - G[n_0]) \tag{196}$$

From the fact that G is differentiable we then find

$$G[n_1] - G[n_0] \geq \lim_{\lambda \to 0} \frac{G[n_0 + \lambda(n_1 - n_0)] - G[n_0]}{\lambda} = \frac{\delta G}{\delta n}[n_1 - n_0] \tag{197}$$

Therefore

$$G[n_1] \geq G[n_0] + \frac{\delta G}{\delta n}[n_1 - n_0] \tag{198}$$

Now $\delta G/\delta n$ is a continuous linear functional which will be identified with a tangent. This is the basis of the following definition. If for a convex functional G there is

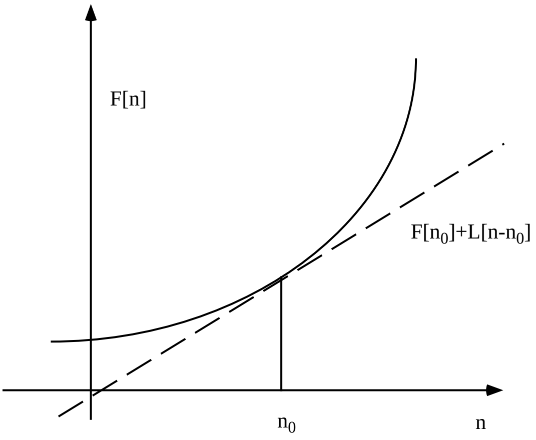

Fig. 1. The convex functional F has a unique tangent functional L in the point n_0.

a continuous linear functional $L : B \longrightarrow \mathcal{R}$ such that

$$G[n_1] \geq G[n_0] + L[n_1 - n_0] \tag{199}$$

then L is called a subgradient or tangent functional in n_0. The geometric idea behind this definition is illustrated in Fig. 1.

For the Lieb functional F_{L} we will now prove the following statement:

Theorem 8. *The functional F_L has a unique tangent functional for every E-V-density and nowhere else. Moreover the tangent functional at an E-V-density n can be identified with $-v$ where v is the potential that generates this density.*

In order to show this we first define the energy functional

$$E[v] = \inf_{\hat{D}} \mathrm{Tr}\, \hat{D}\hat{H}_v \tag{200}$$

where the infimum is searched over all density matrices of the form given in equation (181). This is an extension of the previously defined functional in equation (130) to all potentials in $L^{3/2} + L^{\infty}$. One can further show that if an infimum exists the minimizing density matrix satisfies the Schrödinger equation [1]. Let us first suppose that n_0 is an E-V-density corresponding to potential v of Hamiltonian $\hat{H}_v$. Then

$$\begin{aligned} F_{\mathrm{L}}[n_0] + \int \mathrm{d}^3r\, n_0(\mathbf{r})v(\mathbf{r}) = \mathrm{Tr}\hat{D}[n_0]\hat{H}_v \leq \mathrm{Tr}\hat{D}[n]\hat{H}_v \\ = F_{\mathrm{L}}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v(\mathbf{r}) \end{aligned} \tag{201}$$

and therefore

$$F_{\mathrm{L}}[n] \geq F_{\mathrm{L}}[n_0] - \int \mathrm{d}^3 r\, v(\mathbf{r})(n(\mathbf{r}) - n_0(\mathbf{r})) \tag{202}$$

Therefore the functional L

$$L[n] = -\int \mathrm{d}^3 r\, v(\mathbf{r}) n(\mathbf{r}) \tag{203}$$

defines a linear and continuous functional (continuity follows from equation (192)) and is therefore a tangent functional. Now we have to show its uniqueness. Suppose L' is a different tangent functional. Since F is defined on $B = L^1 \cap L^3$ the tangent functional must represent an element in the dual space $B^* = L^{3/2} + L^{\infty}$ and can be written as:

$$L'[n] = -\int \mathrm{d}^3 r\, \tilde{v}(\mathbf{r}) n(\mathbf{r}) \tag{204}$$

with $\tilde{v} \in L^{3/2} + L^{\infty}$ and $\tilde{v} \neq v + C$. Now since we assumed that L' was also tangent functional we have

$$F_{\mathrm{L}}[n] \geq F_{\mathrm{L}}[n_0] - \int \mathrm{d}^3 r\, \tilde{v}(\mathbf{r})(n(\mathbf{r}) - n_0(\mathbf{r})) \tag{205}$$

and hence

$$F_{\mathrm{L}}[n] + \int \mathrm{d}^3 r\, n(\mathbf{r})\tilde{v}(\mathbf{r}) \geq F_{\mathrm{L}}[n_0] + \int \mathrm{d}^3 r\, n_0(\mathbf{r})\tilde{v}(\mathbf{r}) \tag{206}$$

We take the infimum over all densities in $\mathcal{S}$ on the left hand side. Since we know that there is ground state density matrix corresponding to n_0 we obtain from equation (206):

$$E[\tilde{v}] = \inf_{n \in \mathcal{S}} \{F_{\mathrm{L}}[n] + \int \mathrm{d}^3 r\, n(\mathbf{r})\tilde{v}(\mathbf{r})\} \geq \mathrm{Tr}\hat{D}[n_0]\hat{H}_{\tilde{v}} \tag{207}$$

Now there are two cases, either the Hamiltonian with potential $\tilde{v}$ is able to support a bound ground state or it is not. If it does support a ground state then

$$\mathrm{Tr}\hat{D}[n_0]\hat{H}_{\tilde{v}} > E[\tilde{v}] \tag{208}$$

since $\hat{D}[n_0]$ is not a ground state density matrix for $\tilde{v}$. Together with equation (207) this immediately leads to the contradiction $E[\tilde{v}] > E[\tilde{v}]$. If the Hamiltonian with potential $\tilde{v}$ does not support a bound ground state then there is no normalized density matrix for which the infimum of $E[\tilde{v}]$ as in equation (200) is attained. We then again obtain equation (208) and the same contradiction $E[\tilde{v}] > E[\tilde{v}]$. We therefore conclude that the E-V-density n_0 has a unique tangent functional equal to $-v$ where v is the potential that yields ground state density n_0.

Let us now suppose that n_0 is not an E-V-density. Let us further suppose that there is a tangent functional at n_0, i.e., that for some $\tilde{v}$ equation (205) and therefore also equation (206) are satisfied. The constrained search for $F_\mathrm{L}[n_0]$ always has a minimizing density matrix, which we call $\hat{D}[n_0]$. With this density matrix then also equation (207) is true. Since n_0 is not an E-V-density $\hat{D}[n_0]$ cannot be a ground state density matrix for the Hamiltonian with potential $\tilde{v}$. With the same arguments as before we find that equation (208) must be true which again leads to the contradiction $E[\tilde{v}] > E[\tilde{v}]$. Therefore there is no tangent functional at n_0 if n_0 is not an E-V-density. We have therefore proven our statement, there is a unique tangent functional at every E-V-density and nowhere else.

As a next step we will show that this implies that the functional F_L is Gâteaux differentiable at every E-V-density and nowhere else. For the application of the next theorem it is desirable to extend the domain of F_L to all of $L^1 \cap L^3$. We follow Lieb 1 and define

$$F_\mathrm{L}[n] = \begin{cases} \inf\limits_{\hat{D}\to n} \mathrm{Tr}\hat{D}(\hat{T}+\hat{W}) & \text{if } n \in \mathcal{S} \\ +\infty & \text{if } n \in L^1 \cap L^3 \text{ and } n \notin \mathcal{S} \end{cases} \tag{209}$$

The reader may seem surprised with the appearance of $+\infty$ in this definition. However, infinite values are well defined in the theory of convex functionals [11] and they are usually introduced to deal in a simple way with domain questions. With this definition the functional F_L is a convex lower semicontinuous functional on the whole space $L^1 \cap L^3$. We are now ready to introduce the following key theorem which we will use to prove differentiability of F_L at the set of E-V-densities:

Theorem 9. *Suppose $F : B \longrightarrow \mathcal{R}$ is a lower semicontinous convex functional which is finite at a convex subset $V \subset B$ of a normed linear space B. If F has a unique continuous tangent functional $L : B \longrightarrow \mathcal{R}$ at $n_0 \in V$ then F is Gâteaux differentiable at n_0 and $L = \delta F/\delta n$.*

The fact that uniqueness of a tangent functional implies differentiability is clear from a geometric point of view. In Fig. 2 we display an example of a functional (in this picture the functional is simply a function) which is not differentiable at n_0. Consequently, there is no unique tangent functional at that point. In the example there are in fact infinitely many tangent functionals at n_0 of which there are two drawn in the plot.

In the case of infinitely many dimensions one should, however, be careful in drawing conclusions from simple plots and we have to resort to formal proofs. Since the proof of the previous theorem is important for our discussion and not difficult to follow, we will present it here. Since V is a convex set we have that if $n_0 \in V$ and $n_1 \in V$ then $n_0 + \lambda(n_1 - n_0) \in V$ for $0 \leq \lambda \leq 1$ and since F is convex we obtain

$$F[n_0 + \lambda(n_1 - n_0)] \leq F[n_0] + \lambda(F[n_1] - F[n_0]) \tag{210}$$

Furthermore, since F has a unique continuous tangent functional at n_0 we have

$$F[n_0 + \lambda(n_1 - n_0)] \geq F[n_0] + \lambda L[n_1 - n_0] \tag{211}$$

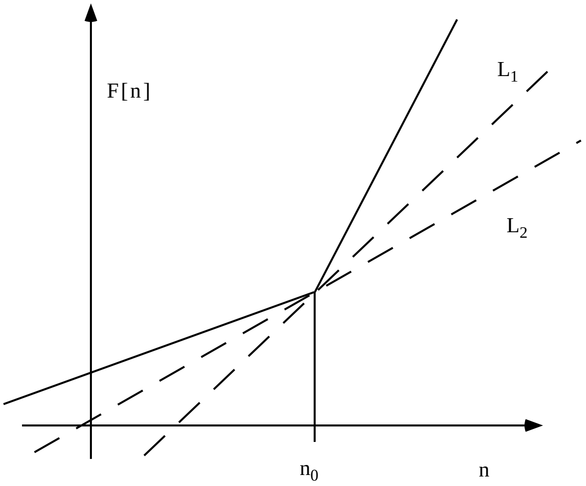

Fig. 2. The convex functional F has no unique tangent functional in the point n_0. Both L_1 and L_2 are tangent functionals.

Note that $n_1 - n_0$ need not be in V but is always in B since that is a linear space. If we combine the two inequalities we find that

$$F[n_1] - F[n_0] \geq \frac{F[n_0 + \lambda(n_1 - n_0)] - F[n_0]}{\lambda} \geq L[n_1 - n_0] \qquad (212)$$

Now since F is convex the function $g(\lambda) = F[n_0 + \lambda(n_1 - n_0)] - F[n_0]$ is a convex real function on the interval $[0, 1]$ and hence continuous. Moreover, as the equation above shows, the function $g(\lambda)/\lambda$ has a finite upper and lower bound and therefore the limit $\lambda \to 0$ of $g(\lambda)/\lambda$ exists. We therefore find

$$F[n_1] - F[n_0] \geq F'[n_0, n_1] \geq L[n_1 - n_0] \qquad (213)$$

where

$$F'[n_0, n_1] = \lim_{\lambda \to 0} \frac{F[n_0 + \lambda(n_1 - n_0)] - F[n_0]}{\lambda} \qquad (214)$$

It remains to show that $F'[n_0, n_1]$ is continuous and linear and equal to L. Now F' has the property that for $n_2 \in V$

$$\begin{aligned} F'[n_0, n_0 + \epsilon(n_2 - n_0)] &= \lim_{\lambda \to 0} \frac{F[n_0 + \lambda\epsilon(n_2 - n_0)] - F[n_0]}{\lambda} \\ &= \epsilon F'[n_0, n_2] \end{aligned} \qquad (215)$$

Therefore from equation (213) we find

$$F[n_0 + \epsilon(n_1 - n_0)] \geq F[n_0] + \epsilon F'[n_0, n_1] \qquad (216)$$

This means that the straight line

$$\mathcal{L} = \{(n_0 + \epsilon(n_1 - n_0), F[n_0] + \epsilon F'[n_0, n_1]) \in B \times \mathcal{R} | \epsilon \in [0,1]\} \tag{217}$$

lies below the graph of functional F. Now since F is convex and lower semicontinuous the set of points above the graph of F (the interior points of epi(F)) form an open convex set which is nonempty since F is finite on V [11]. Now a famous theorem of functional analysis, the Hahn–Banach theorem, tells us that if we have an open convex set A (the interior of epi(F) in our case) and an affine subspace $\mathcal{L}$ (which is the line $\mathcal{L}$ in our case) that does not intersect A then there is a hyperplane $\mathcal{H}$ that contains $\mathcal{L}$ in which the hyperplane $\mathcal{H}$ has the form:

$$\mathcal{H} = \{(n, r) \in B \times \mathcal{R} | L'[n] + \alpha r = \beta\} \tag{218}$$

where $L' : B \rightarrow \mathcal{R}$ is a continuous linear functional and α and β are real numbers (We can take $\alpha \neq 0$ since $F'[n_0, n_1]$ is finite and we will have no vertical line $\mathcal{L}$ or vertical hyperplane $\mathcal{H}$.) We will not prove the Hahn–Banach theorem as it is geometrically intuitive and can be found in most textbooks on functional analysis [20,21]. We will just use its consequences.

Now we know that our line $\mathcal{L}$ is contained in $\mathcal{H}$. The coefficient β is then determined by the fact that $(n_0, F[n_0]) \in \mathcal{H}$ and we find $\beta = L'[n_0] + \alpha F[n_0]$ and therefore

$$\mathcal{H} = \{(n, r) \in B \times \mathcal{R} | L'[n - n_0] + \alpha(r - F[n_0]) = 0\} \tag{219}$$

Now from the fact that $(n_0 + \epsilon(n_1 - n_0), F[n_0] + \epsilon F'[n_0, n_1]) \in \mathcal{H}$ we find that

$$L'[n_1 - n_0] + \alpha F'[n_0, n_1] = 0 \tag{220}$$

From equation (220) and (213) we then see immediately that $-L'/\alpha$ is a continuous tangent functional at n_0 which then must be equal to L since that was the only continuous tangent functional at n_0. Consequently,

$$F'[n_0, n_1] = L[n_1 - n_0] \tag{221}$$

and thus

$$\frac{\delta F}{\delta n}[n_1 - n_0] = \lim_{\lambda \to 0} \frac{F[n_0 + \lambda(n_1 - n_0)] - F[n_0]}{\lambda} = L[n_1 - n_0] \tag{222}$$

We therefore obtained what we wanted to prove, F is Gâteaux differentiable at n_0 and $\delta F/\delta n = L$. Now we can apply this theorem to the Lieb functional. If we take $F = F_{\mathrm{L}}$, $B = L^1 \cap L^3$, $V = \mathcal{S}$ and use that F_{L} has a unique tangent functional $L = -v$ at every E-V-density and nowhere else, we obtain:

Theorem 10. *The functional F_{L} is Gâteaux differentiable for every E-V-density in the set $\mathcal{S}$ and nowhere else. Moreover, the functional derivative at an E-V-density is equal to $-v$ where v is the potential that generates this density.*

This leaves us with the question which densities in set $\mathcal{S}$ actually are E-V-densities. A useful result on this point is obtained in the next section.

14. ENSEMBLE $\boldsymbol{v}$-REPRESENTABILITY

We have seen that the Lieb functional F_{L} is differentiable at the set of E-V-densities in $\mathcal{S}$ and nowhere else. For this reason it is desirable to know a bit more about these densities. The question therefore is: which densities are ensemble v-representable? In this section we will prove a useful result which will enable us to put the Kohn–Sham approach on a rigorous basis.

Theorem 11. *The set of E-V-densities is dense in the set $\mathcal{S}$ with respect to the norm on $L^1 \cap L^3$.*

This statement means the following. Suppose we take an arbitrary density n_0 from the set $\mathcal{S}$, then for every $\epsilon > 0$ we can find an E-V-density n such that $\|n_0 - n\|_1 \leq \epsilon$ and $\|n_0 - n\|_3 \leq \epsilon$. In other words, for every density in the set $\mathcal{S}$ there is an E-V-density arbitrarily close to it. This can also be phrased differently. For every density n_0 in the set $\mathcal{S}$ there is a series of E-V-densities n_k such that

$$\lim_{k \to \infty} \|n_0 - n_k\|_p = 0 \tag{223}$$

where the subindex for the norm takes the values $p = 1$ and $p = 3$. In order to establish this result we need to use a theorem due to Bishop and Phelps. For the clarity of the discussion we split the theorem into two parts which both yield interesting results for our functional F_{L}. The first part gives some insight in the set of potentials $\mathcal{V}$ that generate a bound ground state. From the relation

$$E[v] = \inf_{n \in \mathcal{S}} \left\{ F_{\mathrm{L}}[n] + \int \mathrm{d}^3 r\, n(\mathbf{r}) v(\mathbf{r}) \right\} \tag{224}$$

we obtain immediately that for any $n \in \mathcal{S}$ and any $v \in L^{3/2} + L^{\infty}$

$$F_{\mathrm{L}}[n] \geq -\int \mathrm{d}^3 r\, n(\mathbf{r}) v(\mathbf{r}) + E[v] \tag{225}$$

Now the functional on the right hand side of the inequality sign is, for a given v, a linear functional of n. The inequality sign tells us that this functional lies below the graph of $F_{\mathrm{L}}[n]$. A linear functional with this property is called F_{L}-bounded. Let us give a general definition of these linear functionals. Let F be a functional $F : B \longrightarrow \mathcal{R}$ from a normed function space (a Banach space) B to the real numbers. Let B^* be the dual space of B, i.e., the set of continuous linear functionals on B. Then $L \in B^*$ is said to be F-bounded if there is a constant C such that for all $n \in B$

$$F[n] \geq L[n] + C \tag{226}$$

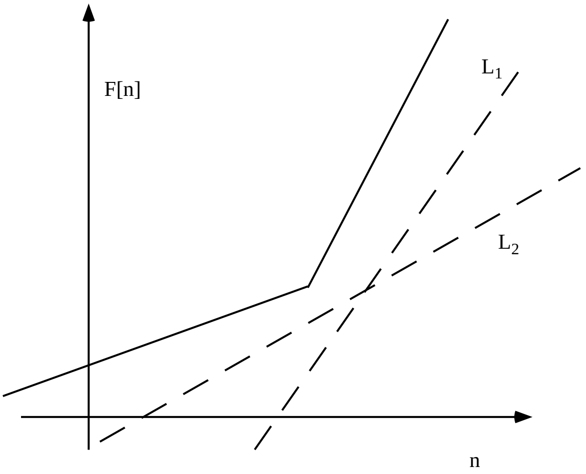

Fig. 3. Both L_1 and L_2 are F-bounded by the convex functional F.

where the constant C may depend on L but not on n. We therefore see from equation (225) that every $v \in L^{3/2} + L^{\infty}$ defines an F_{L}-bounded functional where L is defined as in equation (203). The geometric picture of an F-bounded functional is displayed in Fig. 3.

Note that the tangent functionals of F_{L} are special cases of F_{L}-bounded functionals, they are the F_{L} bounded functionals that also touch the graph of F_{L}. Therefore the set of tangent functionals is a subset of the set of F_{L}-bounded functionals. This can be illustrated with an example. Consider the function $f(x) = \exp(x)$ on the real axis. This function is convex and all tangent functions are of the form $g_{\alpha}(x) = \alpha x + \beta$ where $\alpha > 0$ and $\beta(\alpha) \leq 1$. The constant function $g_0(x) = \beta$ with $\beta \leq 0$ is an f-bounded function, but not a tangent. However, we can always find a tangent with a slope arbitrary close to zero, i.e., arbitrary close to the slope of the constant f-bounded function g_0. The following theorem (due to Bishop and Phelps) ensures that a similar situation occurs for the case of general Banach spaces:

Theorem 12 (Bishop–Phelps I). *Let $F : B \to \mathcal{R}$ be a lower semicontinuous convex functional on a real Banach space B. The functional F can take the value $+\infty$ but not everywhere. Then the continuous tangent functionals to F are B^*-norm dense in the set of F-bounded functionals in B^*.*

This means that if L_0 is some F-bounded functional then we can find a set of tangent functionals L_k such that

$$\lim_{k \to \infty} \|L_0 - L_k\|_{B^*} = 0 \tag{227}$$

where the limit is taken in the norm on B^*. We will not prove this theorem here. The proof is clearly described with a geometric interpretation in Ref. [22]. Let us apply this theorem to our functional F_{L}. We know that every tangent functional of F_{L} can be identified with $-v$, where v is a potential that yields a bound ground state, i.e., $v \in \mathcal{V}$. Now we know that every element $-v_0$ for an arbitrary $v_0 \in L^{3/2} + L^{\infty}$ corresponds to an F_{L}-bounded functional. Therefore for such a v_0 there is a series of $v_k \in \mathcal{V}$ such that

$$\lim_{k \to \infty} \|v_0 - v_k\| = 0 \tag{228}$$

where the norm is the $L^{3/2} + L^{\infty}$-norm described in equation (24). Therefore every potential $v_0 \in L^{3/2} + L^{\infty}$ can be approximated to arbitrary accuracy by a potential that yields a bound ground state. This may seem counterintuitive at first sight as one can imagine v_0 to be a repulsive potential, until one realizes that one may put the system in big box with a wall of finite height. This system will have a bound state if the size of the box is chosen to be big enough. The particles will then spread out over the box in order to minimize the repulsion between them. If we choose $v_k = v_0 + w_k$ where w_k describes a series of boxes of increasing size but with decreasing height of the potential wall then we see that we have created a series of potentials in $\mathcal{V}$ that approaches v_0 to an arbitrary accuracy. Let us now discuss the second part of the Bishop–Phelps theorem.

Theorem 13 (Bishop–Phelps II). *Let $F : B \to \mathcal{R}$ be a lower semicontinuous convex functional on a real Banach space B. The functional F can take the value $+\infty$ but not everywhere. Suppose $n_0 \in B$ with $F[n_0] < \infty$ and let $L_0 \in B^*$ be an F-bounded functional. Then for every $\epsilon \geq 0$ there exists $n_\epsilon \in B$ and a functional $L_\epsilon \in B^*$ such that*

1. $\|L_\epsilon - L_0\|_{B^*} \leq \epsilon$.
2. $F[n] \geq F[n_\epsilon] + L_\epsilon[n - n_\epsilon]$ *for all n.*
3. $\epsilon \|n_\epsilon - n_0\|_B \leq F[n_0] - L_0[n_0] - \mathit{inf}_{n \in B}\{F[n] - L_0[n]\}$.

For the details of the proof we again refer to Ref. [22]. The first two points of this theorem are equivalent to the previous theorem. They say that any F-bounded functional L_0 can be approximated to arbitrary accuracy by a tangent functional L_ϵ. The inequality in the third point of this theorem allows us to make statements about distances between elements in B, which in our case will be densities. Note that the right hand side of this inequality has the geometric meaning of being the difference of the vertical distance of the functionals L_0 and F in n_0 and the shortest possible distance between L_0 and F. Let us now apply this theorem to the functional F_{L} and show that that every density in $\mathcal{S}$ is arbitrarily close to an E-V-density. We first need some preliminaries. From equation (224) we see that we can write

$$F_{\mathrm{L}}[n] = \sup_{v \in L^{3/2} + L^{\infty}} \left\{ E[v] - \int \mathrm{d}^3 r \, n(\mathbf{r}) v(\mathbf{r}) \right\} \tag{229}$$

If the supremum is attained for some v then n is an E-V-density. This follows because then there is a density matrix $\hat{D}[n]$ that yields density n (see Theorem 5) such that

$$\mathrm{Tr}\hat{D}[n]\hat{H}_v = F_{\mathrm{L}}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v(\mathbf{r}) = E[v] = \inf_{\hat{D}} \mathrm{Tr}\hat{D}\hat{H}_v \tag{230}$$

The density matrix $\hat{D}[n]$ must therefore be a ground state density matrix. If n is not an E-V-density then the supremum is not attained for any v. In any case, for every integer k and any density $n_0 \in \mathcal{S}$ we can always find some v_k such that

$$\begin{aligned} E[v_k] - \int \mathrm{d}^3r\, n_0(\mathbf{r})v_k(\mathbf{r}) &\geq \sup_{v \in L^{3/2}+L^{\infty}} \left\{ E[v] - \int \mathrm{d}^3r\, n_0(\mathbf{r})v(\mathbf{r}) \right\} - \frac{1}{k} \\ &= F_{\mathrm{L}}[n_0] - \frac{1}{k} \end{aligned} \tag{231}$$

where we note that the series v_k does not converge to any v if n_0 is not an E-V-density. Furthermore, for any n we have

$$E[v_k] = \inf_{n \in \mathcal{S}} \left\{ F_{\mathrm{L}}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v_k(\mathbf{r}) \right\} \leq F_{\mathrm{L}}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v_k(\mathbf{r}) \tag{232}$$

which in combination with the previous inequality yields

$$F_{\mathrm{L}}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v_k(\mathbf{r}) \geq E[v_k] \geq F_{\mathrm{L}}[n_0] + \int \mathrm{d}^3r\, n_0(\mathbf{r})v_k(\mathbf{r}) - \frac{1}{k} \tag{233}$$

We are now ready to apply the Bishop–Phelps theorem to the Lieb functional F_{L}. We take $\epsilon = 1$, $n_0 \in \mathcal{S}$ and let $-v_k$ correspond to the F-bounded functional L_0 of the theorem. According to the theorem we can then find a tangent functional $-w_k$ (the L_ϵ of the theorem) such that

$$\|v_k - w_k\| \leq 1 \tag{234}$$

in the norm on $L^{3/2} + L^{\infty}$. From our previous investigations we know that the tangent $-w_k$ touches the graph of F_{L} in an E-V-density n_k, i.e.,

$$F_{\mathrm{L}}[n] \geq F_{\mathrm{L}}[n_k] - \int \mathrm{d}^3r\, w_k(\mathbf{r})(n(\mathbf{r}) - n_k(\mathbf{r})) \tag{235}$$

where w_k is the potential that generates density n_k. The Bishop–Phelps theorem then tells us that

$$\begin{aligned}\|n_k - n_0\|_p \leq F_\mathrm{L}[n_0] &+ \int \mathrm{d}^3r\, n_0(\mathbf{r})v_k(\mathbf{r}) \\ &- \inf_{n\in\mathcal{S}}\left\{F_\mathrm{L}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v_k(\mathbf{r})\right\}\end{aligned} \tag{236}$$

where the normindex has the values $p = 1$ and $p = 3$. Note that the infimum in this equation can be taken over $\mathcal{S}$ rather than $L^1 \cap L^3$ since F_L is defined to be $+\infty$ outside $\mathcal{S}$. Then from equation (233) we see immediately that

$$\inf_{n\in\mathcal{S}}\left\{F_\mathrm{L}[n] + \int \mathrm{d}^3r\, n(\mathbf{r})v_k(\mathbf{r})\right\} \geq F_\mathrm{L}[n_0] + \int \mathrm{d}^3r\, n_0(\mathbf{r})v_k(\mathbf{r}) - \frac{1}{k} \tag{237}$$

and therefore

$$\|n_k - n_0\|_p \leq \frac{1}{k} \tag{238}$$

for $p = 1$ and $p = 3$. Since this equation is true for any k we see that any density $n_0 \in \mathcal{S}$ can be approximated to any accuracy by the E-V-density n_k in the norms on $L^1 \cap L^3$. This proves the theorem in the beginning of this section.

15. THE KOHN–SHAM APPROACH AND NONINTERACTING v-REPRESENTABILITY

We have now come to the discussion of the central equations which form the basis of almost any practical application of density functional theory: the Kohn–Sham equations. Kohn and Sham [8] introduced an auxiliary noninteracting system of particles with the property that it yields the same ground state density as the real interacting system. In order to put the Kohn–Sham procedure on a rigorous basis we introduce the functional

$$T_\mathrm{L}[n] = \inf_{\hat{D}\rightarrow n} \mathrm{Tr}\hat{D}\hat{T} \tag{239}$$

We see that this is simply the Lieb functional with the two-particle interaction omitted. All the properties of the functional F_L carry directly over to T_L. The reason is that all these properties were derived on the basis of the variational principle in which we only required that $\hat{T} + \hat{W}$ is an operator that is bounded from below. This is, however, still true if we omit the Coulomb repulsion $\hat{W}$. We therefore conclude that T_L is a convex lower semicontinuous functional which is differentiable for any density n that is ensemble v-representable for the noninteracting system and nowhere else. We refer to such densities as noninteracting E-V-densities and denote the set of all noninteracting E-V-densities by $\mathcal{B}_0$. Let us collect all the results for T_L in a single theorem:

Theorem 14. *T_L is a convex lower semicontinuous functional with the following properties:*

1. *For any $n \in \mathcal{S}$ there is a minimizing density matrix $\hat{D}[n]$ with the property $T_L[n] = Tr\hat{D}[n]\hat{T}$.*
2. *T_L is Gâteaux differentiable at the set of noninteracting E-V-densities and nowhere else.*
3. *The functional derivative at a noninteracting E-V-density n is given by:*

$$\frac{\delta T_L}{\delta n(\boldsymbol{r})} = -v_s[n](\boldsymbol{r})$$

where the potential v_s generates the density n in a noninteracting system.

From the last point in this theorem we see that if we want to know if a given density n from the set $\mathcal{S}$ can be obtained as an E-V-density of a noninteracting system we may try to calculate the derivative of T_{L} for this density. If it exists then the derivative yields the potential that we were looking for. Now Kohn and Sham [8] assumed that for any density of an interacting system there is a noninteracting system that has the same density as its ground state. We can now ask the question whether the sets of interacting and noninteracting E-V-densities are equal. This is currently not known. However, we can make a number of useful conclusions. First of all, if we apply the Bishop–Phelps theorem to the functional T_{L} we obtain the following result:

Theorem 15. *The set of noninteracting E-V-densities is dense in the set $\mathcal{S}$ with respect to the norm on $L^1 \cap L^3$.*

This means that for any density $n \in \mathcal{S}$ there is an noninteracting E-V-density arbitrarily close. We can in particular choose n to be an interacting E-V-density, i.e., $n \in \mathcal{B}$ and find a noninteracting E-V-density arbitrarily close. We also know from the Bishop–Phelps theorem applied to F_{L} that the set of interacting E-V-densities is dense in $\mathcal{S}$ and therefore for any $n \in \mathcal{S}$, in particular $n \in \mathcal{B}_0$, we can find an interacting E-V-density arbitrarily close. We therefore conclude:

Theorem 16. *The set $\mathcal{B}_0$ of noninteracting E-V-densities is dense in the set $\mathcal{B}$ of interacting E-V-densities, and vice versa.*

If we combine this result with previous theorems we obtain the following important consequence for the Kohn–Sham scheme:

Theorem 17. *Suppose $n \in \mathcal{B}$ is an interacting E-V-density. Then for every $\epsilon > 0$ there is a noninteracting E-V-density $n_\epsilon \in \mathcal{B}_0$ such that*

1. $\|n - n_\epsilon\|_p \leq \epsilon$ *for* $p = 1$ *and* $p = 3$.
2. *The density* n_ϵ *is a ground state ensemble density of a noninteracting system with potential*

$$v_{s,\epsilon}(\boldsymbol{r}) = -\frac{\delta T_L}{\delta n(\boldsymbol{r})}(n_\epsilon)$$

i.e., we can always set up a Kohn–Sham scheme that produces a given interacting E-V-density to arbitrary accuracy.

This theorem tells us that in practice we can always set up a Kohn–Sham scheme. We also see that if we want to prove that the sets $\mathcal{B}$ and $\mathcal{B}_0$ of interacting and noninteracting E-V-densities are equal, then we have to show that the potentials $v_{s,\epsilon}$ in this theorem approach some potential $v_{s,0}$ for $\epsilon \longrightarrow 0$ in some smooth way. This, however, has not been proven until now. In numerical calculations (see the discussion at the end of this section) one has indeed always succeeded in obtaining a Kohn–Sham potential for given interacting E-V-densities obtained from accurate configuration interaction (CI) calculations. In these calculations convergence to a given Kohn–Sham potential is sometimes difficult to obtain, but seems to happen in a rather smooth way. One might therefore expect that the sets of interacting and noninteracting E-V-densities are in fact equal. In order to encourage further work in this field we put it here as a conjecture.

Conjecture 1. *The sets* $\mathcal{B}$ *and* $\mathcal{B}_0$ *of interacting and noninteracting E-V-densities are equal, i.e.,* $\mathcal{B} = \mathcal{B}_0$.

Let us describe a couple of cases for which we know this conjecture to be true. Consider a system of two particles. Let the interacting system have density n. Then we can construct a noninteracting Kohn–Sham system with ground state wavefunction

$$\Psi_{\mathrm{KS}}(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \frac{1}{\sqrt{2}}\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)(\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)) \tag{240}$$

where α and β are the usual spin functions with $\alpha(1/2) = \beta(-1/2) = 1$ and $\alpha(-1/2) = \beta(1/2) = 0$. This wavefunction has a density $n(\mathbf{r}) = 2|\varphi(\mathbf{r})|^2$ and the Kohn–Sham orbital φ satisfies

$$(-\tfrac{1}{2}\nabla^2 + v_s[n](\mathbf{r}))\varphi(\mathbf{r}) = \epsilon\varphi(\mathbf{r}) \tag{241}$$

If we now choose $\varphi(\mathbf{r}) = \sqrt{\varphi(\mathbf{r})/2}$ then for an interacting E-V-density n the Kohn–Sham Hamiltonian with potential

$$v_s[n](\mathbf{r}) = \frac{1}{2}\frac{\nabla^2\sqrt{n}}{\sqrt{n}} + \epsilon \tag{242}$$

has orbital φ as an eigenfunction. Because the density is positive the orbital $\varphi = \sqrt{n/2}$ has no nodes and must be a ground state orbital. We therefore have constructed a noninteracting system with ground state n, which is even a pure state density.

Another case where the conjecture is true is for lattice systems. The lattice system is obtained by discretizing the many-body Hamiltonian on a grid, i.e., we replace the differential equation by a difference equation as one might do to solve the Schrödinger equation numerically. Then any interacting E-V-density on the grid is also a noninteracting E-V-density. This was proven by Chayes, Chayes, and Ruskai [23]. This work may be used to prove the general conjecture above if one can prove that the continuum limit can be taken in some smooth way.

Let us finally discuss the exchange–correlation functional which is the central object in any application of density functional theory. We define the exchange–correlation functional E_{xc} by

$$F_{\mathrm{L}}[n] = T_{\mathrm{L}}[n] + \frac{1}{2}\int \mathrm{d}^3r_1\, \mathrm{d}^3r_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_{\mathrm{xc}}[n] \tag{243}$$

Since both T_{L} and F_{L} are defined on the set $\mathcal{S}$ the exchange–correlation functional E_{xc} is also defined on that set. Since F_{L} and T_{L} are differentiable, respectively, on the sets $\mathcal{B}$ and $\mathcal{B}_0$ and nowhere else, the functional E_{xc} is differentiable on $\mathcal{B} \cap \mathcal{B}_0$ and nowhere else. The derivative of equation (243) on that set is given by

$$-v(\mathbf{r}) = -v_s(\mathbf{r}) + \int \mathrm{d}^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})} \tag{244}$$

If we define the exchange–correlation potential by

$$v_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})} \tag{245}$$

then we see that the Kohn–Sham potential can be written as:

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int \mathrm{d}^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\mathrm{xc}}(\mathbf{r}) \tag{246}$$

We see that on the set $\mathcal{B} \cap \mathcal{B}_0$ we have obtained the usual Kohn–Sham equations

$$[\hat{T} + \hat{V} + \hat{V}_H[n] + \hat{V}_{\mathrm{xc}}[n]|\Phi_i\rangle = E_0|\Phi_i\rangle \tag{247}$$

where $i = 1\cdots q$ runs over the q degenerate ground states $|\Phi_i\rangle$ of the Kohn–Sham system. The density must now be calculated from a ground state ensemble

$$\hat{D}_s[n] = \sum_{i=1}^{q} \mu_i |\Phi_i\rangle\langle\Phi_i| \tag{248}$$

of the Kohn–Sham system and is explicitly given as:

$$n(\mathbf{r}) = \mathrm{Tr}\hat{D}_s[n]\hat{n}(\mathbf{r}) = \sum_{i=1}^{q} \mu_i \langle\Phi_i|\hat{n}(\mathbf{r})|\Phi_i\rangle \tag{249}$$

These equations can be written more explicitly in terms of Kohn–Sham orbitals defined to be the eigenstates of the single particle equation

$$(-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r}))\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \tag{250}$$

It is then easily seen that any Slater determinant

$$|\Phi\rangle = |\varphi_{i_1}\cdots\varphi_{i_N}\rangle \tag{251}$$

built out of Kohn–Sham orbitals is an eigenstate of the Kohn–Sham system with eigenvalue $E_0 = \epsilon_{i_1} + \cdots + \epsilon_{i_N}$. However, not every eigenstate is necessarily a Slater determinant. For instance, if two Slater determinants have the same energy eigenvalue, then a linear combination of them also has the same eigenvalue. This leads to a subtle point for Kohn–Sham theory of degenerate states. In equation (249) we require that the density is representable by a ground state ensemble of a noninteracting system. However, we did not require that it must be representable by an ensemble of ground state Slater determinants. That one should be careful at this point, has been shown by Englisch and Englisch [3] and Lieb [1]. They constructed an explicit example of a pure state density of a noninteracting system that cannot be obtained from a single Slater determinant. We will therefore in general have

$$|\Phi_i\rangle = \sum_{j=1}^{q} \alpha_{ij}|D_j\rangle \tag{252}$$

where $|D_j\rangle$ is a Slater determinant. We further know that every $|\Phi_i\rangle$ must be a ground state for potential v_s. This means that all orbitals below the highest occupied level must be occupied. If this were not the case then we could lower the energy by transferring an electron from the highest level to a lower level which would lower the energy and therefore $|\Phi_i\rangle$ would not be a ground state for potential v_s. This also means that if two determinants $|D_i\rangle$ and $|D_j\rangle$ differ, then this difference must be due to different orbitals in the highest level. Because both determinants are eigenfunctions of the Kohn–Sham Hamiltonian it is easily seen that these different orbitals must have the same Kohn–Sham eigenvalue. This eigenvalue is the Kohn–Sham orbital energy of the highest occupied state which we will denote by μ. From these considerations we find that the density is of the general form

$$n(\mathbf{r}) = \sum_{\epsilon_i<\mu} |\varphi_i(\mathbf{r})|^2 + \sum_{\epsilon_k=\epsilon_l=\mu} \beta_{kl}\varphi_k(\mathbf{r})\varphi_l^*(\mathbf{r}) \tag{253}$$

where β_{kl} is an Hermitian matrix with eigenvalues between 0 and 1. This means that we can diagonalize this matrix with a unitary matrix U_{ij}. We then introduce new orbitals for the highest occupied level:

$$\tilde{\varphi}_i(\mathbf{r}) = \sum_j U_{ij}\varphi_j(\mathbf{r}) \tag{254}$$

Since these orbitals are linear combinations of degenerate orbitals, they are again eigenfunctions of the Kohn–Sham single-particle Hamiltonian for the highest occupied level. We can now write the density as:

$$n(\mathbf{r}) = \sum_{\epsilon_i<\mu} |\varphi_i(\mathbf{r})|^2 + \sum_{\epsilon_k=\mu} n_k |\tilde{\varphi}_k(\mathbf{r})|^2 \tag{255}$$

with occupation numbers n_k between 0 and 1. We see that for the case of a degenerate ground state we have to solve equation (250) together with equation (255) in which the coefficients n_k must also be determined. When do we need fractional occupation numbers in practice? In practice one sometimes finds that when solving the Kohn–Sham equations with occupations equal to one that the converged solution has a hole below the highest level. This happens, for instance, for the iron atom within the local density approximation [24]. This is an indication that the true Kohn–Sham density could be an E-V-density. In practice, the lowest energy state is then obtained by a procedure called 'evaporation of the hole'. In this method one increases the occupation of the hole while decreasing the occupation of the highest level until both levels are degenerate [24,25]. The matter has been investigated in detail by Schipper *et al.* [26,27]. These authors calculated by CI-methods accurate charge densities for a couple of molecules. Subsequently they constructed the Kohn–Sham potentials that generate these densities. A particularly interesting case is the C_2 molecule [26]. When one tries to construct a Kohn–Sham potential that produces the ground state density of the C_2 molecule using occupation numbers equal to one, i.e., for a pure state, one finds that the solution corresponds to a state with a hole below the highest occupied level. This is then not a proper Kohn–Sham state since it is not the state of lowest energy for the corresponding potential, but an excited state. If one then tries to construct an ensemble solution by the technique of 'evaporation of the hole', one does find a proper ground state ensemble for the Kohn–Sham system. From this we can conclude that the ground state density of the C_2 molecule is a noninteracting E-V-density but not a noninteracting PS-V-density. This means that the extension of density functionals to E-V-densities is not only of theoretical, but also practical interest. As an illustration we display in Fig. 4, the exchange–correlation potentials of the C_2 molecule for four bonding distances. The potentials are plotted along the C–C bond axis as functions of the distance z from the bond midpoint. The corresponding bond distances R(C–C) are displayed in the inset. The potentials $v_{\text{xc}}^{\text{PS-hole}}$ correspond to the exchange–correlation potentials of the improper Kohn–Sham solutions with a hole. The corresponding state is a pure state consisting of a single Slater determinant. The potentials v_{xc}^{E} are the Kohn–Sham potentials corresponding to a ground state ensemble. Both $v_{\text{xc}}^{\text{PS-hole}}$ and v_{xc}^{E} give an accurate representation of the true density of the molecule, although the accuracy attained with v_{xc}^{E} is a bit higher. The potential v_{xc}^{E} has the features found in many diatomic molecules, i.e., the usual well around the atom, the small intershell peaks and a plateau around the bond midpoint. The potential $v_{\text{xc}}^{\text{PS-hole}}$ on the other hand, is heavily distorted as compared to v_{xc}^{E}. This may be explained by the fact that the wavefunction of the C_2 molecule has a strong multideterminantial character. With this we mean that the simple Hartree–Fock approximation has a relatively small

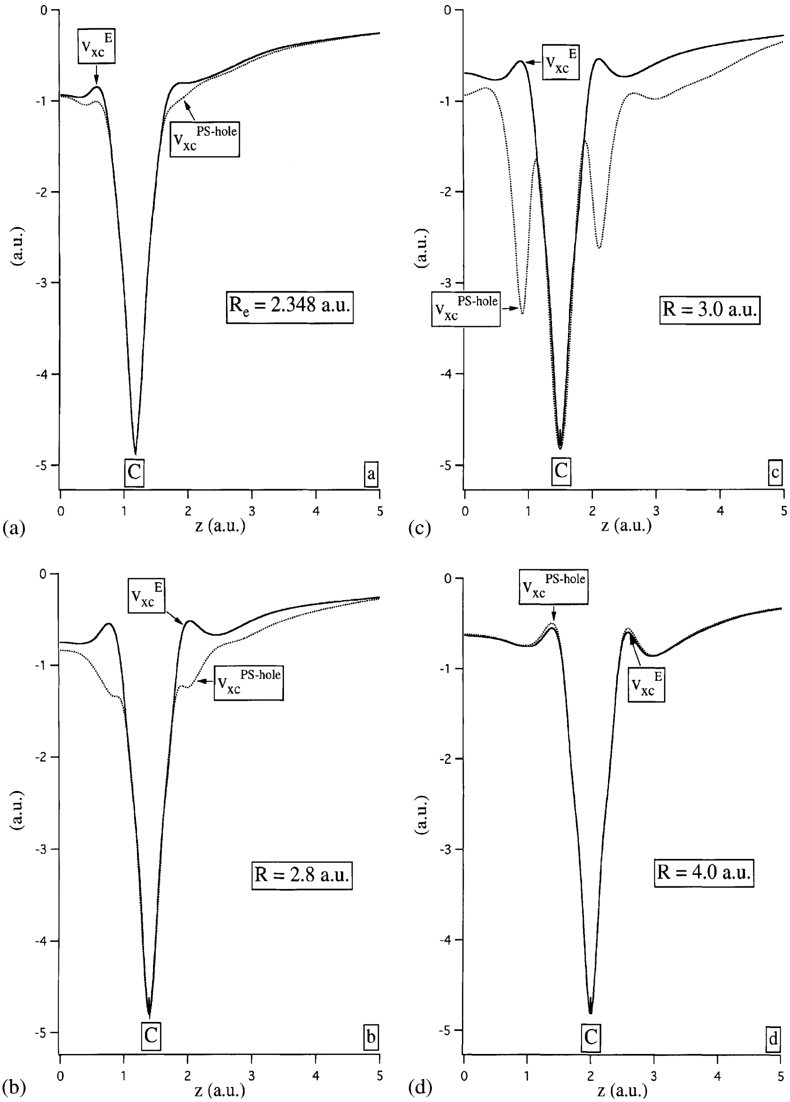

Fig. 4. Exchange–correlation potentials producing the accurate interacting ground state density of the C_2 molecule at various bonding distances. The potential v_{xc}^{E} is the exchange–correlation potential for a ground state ensemble. The potential $v_{xc}^{\text{PS-hole}}$ is an exchange–correlation potential that reproduces the same density for a single Slater determinant with a hole.

coefficient in the CI-expansion of the wavefunction. The distortions in $v_{xc}^{\text{PS-hole}}$ therefore appear to be a price we have to pay for producing the density of such a strongly multideterminantial state with a single Slater determinant. The use of an ensemble formulation of Kohn–Sham theory seems therefore especially relevant in cases of strong electron correlations. Other examples are provided by near-degeneracy situations such as in avoided crossings [25] and the $H_2 + H_2$ reaction [27]. A recent discussion on Kohn–Sham theory for ensembles can be found in Ref. [28] which also gives the beryllium series as an explicit example of systems which are ensemble v-representable but not pure state v-representable.

16. THE GRADIENT EXPANSION

Until now we only considered the formal framework of density functional theory. However, the theory would be of little use if we would not be able to construct good approximate functionals for the exchange–correlation energy and exchange–correlation functional. Historically the first approximation for the exchange–correlation functional to be used was the local density approximation. In this approximation the exchange–correlation functional is taken to be

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int \mathrm{d}^3 r \, \epsilon_{\mathrm{xc}}(n(\mathbf{r})) \tag{256}$$

where $\epsilon_{\mathrm{xc}}(n)$ is the exchange–correlation energy per volume unit for a homogeneous electron gas with density n. We therefore treat the inhomogeneous system locally as an electron gas. This simple and crude approximation turns out to be surprisingly successful for realistic and very inhomogeneous systems although one would expect that the LDA would only be accurate for systems with slowly varying densities. The LDA therefore seems a suitable starting point for more accurate approximations. In this section we will show that the LDA is in fact the first term in a systematic expansion of the exchange–correlation functional in terms of spatial derivatives with respect to the density. This expansion is commonly referred to as the gradient expansion [5,29,30] and has the following form:

$$\begin{aligned} E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}[n] &+ \int \mathrm{d}^3 r \, g_1(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 \\ &+ \int \mathrm{d}^3 r \, g_2(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))^2 + \cdots \end{aligned} \tag{257}$$

where the functions $g_i(n)$ are uniquely determined by the density response functions (of arbitrary order) of the homogeneous electron gas. The gradient expansion presents an, in principle, exact way to construct the exchange–correlation functional for solids, provided the series converges. We will come back to the question of convergence. To derive the gradient expansion we start out by expanding the exact exchange–correlation energy functional around its homogeneous electron gas value n_0 as follows:

$$E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}[n_0] + \sum_{m=1}^{\infty} \frac{1}{m!} \int \mathrm{d}^{3m} r \, K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \cdots \mathbf{r}_m) \, \delta n(\mathbf{r}_1) \cdots \delta n(\mathbf{r}_m) \tag{258}$$

where $\mathrm{d}^{3m}r = \mathrm{d}^3r_1\cdots\mathrm{d}^3r_m$ and $n(\mathbf{r}) = n_0 + \delta n(\mathbf{r})$. We further defined

$$K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) = \left.\frac{\delta^m E_{\mathrm{xc}}}{\delta n(\mathbf{r}_1)\cdots\delta n(\mathbf{r}_m)}\right|_{n=n_0} \tag{259}$$

The first term $E_{\mathrm{xc}}[n_0]$ in equation (258) is the exchange–correlation energy of a homogeneous system with constant density n_0 and is therefore a function of n_0 rather than a functional. We will therefore write this term as $E_{\mathrm{xc}}(n_0)$. This function is by now well-known from extensive investigations of the homogeneous electron gas [31]. Since the electron gas has translational, rotational, and inversion symmetry the functions functions $K_{\mathrm{xc}}^{(m)}$ satisfy

$$K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) = K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1+\mathbf{a}\cdots\mathbf{r}_m+\mathbf{a}) \tag{260}$$

$$K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) = K_{\mathrm{xc}}^{(m)}(n_0;R\mathbf{r}_1\cdots R\mathbf{r}_m) \tag{261}$$

$$K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) = K_{\mathrm{xc}}^{(m)}(n_0;-\mathbf{r}_1\cdots-\mathbf{r}_m) \tag{262}$$

where $\mathbf{a}$ is an arbitrary translation vector and where R is an arbitrary rotation matrix. Furthermore, the function $K_{\mathrm{xc}}^{(m)}$ has full permutational symmetry, i.e.,

$$K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) = K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_{P(1)}\cdots\mathbf{r}_{P(m)}) \tag{263}$$

for an arbitrary permutation P of the indices $1\cdots m$. If we choose $\mathbf{a} = -\mathbf{r}_1$ in equation (260) we see that

$$\begin{aligned} K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) &= K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{0},\mathbf{r}_2-\mathbf{r}_1\cdots\mathbf{r}_m-\mathbf{r}_1) \\ &= L^{(m)}(n_0;\mathbf{r}_2-\mathbf{r}_1\cdots\mathbf{r}_m-\mathbf{r}_1) \end{aligned} \tag{264}$$

where the latter equation defines the function $L^{(m)}$ as a function of $m-1$ variables. Let us give some specific examples. The function $K_{\mathrm{xc}}^{(1)}$ is given by

$$K_{\mathrm{xc}}^{(1)}(n_0;\mathbf{r}_1) = \left.\frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r}_1)}\right|_{n=n_0} = v_{\mathrm{xc}}(n_0) \tag{265}$$

and we see that this function is simply the exchange–correlation potential of the electron gas which, due to translational invariance, does not depend on $\mathbf{r}_1$. Since $\delta n(\mathbf{r})$ integrates to zero the term with $K_{\mathrm{xc}}^{(1)}$ in the expansion equation (258) does not contribute to $E_{\mathrm{xc}}[n]$. The first nontrivial term is therefore

$$K_{\mathrm{xc}}^{(2)}(n_0;\mathbf{r}_1,\mathbf{r}_2) = \left.\frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n=n_0} = L^{(2)}(n_0;\mathbf{r}_2-\mathbf{r}_1) \tag{266}$$

which leads to an expansion of the form:

$$E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}(n_0) + \frac{1}{2}\int \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,L^{(2)}(n_0;\mathbf{r}_2-\mathbf{r}_1)\,\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2) + \cdots \tag{267}$$

The function $L^{(2)}$ (often denoted by K_{xc} in the literature) has been the subject of many investigations [32,33]. Let us now go back to the more general case. If we introduce the Fourier transform of a function f as follows:

$$\tilde{f}(\mathbf{q}_1\cdots\mathbf{q}_m) = \int d^{3m}r\, f(\mathbf{r}_1\cdots\mathbf{r}_m)e^{-i\mathbf{q}_1\cdot\mathbf{r}_1-\cdots-\mathrm{i}\mathbf{q}_m\cdot\mathbf{r}_m} \tag{268}$$

then

$$\tilde{K}_{\mathrm{xc}}^{(m)}(n_0;\mathbf{q}_1\cdots\mathbf{q}_m) = (2\pi)^3\delta(\mathbf{q}_1+\cdots+\mathbf{q}_m)\tilde{L}^{(m)}(n_0;\mathbf{q}_2\cdots\mathbf{q}_m) \tag{269}$$

The expansion for E_{xc} then becomes

$$E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}(n_0) + \sum_{m=1}^{\infty}\frac{1}{m!}\int\frac{\mathrm{d}^{3m}q}{(2\pi)^{3m}}\tilde{K}_{\mathrm{xc}}^{(m)}(n_0;\mathbf{q}_1\cdots\mathbf{q}_m)\delta\tilde{n}(\mathbf{q}_1)\cdots\delta\tilde{n}(\mathbf{q}_m) \tag{270}$$

where $\mathrm{d}^{3m}q = \mathrm{d}^3q_1\cdots\mathrm{d}^3q_m$. This can also be written in terms of the functions $L^{(m)}$ as follows:

$$\begin{aligned} E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}(n_0) + \sum_{m=1}^{\infty}\frac{1}{m!}\int\frac{\mathrm{d}^3q_2}{(2\pi)^3}\cdots\frac{\mathrm{d}^3q_m}{(2\pi)^3}\tilde{L}^{(m)}(n_0;\mathbf{q}_2\cdots\mathbf{q}_m) \\ \times\,\delta\tilde{n}(-\mathbf{q}_2-\cdots-\mathbf{q}_m)\delta\tilde{n}(\mathbf{q}_2)\cdots\delta\tilde{n}(\mathbf{q}_m) \end{aligned} \tag{271}$$

The gradient expansion is then obtained by expanding $L^{(m)}$ in powers of $\mathbf{q}_i$ around $\mathbf{q}_i = 0$ and subsequently transforming back to real space. If we do this our final expansion will then still depend on our reference density n_0 which is undesirable for application of the functional to general systems. However, we will show that we can get rid of this dependence on n_0 by doing infinite resummations. The key formula that will enable us to do these resummations is the following first order change of $K_{\mathrm{xc}}^{(m)}$:

$$\delta K_{\mathrm{xc}}^{(m)}(\mathbf{r}_1\cdots\mathbf{r}_m) = \int\mathrm{d}^3r\, K_{\mathrm{xc}}^{(m+1)}(n_0;\mathbf{r},\mathbf{r}_1\cdots\mathbf{r}_m)\,\delta n(\mathbf{r}) \tag{272}$$

If we take $\delta n(\mathbf{r}) = \delta n_0$ to be a constant change we obtain

$$\frac{\partial K_{\mathrm{xc}}^{(m)}}{\partial n_0}(n_0;\mathbf{r}_1\cdots\mathbf{r}_m) = \int\mathrm{d}^3r\, K_{\mathrm{xc}}^{(m+1)}(n_0;\mathbf{r},\mathbf{r}_1\cdots\mathbf{r}_m) \tag{273}$$

Note that by taking $\delta n(\mathbf{r}) = \delta n_0$ we violate the condition that $\delta n(\mathbf{r})$ integrates to zero. Nevertheless equation (273) can alternatively be derived directly from the properties of the response functions [30] and is related to a generalized form of the well-known compressibility sumrule of the electron gas. An important special case is obtained for $m = 1$:

$$\begin{aligned}\frac{\partial v_{\rm xc}}{\partial n_0} &= \frac{\partial K^{(1)}_{\rm xc}}{\partial n_0}(n_0) = \int {\rm d}^3 r_2\, K^{(2)}_{\rm xc}(n_0; \mathbf{r}_1, \mathbf{r}_2) = \int {\rm d}^3 r_2\, L^{(2)}(n_0; \mathbf{r}_2 - \mathbf{r}_1)\\ &= \tilde{L}^{(2)}(\mathbf{q} = \mathbf{0}) \end{aligned} \tag{274}$$

We see that the $\mathbf{q} = 0$ value of $\tilde{L}^{(2)}$ can be directly calculated from the knowledge of $v_{\rm xc}(n_0)$. For $m \geq 2$ relation (273) directly implies the following relation between $L^{(m)}$ and $L^{(m+1)}$

$$\frac{\partial L^{(m)}}{\partial n_0}(n_0; \mathbf{q}_2 \cdots \mathbf{q}_m) = L^{(m+1)}(n_0; -\mathbf{q}_2 - \cdots - \mathbf{q}_m, \mathbf{q}_2 \cdots \mathbf{q}_m) \tag{275}$$

The importance of this formula will become clear if we work out, as an explicit example, the lowest order in the gradient expansion. From the symmetry properties of $K^{(m)}_{\rm xc}$ one finds that its Fourier transform has the following expansion in powers of $\mathbf{q}_i$:

$$\begin{aligned}\tilde{K}^{(m)}_{\rm xc}(n_0; \mathbf{q}_1 \cdots \mathbf{q}_n) = (2\pi)^3 \delta(\mathbf{q}_1 + \cdots + \mathbf{q}_m) \times (K^{(m)}_0 + K^{(m)}_1 P^{(m)}_1(\mathbf{q}_1 \cdots \mathbf{q}_m)\\ + K^{(m)}_2 P^{(m)}_2(\mathbf{q}_1 \cdots \mathbf{q}_m) + \cdots)\end{aligned} \tag{276}$$

in which the $K^{(m)}_i$ are coefficients and $P^{(m)}_i$ are symmetric polynomials. This is a direct consequence of the permutational symmetry of $K_{\rm xc}$. The first polynomial $P^{(m)}_1$ (taking into account the δ-function) has the explicit form

$$P^{(m)}_1(\mathbf{q}_1 \cdots \mathbf{q}_m) = \mathbf{q}_1^2 + \cdots + \mathbf{q}_m^2 \tag{277}$$

and is invariant under permutation of the indices, i.e., it transforms according to a one-dimensional representation of the permutation group. More details on the group theoretical treatment of these response functions can be found in the work of Svendsen and von Barth [34]. From the properties of $\tilde{K}^{(m)}_{\rm xc}$ we find that for $m \geq 2$ the function $L^{(m)}$ has the following expansion:

$$L^{(m)}(n_0; \mathbf{q}_2 \cdots \mathbf{q}_m) = L^{(m)}_0(n_0) + L^{(m)}_1(n_0) p^{(m)}(\mathbf{q}_2 \cdots \mathbf{q}_m) + \cdots \tag{278}$$

where the polynomial $p^{(m)}$ is given by

$$\begin{aligned} p^{(m)}(\mathbf{q}_2 \cdots \mathbf{q}_m) &= (-\mathbf{q}_2 - \cdots - \mathbf{q}_m)^2 + \mathbf{q}_2^2 + \cdots + \mathbf{q}_m^2\\ &= 2\sum_{i=2}^{m} \mathbf{q}_i^2 + 2 \sum_{i>j\geq 2}^{m} \mathbf{q}_i \cdot \mathbf{q}_j \end{aligned} \tag{279}$$

It is easily seen that this polynomial has the property

$$p^{(m+1)}(-\mathbf{q}_2 - \cdots - \mathbf{q}_m, \mathbf{q}_2 \cdots \mathbf{q}_m) = p^{(m)}(\mathbf{q}_2 \cdots \mathbf{q}_m) \tag{280}$$

If we use this property together with equation (278) and equation (275) we obtain for the coefficients in the expansion of $L^{(m)}$ the following equations:

$$\frac{\partial L_0^{(m)}}{\partial n_0} = L_0^{(m+1)}(n_0) \tag{281}$$

$$\frac{\partial L_1^{(m)}}{\partial n_0} = L_1^{(m+1)}(n_0) \tag{282}$$

where $m \geq 2$. Together with

$$\tilde{L}^{(2)}(\mathbf{q} = \mathbf{0}) = \frac{\partial v_{\mathrm{xc}}}{\partial n_0}(n_0) = \frac{\partial^2 \epsilon_{\mathrm{xc}}}{\partial n_0^2}(n_0) \tag{283}$$

where $\epsilon_{\mathrm{xc}}(n_0)$ is the exchange energy per volume unit of the electron gas, this yields

$$L_0^{(m)}(n_0) = \frac{\partial^m \epsilon_{\mathrm{xc}}}{\partial n_0^m}(n_0) \tag{284}$$

$$L_1^{(m)}(n_0) = \frac{\partial^{m-2} L_1^{(2)}}{\partial n_0^{m-2}}(n_0) \tag{285}$$

It is these two equations that will allow us to eliminate the dependence on n_0 in the lowest order gradient expansion. If we insert the explicit form of $L^{(m)}$ of equation (278) into equation (271) and Fourier transform back to real space we obtain

$$\begin{aligned} E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}(n_0) &+ \sum_{m=1}^{\infty} \frac{1}{m!} L_0^{(m)}(n_0) \int \mathrm{d}^3 r (\delta n(\mathbf{r}))^m \\ &+ \sum_{m=2}^{\infty} \frac{1}{m!} L_1^{(m)}(n_0) m(m-1) \int \mathrm{d}^3 r (\nabla \delta n(\mathbf{r})^2 (\delta n(\mathbf{r}))^{m-2} + \cdots \end{aligned} \tag{286}$$

Since $\nabla \delta n(\mathbf{r}) = \nabla n(\mathbf{r})$ this can be rewritten with help of equations (284) and (285) as:

$$\begin{aligned} E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}(n_0) &+ \sum_{m=1}^{\infty} \frac{1}{m!} \frac{\partial^m \epsilon_{\mathrm{xc}}(n_0)}{\partial n_0^m} \int \mathrm{d}^3 r (\delta n(\mathbf{r}))^m \\ &+ \sum_{m=2}^{\infty} \frac{1}{(m-2)!} \frac{\partial^{m-2} L_1^{(2)}(n_0)}{\partial n_0^{m-2}} \int \mathrm{d}^3 r (\nabla n(\mathbf{r}))^2 (\delta n(\mathbf{r}))^{m-2} + \cdots \end{aligned} \tag{287}$$

We see that the first two terms simply give the expansion of the LDA functional around the constant density n_0, i.e.,

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int \mathrm{d}^3 r \, \epsilon_{\mathrm{xc}}(n_0 + \delta n(\mathbf{r})) \tag{288}$$

whereas the third term involves an expansion of the coefficient $L_1^{(2)}(n_0 + \delta n(\mathbf{r}))$ around n_0. We obtain

$$E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}[n] + \int \mathrm{d}^3 r \, L_1^{(2)}(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 + \cdots \tag{289}$$

and we see that we succeeded in eliminating the dependence on n_0 in the gradient expansion. Moreover we see that the local density approximation naturally appears as the first term in the gradient expansion. Furthermore we find that the coefficient $g_1(n)$ in our first equation (257) is completely determined by the $\mathbf{q}$-expansion of the function $\tilde{L}^{(2)}(n_0; \mathbf{q})$ to order $\mathbf{q}^2$. We also see that the replacement $n_0 \longrightarrow n(\mathbf{r})$ requires a resummation over response functions of arbitrary order. The dependence on n_0 can also be removed to higher order in powers of $\mathbf{q}$. For an explicit example up to order $\mathbf{q}^4$ we refer again to Svendsen and von Barth [34].

Let us now address the question of convergence of the gradient expansion. This question has been investigated for the gradient expansion of the exchange-energy functional for which a comparison with exact exchange energies is possible. For this case the analytic form of $\tilde{L}^{(2)}(n_0; \mathbf{q})$ is known from the impressive work of Engel and Vosko [35,36] and some higher order gradient coefficients have been determined by Svendsen, Springer, and von Barth [34,37]. One finds [37] that the gradient expansion performs very well for metallic systems, but that the quality deteriorates as soon as the system acquires an energy gap. This may not be so surprising if one realizes that the appearance of a gap drastically changes the low $\mathbf{q}$-behavior of the response functions $K_{\mathrm{xc}}^{(m)}$ which determine the gradient coefficients [38]. This means that the standard gradient expansion cannot deal with insulators or finite systems (which may be modelled as insulators by repeating them periodically with a large lattice constant). Further progress along the lines of the gradient expansion may be obtained by study of the so-called gapped electron gas [39]. Currently the most fruitful approach to the construction of simple and accurate functionals is the so-called Generalized Gradient Approximation (GGA) [40,41]. In this approach one specifies a form of the pair-correlation function of the many-electron system and determines the parameters in this function by sumrules and information from the straightforward gradient expansion. These functionals have led to large improvements in molecular binding energies as compared to the local density approximation [42]. However, since the approach is not systematic it is difficult to improve the quality of the current GGA functionals.

17. THE OPTIMIZED POTENTIAL METHOD AND THE e^2-EXPANSION

In this section we will describe a second systematic method to construct density functionals, namely perturbation theory starting from the Kohn–Sham Hamiltonian [43,44]. The method is based on traditional perturbation theory and is comparable in computational cost. For this reason the method is less suited to the calculation of properties of large systems. However, the method has the theoretical advantage that it can be used as a benchmark to test the quality of different approximate density functionals. We consider the Hamiltonian

$$\hat{H}_\epsilon = \hat{H}_s + \epsilon(\hat{H} - \hat{H}_s) = \hat{H}_s + \epsilon(\hat{W} - \hat{V}_{H\mathrm{xc}}) \tag{290}$$

where

$$\hat{W} = \sum_{i>j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{291}$$

$$\hat{V}_{H\mathrm{xc}} = \sum_{i=1}^{N} v_H(\mathbf{r}_i) + v_{\mathrm{xc}}(\mathbf{r}_i) \tag{292}$$

where e^2 is the square of the electronic charge and v_H is the usual Hartree potential

$$v_H(\mathbf{r}) = e^2 \int \mathrm{d}^3 r' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{293}$$

and v_{xc} the exchange–correlation potential. The perturbation term is simply the difference between the true and the Kohn–Sham Hamiltonian and we are interested in the case $\epsilon = 1$ although this makes expansion in powers of ϵ rather doubtful. We will come back to the point of convergence later. We can now do standard perturbation theory and obtain the ground state energy

$$E(\epsilon) = E_s + \epsilon E^{(1)} + \epsilon^2 E^{(2)} + \cdots \tag{294}$$

where E_s is ground state energy of the auxiliary Kohn–Sham system, i.e., simply a sum over orbital energies and the terms $E^{(i)}$ is the energy to order i in powers of ϵ. The first two terms are explicitly given by [43,44]

$$E^{(1)} = \langle \Phi_s | \hat{W} - \hat{V}_{H_{\mathrm{xc}}} | \Phi_s \rangle \tag{295}$$

$$E^{(2)} = \sum_{i=1}^{\infty} \frac{|\langle \Phi_s | \hat{W} - \hat{V}_{H_{\mathrm{xc}}} | \Phi_{s,i} \rangle|^2}{E_s - E_{s,i}} \tag{296}$$

where $E_{s,i}$ and $\Phi_{s,i}$ are the excited state energies and wavefunctions of the Kohn–Sham system. We now note that the energies $E^{(i)}$ are implicit functionals of the density through their dependence on the Kohn–Sham potential, orbitals, and energies, i.e.,

$$E^{(i)}[n] = E^{(i)}[\{\varphi_k[n]\}, \{\epsilon_k[n]\}, v_{\mathrm{xc}}[n]] \tag{297}$$

This follows directly from the Hohenberg–Kohn theorem applied to a noninteracting system. The density n uniquely determines the Kohn–Sham potential v_s (up to a constant) and therefore the also the orbitals (up to a phase factor) and eigenvalues (up to constant). The arbitrariness with respect to a constant shift and with respect to the phase factor cancels out in the energy expression and therefore the ith-order energy becomes a pure density functional. We therefore have the following series of implications:

$$n(\mathbf{r}) \rightarrow v_s(\mathbf{r}) \rightarrow \{\varphi_k(\mathbf{r}), \epsilon_k\} \rightarrow E^{(i)} \tag{298}$$

Note that the perturbation theory that we constructed is not yet in a form that we can use in practical calculations. This is because the perturbing Hamiltonian contains the exchange–correlation potential which is unknown from the start and has to be determined self-consistently from the perturbation series. However, the equations can be simplified if we expand the energies and potentials in powers of the interaction strength e^2 and take $\epsilon = 1$. This leads to the following set of equations [44]:

$$E[n] = T_s[n] + \int d^3r\, n(\mathbf{r})v(\mathbf{r}) + \frac{e^2}{2}\int d^3r\, d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \sum_{i=1}^{\infty} e^{2i} E_{\mathrm{xc}}^{(i)} \tag{299}$$

$$v_{H_{\mathrm{xc}}}(\mathbf{r}) = v_H(\mathbf{r}) + \sum_{i=1}^{\infty} e^{2i} v_{\mathrm{xc}}^{(i)}(\mathbf{r}) \tag{300}$$

$$v_{\mathrm{xc}}^{(i)}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{(i)}}{\delta n(\mathbf{r})} \tag{301}$$

The e^2 and e^4 terms in the expansion of the exchange–correlation energy have the explicit form

$$e^2 E_{\mathrm{xc}}^{(1)}[n] = \langle \Phi_s|\hat{W}|\Phi_s\rangle - \frac{e^2}{2}\int d^3r\, d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{302}$$

and

$$e^4 E_{\mathrm{xc}}^{(2)}[n] = \sum_{i=1}^{\infty} \frac{|\langle \Phi_s|\hat{W} - \hat{V}_H - e^2\hat{V}_{\mathrm{xc}}^{(1)}|\Phi_{s,i}\rangle|^2}{E_s - E_{s,i}} \tag{303}$$

The term of order e^2 can be written explicitly in terms of the Kohn–Sham orbitals as follows:

$$E_{\mathrm{xc}}^{(1)}[n] = -\frac{1}{2}\sum_{k,l=1}^{N} \int d^3r\, d^3r'\, \frac{\varphi_k^*(\mathbf{r})\varphi_l(\mathbf{r})\varphi_l^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{304}$$

We see that this expression has exactly the same form as the usual expression of the exchange energy within the Hartree–Fock approximation. The difference, however, is that the orbitals in this expression are Kohn–Sham orbitals which, in contrast to the Hartree–Fock orbitals, are eigenfunctions of a single-particle Hamiltonian with a local potential. The numerical value of $E_{\mathrm{xc}}^{(1)}[n]$ and the Hartree–Fock exchange will therefore in general differ from each other. However, because of the similarity to the Hartree–Fock definition of exchange we will define the exchange functional within density functional theory to be $E_x[n] = E_{\text{xc}}^{(1)}[n]$. Corresponding to the exchange-functional there is a local exchange potential defined as:

$$v_x(\mathbf{r}) = \frac{\delta E_x}{\delta n(\mathbf{r})} = \frac{\delta E_{\text{xc}}^{(1)}}{\delta n(\mathbf{r})} = v_{\text{xc}}^{(1)}(\mathbf{r}) \tag{305}$$

We see from equation (303) that we need to know this potential in order to calculate the e^4 contribution to the exchange–correlation energy. This is a general feature of the present perturbation theory. In order to calculate $E_{\text{xc}}^{(i)}$ we need to calculate $v_{\text{xc}}^{(i-1)}$ first. Let us therefore start by calculating v_x. For this we have to calculate the first order change δE_x in the exchange functional due to a change δn in the density. Since densities and potential are in $1-1$-correspondence this task amounts to calculating the change in E_x due to a change δv_s in the Kohn–Sham potential. This is readily done by perturbation theory. The change $\delta\varphi_k$ and $\delta\epsilon_k$ of the orbitals and orbital energies of the Kohn–Sham system due to a small change δv_s in the potential is given by solution of the equation

$$(-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r}) - \epsilon_k)\delta\varphi_k(\mathbf{r}) = (\delta\epsilon_k - \delta v_s(\mathbf{r}))\varphi_k(\mathbf{r}) \tag{306}$$

This gives

$$\delta\epsilon_k = \int \mathrm{d}^3r\ \varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r})\ \delta v_s(\mathbf{r}) \tag{307}$$

$$\delta\varphi_k(\mathbf{r}) = -\int \mathrm{d}^3r'\ G_k(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{r}')\ \delta v_s(\mathbf{r}') \tag{308}$$

$$G_k(\mathbf{r},\mathbf{r}') = \sum_{l\neq k} \frac{\varphi_l(\mathbf{r})\varphi_l^*(\mathbf{r}')}{\epsilon_l - \epsilon_k} \tag{309}$$

From these equations we obtain the following functional derivatives

$$\frac{\delta\epsilon_k}{\delta v_s(\mathbf{r})} = \varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r}) \tag{310}$$

$$\frac{\delta\varphi_k(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -G_k(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{r}') \tag{311}$$

The density change δn is given by

$$\delta n(\mathbf{r}) = \sum_{k=1}^{N} \varphi_k^*(\mathbf{r})\ \delta\varphi_k(\mathbf{r}) + \text{c.c.} = \int \mathrm{d}^3r'\ \chi_s(\mathbf{r},\mathbf{r}')\ \delta v_s(\mathbf{r}') \tag{312}$$

where we defined the static density response function χ_s of the Kohn–Sham system by

$$\chi_s(\mathbf{r},\mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -\sum_{k=1}^{N} \varphi_k^*(\mathbf{r})G_k(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{r}') + \text{c.c.} \tag{313}$$

We can now readily derive the following integral equation for v_x:

$$\Lambda_x(\mathbf{r}) = \frac{\delta E_x}{\delta v_s(\mathbf{r})} = \int d^3r' \frac{\delta E_x}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \int d^3r' \, \chi_s(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') \tag{314}$$

where the inhomogeneity Λ_x is given by

$$\Lambda_x(\mathbf{r}) = -\sum_{k=1}^{N} \int d^3r' \frac{\delta E_x}{\delta \varphi_k(\mathbf{r}')} G_k(\mathbf{r}', \mathbf{r}) \varphi_k(\mathbf{r}) + \text{c.c.} \tag{315}$$

Since both Λ_x and χ_s are given as explicit functionals of the Kohn–Sham orbitals and orbital energies, the exchange potential can be found from simultaneous solution of the equations

$$\epsilon_k \varphi_k(\mathbf{r}) = (-\tfrac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + e^2 v_x(\mathbf{r}))\varphi_k(\mathbf{r}) \tag{316}$$

$$\Lambda_x(\mathbf{r}) = \int d^3r' \, \chi_s(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') \tag{317}$$

Once we have solved these equations and determined v_x we can go on and calculate $E_{\text{xc}}^{(2)}$ from equation (303). To calculate the e^6 contribution to the exchange–correlation energy we first have to evaluate $v_{\text{xc}}^{(2)}$. This potential is the solution of the integral equation

$$\Lambda_{\text{xc}}^{(2)}(\mathbf{r}) = \frac{\delta E_{\text{xc}}^{(2)}}{\delta v_s(\mathbf{r})} = \int d^3r' \, \chi_s(\mathbf{r}, \mathbf{r}') v_{\text{xc}}^{(2)}(\mathbf{r}') \tag{318}$$

Since $E_{\text{xc}}^{(2)}$ is an explicit functional of the orbitals, orbital energies and v_x the inhomogeneity $\Lambda_{\text{xc}}^{(2)}$ can be calculated from

$$\begin{aligned}\Lambda_{\text{xc}}^{(2)}(\mathbf{r}) = &\left[\sum_{k=1}^{\infty} \int d^3r' \frac{\delta E_{\text{xc}}^{(2)}}{\delta \varphi_k(\mathbf{r}')} \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \text{c.c.}\right] + \sum_{k=1}^{\infty} \int d^3r' \frac{\delta E_{\text{xc}}^{(2)}}{\delta \epsilon_k} \frac{\delta \epsilon_k}{\delta v_s(\mathbf{r})} \\ &+ \int d^3r' \frac{\delta E_{\text{xc}}^{(2)}}{\delta v_x(\mathbf{r}')} \frac{\delta v_x(\mathbf{r}')}{\delta v_s(\mathbf{r})}\end{aligned} \tag{319}$$

All terms in this equation are explicitly known, except for the term $\delta v_x / \delta v_s$. However, for this term we can find an integral equation by differentiation of equation (317) with respect to v_s:

$$\frac{\delta \Lambda_x(\mathbf{r}_1)}{\delta v_s(\mathbf{r}_2)} = \int d^3r_3 \frac{\delta \chi_s(\mathbf{r}_1, \mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)} v_x(\mathbf{r}_3) + \int d^3r_3 \, \chi_s(\mathbf{r}_1, \mathbf{r}_3) \frac{\delta v_x(\mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)} \tag{320}$$

Since both Λ_x and χ_s are explicitly known in terms of orbitals and orbital energies their derivatives with respect to v_s are also explicitly known in terms of these quantities (see Ref. [44] for more details) and therefore equation (320) determines $\delta v_x / \delta v_s$ uniquely. So we see that in order to determine $v_{\text{xc}}^{(2)}$ we have to solve two integral equations. For realistic systems these equations have only be solved approximately (for an explicit solution of equation (320) see

Ref. [34]). From $v_{\mathrm{xc}}^{(2)}$ one could go on along the same lines to determine $E_{\mathrm{xc}}^{(3)}$ and subsequently $v_{\mathrm{xc}}^{(3)}$. The determination of these higher order energies and potentials becomes more involved. Nevertheless, the perturbation series represents an explicit construction procedure for the exact exchange–correlation energy and potential, provided that the series converges. Before we go on to discuss the convergence properties of this series, let us briefly review the first order equations from a different viewpoint. It is readily seen that one can write the total energy to order e^2, which we denote by $E_1[n]$, as:

$$\begin{aligned} E_1[n] &= T_s[n] + \int \mathrm{d}^3 r\, n(\mathbf{r}) v(\mathbf{r}) + \frac{e^2}{2} \int \mathrm{d}^3 r\, \mathrm{d}^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + e^2 E_x[n] \\ &= \langle \Phi_s | \hat{H} | \Phi_s \rangle \end{aligned} \tag{321}$$

This is just the expectation value of the true Hamiltonian $\hat{H}$ of the system with the Kohn–Sham wavefunction $|\Phi_s\rangle$. Because of the 1–1-correspondence between the density n and the potential v_s we can also regard E_1 as a functional of the potential v_s, i.e.,

$$E_1[v_s] = \langle \Phi_s[v_s] | \hat{H} | \Phi_s[v_s] \rangle \tag{322}$$

We may now try to find an approximation to the true total energy of the system by choosing a local potential v_s that minimizes the energy expression $E_1[v_s]$. This means that we have to solve the variational equation

$$0 = \frac{\delta E_1}{\delta v_s(\mathbf{r})} = \sum_{k=1}^{N} \int \mathrm{d}^3 r' \frac{\delta E_1}{\delta \varphi_k(\mathbf{r}')} \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \mathrm{c.c.} \tag{323}$$

If one works out this expression one obtains equations that are identical to equations (316) and (317). These equations were first derived by Talman and Shadwick [45]. Since in our procedure we optimized the energy of a Slater determinant wavefunction under the constraint that the orbitals in the Slater determinant come from a local potential, the method is also known as the optimized potential method (OPM). We have therefore obtained the result that the OPM and the expansion to order e^2 are equivalent procedures. The OPM has many similarities to the Hartree–Fock approach. Within the Hartree–Fock approximation one minimizes the energy of a Slater determinant wavefunction under the constraint that the orbitals are orthonormal. One then obtains one-particle equations for the orbitals that contain a nonlocal potential. Within the OPM, on the other hand, one adds the additional requirement that the orbitals must satisfy single-particle equations with a local potential. Due to this constraint the OPM total energy E_1 will in general be higher than the Hartree–Fock energy E_{HF}, i.e., $E_1 \geq E_{\mathrm{HF}}$. We refer to Refs. [46,47] for an application of the OPM method for molecules.

We finally make some comments on the calculation of functional derivatives in this section. We stress this point since careless use of the chain rule for differentiation has led to wrong results in the literature [48]. As an example we consider the exchange functional E_x. When we regard this functional as an explicit functional of the orbitals then the functional derivative with respect to φ_k is given by

$$\left(\frac{\delta E_x}{\delta \varphi_k(\mathbf{r})}\right)_e = -\sum_{i=1}^{N} \int \mathrm{d}^3 r' \, \frac{\varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, \varphi_k^*(\mathbf{r}') \tag{324}$$

where we used the subindex e to indicate that we regard the functional as an explicit orbital functional. This functional derivative represents the change in E_x due to a change $\delta\varphi_k$ in orbital φ_k, while keeping all other orbitals fixed. Moreover, we regard φ_k and φ_k^* as independent variables. If we regard E_x as a density functional we must require that all orbitals are eigenfunctions of a noninteracting Hamiltonian with a local potential v_s. It is clear that we can we can never find a change δv_s in a local potential that induces a change in only one orbital, while keeping the other orbitals fixed. If a potential changes one orbital φ_k to $\varphi_k + \delta\varphi_k$ then all other orbitals will change too. The change in E_x regarded as a functional of v_s is then given by the functional derivative

$$\begin{aligned}\frac{\delta E_x}{\delta v_s(\mathbf{r})} &= \sum_{k=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_x}{\delta \varphi_k(\mathbf{r}')}\right)_e \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} \\ &\quad + \sum_{k=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_x}{\delta \varphi_k^*(\mathbf{r}')}\right)_e \frac{\delta \varphi_k^*(\mathbf{r}')}{\delta v_s(\mathbf{r})}\end{aligned} \tag{325}$$

We see that in this case the explicit orbital derivatives only occur in the sum in which all the orbital changes must be taken into account. We may also introduce an implicit derivative $(\delta E_x/\delta\varphi_k)_i$, which can be given the meaning of giving the change in E_x if we know that there is a potential change δv_s that changes φ_k to $\varphi_k + \delta\varphi_k$. This implicit orbital derivative, which we denote by subindex i is expressed in terms of the explicit orbital derivatives as follows:

$$\begin{aligned}\left(\frac{\delta E_x}{\delta \varphi_k(\mathbf{r})}\right)_i &= \sum_{i=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_x}{\delta \varphi_i(\mathbf{r}')}\right)_e \frac{\delta \varphi_i(\mathbf{r}')}{\delta \varphi_k(\mathbf{r})} \\ &\quad + \sum_{i=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_x}{\delta \varphi_i^*(\mathbf{r}')}\right)_e \frac{\delta \varphi_i^*(\mathbf{r}')}{\delta \varphi_k(\mathbf{r})}\end{aligned} \tag{326}$$

The derivatives $\delta\varphi_i/\delta\varphi_k$ appear now to take into account that, if orbital φ_k changes to $\varphi_k + \delta\varphi_k$ by some potential change δv_s, then the other orbitals φ_i change to $\varphi_i + \delta\varphi_i$. By using the implicit orbital derivative we regard E_x as a functional of the potential, or equivalently of the density, and we can therefore use the chain rule

$$\left(\frac{\delta E_x}{\delta \varphi_k(\mathbf{r})}\right)_i = \int \mathrm{d}^3 r' \, \frac{\delta E_x}{\delta n(\mathbf{r}')} \left(\frac{\delta n(\mathbf{r}')}{\delta \varphi_k(\mathbf{r})}\right)_i = \int \mathrm{d}^3 r' \, v_x(\mathbf{r}') \left(\frac{\delta n(\mathbf{r}')}{\delta \varphi_k(\mathbf{r})}\right)_i \tag{327}$$

In this equation $(\delta n/\delta\varphi_k)_i$ is also an implicit derivative given by:

$$\left(\frac{\delta n(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})}\right)_i = \sum_{i=1}^{N} \int d^3r' \left[\varphi_i^*(\mathbf{r}') \frac{\delta\varphi_i(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})} + \varphi_i(\mathbf{r}') \frac{\delta\varphi_i^*(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})} \right] \tag{328}$$

which should be compared to the explicit derivative

$$\left(\frac{\delta n(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})}\right)_e = \varphi_k^*(\mathbf{r}) \tag{329}$$

for $k = 1, \ldots, N$. We stress that equation (327) is only true when using the implicit derivatives. If in equation (327) we replace the implicit derivatives by the explicit ones of equation (324) and equation (329) we obtain a result that is wrong. As pointed out this is due to the fact that a change in just one orbital cannot be induced by a change in a local potential which in density functional theory is in 1–1-correspondence with the density. Most of the confusion can be avoided by regarding all functionals as functionals of the potential v_s and by calculating the change in the functionals by means of perturbation theory. In this way one can avoid use of the implicit orbital derivatives as in equation (326).

Let us finally come back to the question of convergence of the perturbation series. The perturbation series presented in this section is very similar to Møller–Plesset perturbation theory starting from the Hartree–Fock approximation. For the Møller–Plesset perturbation theory it is known that it is in general divergent [49–51]. However, it is well known that when carried out to low orders this perturbation theory gives reasonable answers. The Møller–Plesset perturbation series has therefore all the features of an asymptotic series [52]. Since the perturbation series in this section is very similar to the Møller–Plesset series it will in general also diverge. This has indeed been found in a perturbation theory on the basis of some approximate Kohn–Sham Hamiltonians [53]. Nevertheless, it has been found for the method presented in this section that low orders in perturbation theory give good results [54] and we conclude that our series give at least an asymptotic expansion for the exchange–correlation energy and potential.

18. OUTLOOK AND CONCLUSIONS

In this work we have given on overview of the mathematical foundations of stationary density functional theory. We discussed in great detail the question of differentiability of the functionals and showed that the Kohn–Sham theory can be put on a solid basis for all practical purposes, since the set of noninteracting E-V-densities is dense in the set of interacting E-V-densities. The question whether these two sets are in fact identical is still an open question. We further discussed two systematic approaches for the construction of the exchange–correlation functional and potential. What can we say about future developments within density functional theory? There have been many extensions of density functional theory involving spins, relativistic effects, temperature, superconductivity, and time-dependent phenomena. The last few years we have, for instance, seen many applications of response properties, rather than ground state properties, using time-dependent density functional theory. For these extended density functional theories it is, of course, more difficult to provide a rigorous theoretical basis. This is, however, not particular to density functional theory, but applies to any method that deals with many-body systems, especially if one is interested in phenomena like superconductivity or interactions with laser fields. Nevertheless, also for these complicated cases simple density functionals have provided encouraging results although there is still a clear need for more accurate density functionals. In view of the success of density functional theory for ground state calculations it seems worthwhile to explore these new areas.

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Differentiability in Density-Functional Theory

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Abstract

The differentiability of different functionals used in density-functional theory (DFT) is investigated, and it is shown that the so-called Levy–Lieb functional $F_{\mathrm{LL}}[\rho]$ and the Lieb functional $F_{\mathrm{L}}[\rho]$ are Gâteaux differentiable at pure-state v-representable and ensemble v-representable densities, respectively. The conditions for the Fréchet differentiability of these functionals are also discussed. The Gâteaux differentiability of the Lieb functional has been demonstrated by Englisch and Englisch (Phys. Stat. Solidi **123**, 711 and **124**, 373 (1984)), but the differentiability of the Levy–Lieb functional has not been shown before.

Contents

1. INTRODUCTION

The differentiability of density functionals is of fundamental importance in *density-functional theory* (DFT) and forms the basis for models of Kohn–Sham type [1,2].

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In standard DFT an energy functional, $E[\rho]$, is minimized under the constraint that the density $\rho(\mathbf{r})$ is normalized to the number of electrons, which requires that the functional is differentiable with respect to the density at the minimum. In the Kohn–Sham model, an interacting system is simulated by a system of noninteracting electrons moving in a *local* potential, which requires that the derivative of the functionals involved can be represented by a local function.

The locality of density-functional derivatives has been a controversial issue for some time. It was demonstrated almost 20 years ago by Englisch and Englisch [3,4], based upon works of Lieb [5], that a very large class of functionals is (Gâteaux) differentiable with the derivative in the form of a local function. This result has been challenged by Nesbet [6–9], who in a series of papers claims that the energy-functional derivative cannot be represented by a local potential even for a noninteracting system with more than two electrons. In a recent Comment to the Physical Review [10] we claim that the results of Nesbet are incorrect. There we have demonstrated in a simple way that such a derivative does exist for noninteracting systems in general—in accordance with the more general results of Englisch and Englisch—and, in addition, pointed out where we believe the mistake of Nesbet has been made. In the present work, we shall extend our treatment in the Comment to systems of *interacting electrons* and with a ground state that can also be *degenerate*.

Englisch and Englisch [3,4] have demonstrated the Gâteaux differentiability of the so-called Lieb functional, $F_{\mathrm{L}}[\rho]$, utilizing the convexity of the functional. The question of the differentiability of the so-called Levy–Lieb functional, $F_{\mathrm{LL}}[\rho]$, which is not necessarily convex, is left open in their work. The general situation concerning the differentiability of density functionals has been reviewed by van Leeuwen in this volume [11], confirming the results of Englisch and Englisch. In the present work we shall show that $F_{\mathrm{L}}[\rho]$ and $F_{\mathrm{LL}}[\rho]$ functionals are both Gâteaux differentiable at pure-state-v-(PS-v) and ensemble-v-(E-v) representable densities, respectively. We shall also discuss the conditions for the Fréchet differentiability of these functionals and show that the possible difference between the Gâteaux and Fréchet differentiability is quite subtle.

2. GENERAL CONCEPTS

2.1. The space of wavefunctions and densities

We consider a system of N *interacting electrons* with the Hamiltonian (in Hartree atomic units, i.e., $m = e = \hbar = 4\pi\epsilon_0 = 1$)

$$\hat{H}_v = \hat{T} + \hat{W} + \hat{V} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{i<j=1}^{N} \frac{1}{r_{ij}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{1}$$

Here, $\hat{T} = \sum_i - \frac{1}{2}\nabla_i^2$ represents the kinetic energy, $\hat{W} = \sum_{i<j} 1/r_{ij}$ the interaction between the electrons and $\hat{V} = \sum_i v(\mathbf{r}_i)$ the external (usually nuclear) field. The wavefunctions are assumed to be normalizable (but not necessarily normalized)[1]

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N |\Psi(\mathbf{r}_1, \mathbf{r}_2 \cdots \mathbf{r}_N)|^2 < \infty \tag{2}$$

The electron density is defined as the diagonal of the first-order density matrix,

$$\rho(\mathbf{r}) = N \int d\mathbf{r_2} \int d\mathbf{r}_3 \cdots \int d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r_2} \cdots \mathbf{r}_N)|^2 \tag{3}$$

and we shall use this definition also for wavefunctions that are not normalized. Integration of the density then leads to

$$\int d\mathbf{r}\, \rho(\mathbf{r}) = N\langle \Psi | \Psi \rangle \tag{4}$$

which shows that normalizing the density to N, automatically implies that the wavefunction is normalized to unity. Regardless of the normalization, we have the relation

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d\mathbf{r}\, \rho(\mathbf{r}) v(\mathbf{r}) \tag{5}$$

We shall also restrict the space of wavefunctions to those with *finite kinetic energy*, which implies that

$$\sum_i \int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N |\nabla_i \Psi(\mathbf{r_1}, \mathbf{r_2} \cdots \mathbf{r}_\mathrm{N})|^2 < \infty \tag{6}$$

The wavefunctions then belong to the *Sobolev space* $H^1(\boldsymbol{R}^{3N})$ [2]. The densities corresponding to these wavefunctions form the space

$$S = \{\rho | \rho \geq 0; \qquad \sqrt{\rho} \in H^1(\mathbf{R}^3)\} \tag{7}$$

which is a subset of the intersection of the L^1 and L^3 spaces, $S \subset X = L^1 \cap L^3$ [5,11]. All densities in $\mathcal{S}$ can be generated by at least one function in $H^1(\mathbf{R}^{3N})$. The $\mathcal{S}$ space has the property of being *convex*, which implies that if $\rho_1, \rho_2 \in S$, then also $\lambda\rho_1 + (1-\lambda)\rho_2 \in S$ with $\lambda \in [0, 1]$.

For future reference we shall define the concept of *pure-state v-representable* (PS-v-representable) densities, being the densities corresponding to a single ground-state wavefunction of a Hamiltonian (1) with the potential v, which is in the dual

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[1] The integrals are generally assumed to be of Lebesgue type and normally include a sum over spin coordinates.

[2] Some of the topological concepts used here are defined in the Appendix. See also the review article by van Leeuwen in this volume [11], where some of these concepts are further discussed.

space of X, i.e., $v \in X^* = L^\infty + L^{3/2}$ [5,12,11]. The ground state can be degenerate or nondegenerate.

2.2. The Hohenberg–Kohn theorems

According to the Hohenberg–Kohn (HK) theorems [1], the ground-state energy (E_0) of an electronic system (1) is a functional of the ground-state density (ρ_0),

$$E_0 = E_{\text{HK}}[\rho_0] \tag{8}$$

and the ground-state energy is obtained by minimizing the energy functional

$$E_0 = \min E_{\text{HK}}[\rho] \tag{9}$$

over the set of v-representable normalized densities.

The energy functional can in the HK model be expressed

$$E_{\text{HK}}[\rho_0] = F_{\text{HK}}[\rho_0] + \int \mathrm{d}\mathbf{r}\, \rho_0(\mathbf{r}) v(\mathbf{r}) \tag{10}$$

where

$$F_{\text{HK}}[\rho_0] = \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_0 \rangle \tag{11}$$

is the *universal HK functional*, which is independent of the external potential $v(\mathbf{r})$.

Originally, the HK theorem was derived only for nondegenerate ground states, and the densities were restricted to v-representable densities of such states. Later it has been shown that the theorems hold also if the ground-state is degenerate. ρ_0 can then be any of the ground-state densities and Ψ_0 any ground-state wavefunction yielding this density [12].

2.3. The minimization process

Often the variation of a functional $F[\rho]$ at a density ρ_0 due to a small density change $\delta\rho$ can be expressed in the form

$$\begin{aligned} \delta F(\rho_0, \delta\rho) &= F[\rho_0 + \delta\rho] - F[\rho_0] \\ &= \int \mathrm{d}\mathbf{r} \left(\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} \right)_{\rho=\rho_0} \delta\rho(\mathbf{r}) + \text{higher order terms.} \end{aligned} \tag{12}$$

Then we refer to $(\delta F[\rho]/\delta\rho(\mathbf{r}))_{\rho=\rho_0}$ as the *functional derivative* at the density ρ_0. There are different definitions of this concept, as we shall discuss in the next section. If the functional has an *extremum* (maximum or minimum) at the density ρ_0, then the functional derivative will vanish in that point.

In order to be able to perform the minimization, using standard variational principles, it is necessary that we can make arbitrarily small variations of the density.

With the densities restricted by the v-representability condition, this is not necessarily the case, and standard procedures cannot be generally applied. Therefore, in order to find workable forms of the theory, the definition of the functionals has to be generalized to a larger group of densities. This will be discussed in Section 4.

We have assumed here that the variations are performed within the domain of normalized densities. Alternatively, the minimization can be performed using the *Euler–Lagrange procedure*. Then the densities are allowed to vary also outside the normalization domain. This we shall do by relaxing the normalization constraint of the wavefunctions and by using the definition (3) of the density also in the extended domain. The normalization constraint is enforced by means of a *Lagrange multiplier* (μ),

$$\delta\Big(F[\rho_0] - \mu \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})\Big) = 0 \tag{13}$$

which leads to the Euler equation

$$\left(\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}\right)_{\rho=\rho_0} - \mu = 0 \tag{14}$$

The extension of the functionals into the domain of unnormalized densities can be made in different ways, and the value of the Lagrange multiplier will depend on the way this is done. The process is not trivial, however, as we shall demonstrate below. Certain rules have to be followed in making such an extension (c.f., for instance, analytical continuation in function analysis). The expression must above all fulfill the conditions for a functional in the extended region, which, among other things, implies that it has to be uniquely defined—a certain density must always lead to a unique value of the functional.

2.4. Comments on the treatment of Nesbet

At this point we want to make a brief comment upon the approach of Nesbet, reviewed in another article of this volume [9]. Nesbet's main conclusion is that one of the main fundaments of DFT, the so-called *locality hypothesis*—the assumption that the derivative of the density functionals can be expressed in the form of multiplicative local function—is not generally valid. As we have pointed out in a separate Comment to the Physical Review [10], we believe that the arguments of Nesbet are incorrect and that the mistake is connected to the above-mentioned question of extending the functionals into the domain of unnormalized densities. We summarize our main arguments here and refer to our Comment for further details.

Nesbet considers a system of N noninteracting electrons with a nondegenerate ground state and with the wavefunctions in the form of Slater determinants $\Phi = 1/\sqrt{N!}\,\mathrm{Det}\{\phi_1, \phi_2, \ldots\}$. Restricting ourselves here to a two-electron system, the kinetic energy is then given by the orbital functional

$$T_s[\phi_1, \phi_2] = \langle \Phi | \hat{T} | \Phi \rangle = \langle \phi_1 | \hat{t} | \phi_1 \rangle + \langle \phi_2 | \hat{t} | \phi_2 \rangle \tag{15}$$

with $\hat{t} = -\frac{1}{2}\nabla^2$ and the density by

$$\rho(\mathbf{r}) = |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2 \tag{16}$$

Differentiating the expression (15), yields the orbital derivative

$$\frac{\delta T_s[\phi_1, \phi_2]}{\delta \phi_i^*(\mathbf{r})} = \hat{t}\phi_i(\mathbf{r}) = (\varepsilon_i - v(\mathbf{r}))\phi_i(\mathbf{r}) \tag{17}$$

using the orbital equation

$$\big(\hat{t} + v(\mathbf{r})\big)\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

Considering the kinetic energy (15) also as a *density* functional,

$$T_\mathrm{s}[\phi_1, \phi_2] = T_\mathrm{s}\big[\rho[\phi_1, \phi_2]\big] \tag{18}$$

Nesbet applies the chain rule and obtains

$$\frac{\delta T_\mathrm{s}\big[\rho[\phi_1, \phi_2]\big]}{\delta \phi_i^*(\mathbf{r})} = \frac{\delta T_\mathrm{s}[\rho]}{\delta \rho(\mathbf{r})} \frac{\delta \rho(\mathbf{r})}{\delta \phi_i^*(\mathbf{r})} = \frac{\delta T_\mathrm{s}[\rho]}{\delta \rho(\mathbf{r})} \phi_i(\mathbf{r}) \tag{19}$$

Identification then leads to an *orbital-dependent derivative*

$$\frac{\delta T_\mathrm{s}[\rho]}{\delta \rho(\mathbf{r})} \phi_i(\mathbf{r}) = \big(\varepsilon_i - v(\mathbf{r})\big)\phi_i(\mathbf{r}) \tag{20}$$

which Nesbet interprets so that the *locality hypothesis* is not valid if the system contains different orbital energy eigenvalues.

As we have pointed out in our Comment [10], the expression (15) is in combination with the density expression (16) *not a density functional* outside the normalization domain. Therefore, the identity (18) is not generally valid and the chain rule cannot be used in the way Nesbet does. If the variations are restricted to the normalization domain, then the constant term (orbital eigenvalue) disappears, and the locality hypothesis is restored.

Another approach is to modify the kinetic-energy expression so that it will be a density functional also in the unnormalized domain. This we have performed in our Comment by defining the density according to equation (3)

$$\rho(\mathbf{r}) = |\phi_1(\mathbf{r})|^2 \langle \phi_2 | \phi_2 \rangle + |\phi_2(\mathbf{r})|^2 \langle \phi_1 | \phi_1 \rangle \tag{21}$$

and the kinetic energy similarly by

$$T_\mathrm{s}[\phi_1, \phi_2] = \langle \Phi | \hat{T}_\mathrm{s} | \Phi \rangle = \langle \phi_1 | \hat{t} | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle + \langle \phi_2 | \hat{t} | \phi_2 \rangle \langle \phi_1 | \phi_1 \rangle \tag{22}$$

(Here we relaxed the normalization constraint of the orbitals but maintained the orthogonality constraint.) Then we have shown that the kinetic energy is in fact a density as well as an orbital functional in the close neighborhood of the ground-state density, and hence the relation (18) is valid in that neighborhood. Direct derivation now yields the orbital derivative

$$\begin{aligned}\frac{\delta T_{\mathrm{s}}[\phi_1,\phi_2]}{\delta\phi_1^*} &= [\hat{t}\langle\phi_2|\phi_2\rangle + \langle\phi_2|\hat{t}|\phi_2\rangle]\phi_1(\mathbf{r}) \\ &= \Big[(\varepsilon_1 - v(\mathbf{r}))\langle\phi_2\phi_2\rangle + \langle\phi_2|\varepsilon_2 - v(\mathbf{r})|\phi_2\rangle\Big]\phi_1(\mathbf{r}) \qquad (23)\end{aligned}$$

and application of the chain rule

$$\begin{aligned}\frac{\delta T_{\mathrm{s}}[\rho[\phi_1,\phi_2]]}{\delta\phi_1^*(\mathbf{r})} &= \int \mathrm{d}\mathbf{r}'\,\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r}')}\,\frac{\delta\rho(\mathbf{r}')}{\delta\phi_1^*(\mathbf{r})} \\ &= \left[\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r})}\langle\phi_2|\phi_2\rangle + \left\langle\phi_2\middle|\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho}\middle|\phi_2\right\rangle\right]\phi_1(\mathbf{r}) \qquad (24)\end{aligned}$$

Identification then yields

$$\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r})} = \frac{\varepsilon_1 + \varepsilon_2}{2} - v(\mathbf{r}) \qquad (25)$$

which is *orbital independent* and in the form of a *multiplicative local potential*, and again the locality hypothesis is restored.

This demonstrates the importance of extending the functionals into the domain of unnormalized densities in a proper way in applying the Euler–Lagrange procedure.

3. FUNCTIONAL DERIVATIVES

The functional derivative is a particular important concept in DFT, and we shall here investigate that in some detail. Two forms of functional derivatives are here of interest, the *Gâteaux* derivative and the *Fréchet* derivative.

3.1. Gâteaux derivative

We consider a functional $f : M \longrightarrow \mathbf{R}$, which is a mapping of a normed space (M) on the space of real numbers ($\mathbf{R}$). If at some point $x_0 \in M$ there exists a mapping $\mathrm{d}f(x_0,\cdot) : M \longrightarrow \mathbf{R}$ such that

$$\mathrm{d}f(x_0,h) = \lim_{\lambda\to 0}\frac{f(x_0+\lambda h) - f(x_0)}{\lambda} \qquad (26)$$

then $\mathrm{d}f(x_0,h)$ is the *Gâteaux differential* at the point x_0 in the direction h ([13], p. 46), ([14], p. 448). An equivalent definition is

$$f(x_0+h) = f(x_0) + \mathrm{d}f(x_0,h) + \omega(x_0,h) \qquad (27)$$

where

$$\lim_{\lambda\to 0}\frac{\omega(x_0,\lambda h)}{\lambda}=0 \tag{28}$$

The Gâteaux differential is also termed the *weak differential* ([15], p. 293). In principle, this mapping need neither be linear nor continuous, but we shall follow the convention ([11], equation 60) that

> *a functional is Gâteaux differentiable at a point* x_0 *if and only if the mapping in equation (26) is linear and continuous in h for all h at this point.*

In applying the formalism to DFT, we express the variation of a density functional $F[\rho]$ at a density ρ_0 due to a density change $\delta\rho$ in the form (12)

$$\delta F(\rho_0,\delta\rho)=F[\rho_0+\delta\rho]-F[\rho_0]=\int \mathrm{d}\mathbf{r}\; v([\rho_0];\mathbf{r})\delta\rho(\mathbf{r})+\omega\,(\rho_0,\delta\rho) \tag{29}$$

and the differential (26) then becomes

$$\mathrm{d}f(\rho_v,\delta\rho)=\int \mathrm{d}\mathbf{r}v([\rho_0];\mathbf{r})\delta\rho(\mathbf{r})+\lim_{\lambda\to 0}\frac{1}{\lambda}\,\omega(\rho_0,\lambda\delta\rho) \tag{30}$$

This mapping is linear and continuous if (1) $v([\rho_0];\mathbf{r})$ is a single-valued *bounded* function of $\mathbf{r}$ that may depend on the density ρ_0 but is independent of $\delta\rho$, and (2)

$$\lim_{\lambda\to 0}\frac{1}{\lambda}\,\omega(\rho_0,\lambda\delta\rho)=0 \tag{31}$$

[Note that a linear operator is continuous if and only if it is bounded ([16], p. 197, 213), ([14], p. 22).] We shall refer to the function above as the *Gâteaux derivative* at the density ρ_0 ([11], Eq. 61)

$$\left(\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}\right)_{\rho=\rho_0}=v([\rho_0];\mathbf{r}) \tag{32}$$

A necessary condition for the Gâteaux differentiability is also that the functional is defined for $\rho_0+\lambda\delta\rho$—for all $\lambda\in[0,1]$—if it is defined for ρ_0 and $\rho_0+\delta\rho$. This is the case if the functional is defined on a space that is *convex*, as the $\mathcal{S}$ space (7).

The form (30) represents a differential that is linear and continuous if the conditions specified are fulfilled. A question relevant for the discussion of the differentiability in Section 4, is if the differential of a differentiable functional always can be written in this form. We believe that this can be answered positively.[3]

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[3] In order to show that this is at least plausible, we consider a *discrete* coordinate space, $\mathbf{r}=\mathbf{r}_i$, $i=1\cdots n$ and $\delta\rho_i=\delta\rho(\mathbf{r}_i)$. A functional $l[\delta\rho]$ then becomes a *function* of n variables, $l[\delta\rho]\to l(\delta\rho_1,\dots\delta\rho_n)$. If the functional is *linear*, then

$$l(\delta\rho_1,\dots\delta\rho_n)=l(\delta\rho_1,0,\dots)+l(0,\delta\rho_2,0,\dots)+\cdots=\sum_{i=1}^{n}f_i\delta\rho_i$$

with $l(0,\dots 0,\delta\rho_i,0,\dots)=f_i\delta\rho_i$. In the limit, this approaches an integral,

$$l[\delta\rho]\to l(\delta\rho_1,\dots\delta\rho_n)=\sum_{i=1}^{n}f_i\delta\rho_i\to\int \mathrm{d}\mathbf{r}f(\mathbf{r})\delta\rho(\mathbf{r})$$

If the functional is *continuous*, then all f_i must be finite and the function $f(\mathbf{r})$ *bounded.*

3.2. Fréchet derivative

Another form of functional differential is the *Fréchet differential*, also termed the *strong differential*, which can be defined as follows ([13], p. 37), ([14], p. 451). With M being a subset of a Banach space E with the norm $\|\cdot\|$, the function $f : M \longrightarrow \mathbf{R}$ is *Fréchet differentiable* at a point $x_0 \in M$, if there exists a *continuous and linear operator*, $L(\cdot) : E \longrightarrow \mathbf{R}$, such that (1)

$$f(x_0 + h) - f(x_0) = L(h) + \omega(x_0, h) \tag{33}$$

for all $h \in E$ and $x_0 + h \in M$ and (2) $\omega(x_0, 0) = 0$ and

$$\lim_{\|h\| \to 0} \frac{\omega(x_0, h)}{\|h\|} = 0 \tag{34}$$

The function $L(h)$ is the *Fréchet differential* at the point x_0 in the direction h, and the operator $L(\cdot)$ is sometimes termed the *Fréchet derivative* at x_0. Here, however, we shall reserve the term Fréchet derivative to a function equivalent to the Gâteaux derivative (32). Fréchet differentiability is a stronger requirement than that of Gâteaux differentiability, but—with the interpretations we make—the difference is quite subtle.

3.3. Comparison between Fréchet and Gâteaux differentiabilities

It can be shown that if a Gâteaux derivative exists in a neighborhood of the point x_0, i.e., at all points $\|x - x_0\| < \delta$, and is (uniformly) *continuous* in x in this neighborhood, then the functional is *Fréchet differentiable* at the point x_0 ([13], p. 47), ([15], p. 295). [For a linear mapping the concepts of 'continuity' and 'uniform continuity' are equivalent ([14], p. 23).] In this case there exists a δ for each ε so that the difference between the Gâteaux derivatives at the points x_0 and x is less than ε for all x with $\|x - x_0\| < \delta$. Therefore, a functional that is Gâteaux but not Fréchet differentiable at a point x_0 must have some kind of discontinuity at this point.

In order to demonstrate the difference further, we shall assume that the functional is Gâteaux differentiable and then find out what the additional requirement is to make it Fréchet differentiable. If we make the replacement $h \longrightarrow \lambda h$ and set $\|h\| = 1$, the expression (34) becomes

$$\lim_{\lambda \to 0} \frac{\omega(x_0, \lambda h)}{\lambda} = 0 \tag{35}$$

or formally identical to the corresponding condition (28) in the Gâteaux case. The difference is that in the Gâteaux case it is sufficient that this relation is satisfied for each individual value of h separately, while in the Fréchet case the relation must be fulfilled for the entire neighborhood. In other words, the limit must in the Fréchet case be *uniform*, implying that for each value of $\delta > 0$ there exists a $\lambda > 0$, so that

$$\frac{|\omega(x_0, \lambda h)|}{\lambda} < \delta \quad \text{for all } h \tag{36}$$

If we assume that $\omega(x_0, \lambda h) = C(h)\lambda^2$, where $C(h)$ is a number that depends on h, then the condition for Gâteaux differentiability is that $C(h)$ is *finite*, while for Fréchet differentiability it is has to be *bounded*, implying that there exists a number $D < \infty$, such that $C(h) < D$ for all h. This implies that also $\omega(x_0, h)$ must be bounded within the neighborhood $\|h\| < \varepsilon$. Thus, if the functional is not Fréchet differentiable, this term is unbounded in any neighborhood of x_0, which indicates some kind of singularity.

Fréchet differentiability is obviously a stronger condition than Gâteaux differentiability. Therefore, *if a functional is Fréchet differentiable, it is also Gâteaux differentiable, and the Fréchet and the Gâteaux derivatives are identical.*

4. APPLICATION TO DENSITY FUNCTIONALS

As mentioned, in order to be able to apply the variational principle in DFT, it is necessary to extend the definition of the functionals beyond the domain of v-representable densities, and the standard procedure is here to apply the *Levy constrained-search procedure* [17]. This has led to the functionals known as the Levy–Lieb ($F_{\mathrm{L}}[\rho]$) and Lieb ($F_{\mathrm{L}}[\rho]$) functionals, respectively, and we shall now investigate the differentiability of these functionals. This will represent the main part of our paper.

4.1. The Levy–Lieb functional

We consider a general electronic system with the Hamiltonian (1)

$$\hat{H}_v = \hat{T} + \hat{W} + \hat{V} \tag{37}$$

with a ground-state energy E_v that can be degenerate. By applying the constrained-search procedure to the HK functional (11), Levy [17] and Lieb [5] have defined the functional

$$F_{\mathrm{LL}}[\rho] = \inf_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \tag{38}$$

referred to as the *Levy–Lieb functional*. Here, Ψ is any normalized wavefunction in the Sobolev space $H^1(\mathbf{R}^{3N})$ [equation (6)] that generates the density $\rho(\mathbf{r})$. This extends the definition of the HK functional to all densities of the space $\mathcal{S}$.

The energy functional (10) is generalized accordingly,

$$E_{\mathrm{LL}}[\rho] = F_{\mathrm{LL}}[\rho] + \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})\, v(\mathbf{r}) \tag{39}$$

Here, we shall extend these definitions further by relaxing the normalization restriction of the wavefunctions and densities by using the definition of the density (3) also outside the normalization domain.

Within the normalization domain the energy functional (39) has its minimum equal to the exact ground-state energy E_v of the system, when the density is equal to any of the exact ground-state densities ρ_v,

$$E_v = \min_{\rho \in S} E_{\mathrm{LL}}[\rho] = E_{\mathrm{LL}}[\rho_v] \tag{40}$$

We shall now investigate the differentiability of the Levy–Lieb functional (38), and in doing so we shall largely follow the arguments of our recent Comment to the work of Nesbet [10], extended to the more general situation.

With the normalization constraint, any ground-state wavefunction Ψ_v of $\hat{H}_v$ minimizes $\langle \Psi | \hat{H}_v | \Psi \rangle$ according to the variational principle of quantum mechanics. Hence, any ground-state wavefunction, corresponding to a particular ground-state density ρ_v, also minimizes this quantity when the variation is restricted to that density. In such a restricted variation the potential contribution (5) is constant, and it then follows that also $\langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$ is minimized, or

$$F_{\mathrm{LL}}[\rho_v] = \langle \Psi_v | \hat{T} + \hat{W} | \Psi_v \rangle \tag{41}$$

We then have, using equations (4) and (5),

$$F_{\mathrm{LL}}[\rho_v] = \langle \Psi_v | \hat{H}_v - \hat{V} | \Psi_v \rangle = \int \mathrm{d}\mathbf{r} \left(\frac{E_v}{N} - v(\mathbf{r}) \right) \rho_v(\mathbf{r}) \tag{42}$$

In order to find the differential of the functional (38) at a ground-state density, ρ_v, we make a small change in the density around that density, $\rho = \rho_v + \delta\rho$, and investigate the corresponding change of the functional

$$\begin{aligned} \delta F_{\mathrm{LL}}(\rho_v, \delta\rho) &= F_{\mathrm{LL}}[\rho_v + \delta\rho] - F_{\mathrm{LL}}[\rho_v] \\ &= \inf_{\Psi \to \rho_v + \delta\rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle - \int \mathrm{d}\mathbf{r} \left(\frac{E_v}{N} - v(\mathbf{r}) \right) \rho_v(\mathbf{r}) \end{aligned} \tag{43}$$

We write the minimizing wavefunction as $\Psi = \Psi_v + \delta\Psi$ with Ψ_v being a normalized ground-state wave function, corresponding to the density ρ_v. We do *not* assume that $\delta\Psi$ has to be ‘small’, and we also leave the question of normalization of Ψ open.

Generally, we have

$$\langle\Psi|\hat{T}+\hat{W}|\Psi\rangle=\langle\Psi|\hat{H}_v-\hat{V}|\Psi\rangle=\langle\Psi|\hat{H}_v|\Psi\rangle-\int\mathrm{d}\mathbf{r}\,v(\mathbf{r})\,\rho(\mathbf{r}) \tag{44}$$

and

$$\begin{aligned}\langle\Psi|\hat{H}_v|\Psi\rangle&=E_v\langle\Psi|\Psi\rangle+\langle\Psi_v+\delta\Psi|\hat{H}_v-E_v|\Psi_v+\delta\Psi\rangle\\&=E_v\langle\Psi|\Psi\rangle+\langle\delta\Psi|\hat{H}_v-E_v|\delta\Psi\rangle\end{aligned} \tag{45}$$

This yields

$$\begin{aligned}\langle\Psi|\hat{T}+\hat{W}|\Psi\rangle&=\langle\Psi|\hat{H}_v-\hat{V}|\Psi\rangle\\&=\int\mathrm{d}\mathbf{r}\left(\frac{E_v}{N}-v(\mathbf{r})\right)\rho(\mathbf{r})+\langle\delta\Psi|\hat{H}_v-E_v|\delta\Psi\rangle\end{aligned} \tag{46}$$

and with the definition (38)

$$\begin{aligned}F_{\mathrm{LL}}[\rho_v+\delta\rho]=&\int\mathrm{d}\mathbf{r}\left(\frac{E_v}{N}-v(\mathbf{r})\right)(\rho_v(\mathbf{r})+\delta\rho(\mathbf{r}))\\&+\inf_{\Psi\to\rho_v+\delta\rho}\langle\delta\Psi|\hat{H}_v-E_v|\delta\Psi\rangle\end{aligned} \tag{47}$$

The variation (43) now becomes, using equation (42),

$$\begin{aligned}\delta F_{\mathrm{LL}}(\rho_v,\delta\rho)=F_{\mathrm{LL}}[\rho_v+\delta\rho]-F_{\mathrm{LL}}[\rho_v]=&\int\mathrm{d}\mathbf{r}\left(\frac{E_v}{N}-v(\mathbf{r})\right)\delta\rho(\mathbf{r})\\&+\inf_{\Psi_v+\delta\Psi\to\rho_v+\delta\rho}\langle\delta\Psi|\hat{H}_v-E_v|\delta\Psi\rangle\end{aligned} \tag{48}$$

This is of the form (29), with the potential $v(\mathbf{r})\in L^{\infty}+L^{3/2}$ being finite. Therefore, the functional is Gâteaux differentiable, if the last term

$$\omega(\rho_v,\delta\rho)=\inf_{\Psi_v+\delta\Psi\to\rho_v+\delta\rho}\langle\delta\Psi|\hat{H}_v-E_v|\delta\Psi\rangle \tag{49}$$

vanishes faster than $\delta\rho$ or

$$\lim_{\lambda\to0}\frac{1}{\lambda}\inf_{\Psi_v+\delta\Psi\to\rho_v+\lambda\delta\rho}\langle\delta\Psi|\hat{H}_v-E_v|\delta\Psi\rangle=0 \tag{50}$$

for all $\delta\rho$.

We know that the kinetic energy is finite with the wavefunctions of the space we consider [equation (6)], and since the electrostatic energy is finite and the potential energy can be expected to be finite, it follows that the matrix element in equation (50) is finite. Then we can show the differentiability by scaling.

We consider one specific wavefunction $\Psi_v+\delta\Psi_{\delta\rho}$ that yields a particular density $\rho_v+\delta\rho$. We know that all densities in the $\mathcal{S}$ space (7) can be generated by at least one wavefunction in our space. We then scale the wavefunction increment by $\lambda \in [0,1]$, i.e., $\Psi_v \longrightarrow \Psi_v + \lambda\delta\Psi_{\delta\rho}$, which generates the density change

$$\lambda\delta\rho_1 + \lambda^2\delta\rho_2 = \lambda\delta\rho' \tag{51}$$

With the scaled wavefunction we have

$$\lim_{\lambda\to 0}\frac{1}{\lambda}\langle\lambda\delta\Psi_{\delta\rho}|\hat{H}_v - E_v|\lambda\delta\Psi_{\delta\rho}\rangle = 0$$

which means that

$$\lim_{\lambda\to 0}\frac{1}{\lambda}\inf_{\Psi_v+\delta\Psi\to\rho_v+\lambda\delta\rho'}\langle\delta\Psi|\hat{H}_v - E_v|\delta\Psi\rangle = 0 \tag{52}$$

The infimum in equation (52) is searched over the density $\rho_v + \lambda\delta\rho'$, which is not identical to the density $\rho_v + \lambda\delta\rho$ of equation (50). For that reason we consider instead of equation (48) the variation

$$\begin{aligned}\delta F_{\mathrm{LL}}(\rho_v, \lambda\delta\rho') &= F_{\mathrm{LL}}[\rho_v + \lambda\delta\rho'] - F_{\mathrm{LL}}[\rho_v] \\ &= \int d\mathbf{r}\left(\frac{E_v}{N} - v(\mathbf{r})\right)\lambda\delta\rho'(\mathbf{r}) + \omega(\rho_v, \lambda\delta\rho')\end{aligned} \tag{53}$$

where

$$\omega(\rho_v, \lambda\delta\rho') = \inf_{\Psi_v+\delta\Psi\to\rho_v+\lambda\delta\rho'}\langle\delta\Psi|\hat{H}_v - E_v|\delta\Psi\rangle$$

vanishes faster than λ in view of equation (52). The expression (53) can be rewritten as

$$\frac{\delta F_{\mathrm{LL}}(\rho_v, \lambda\delta\rho')}{\lambda} = \int d\mathbf{r}\left(\frac{E_v}{N} - v(\mathbf{r})\right)\delta\rho'(\mathbf{r}) + \frac{\omega(\rho_v, \lambda\delta\rho')}{\lambda} \tag{54}$$

where the last term goes to zero as $\lambda \longrightarrow 0$. This leads to

$$\lim_{\lambda\to 0}\frac{\delta F_{\mathrm{LL}}(\rho_v, \lambda\delta\rho')}{\lambda} = \int d\mathbf{r}\left(\frac{E_v}{N} - v(\mathbf{r})\right)\delta\rho_1(\mathbf{r}) \tag{55}$$

The r.h.s of equation (55) is *continuous* with respect to changes in $\delta\rho'$, which we can show by replacing $\delta\rho'$ in equation (54) by $\delta\rho' + \delta^2\rho'$ and let $\delta^2\rho' \longrightarrow 0$. Then the corresponding change of the r.h.s. vanishes in the limit $\lambda \longrightarrow 0$. Furthermore, the various ‘paths’ $\delta\rho'$ cover all possible densities, so that we can make infinitesimal changes. By setting $\delta^2\rho' = -\lambda\delta\rho_2$, we then obtain

$$\lim_{\lambda\to 0}\frac{\delta F_{\mathrm{LL}}(\rho_v, \lambda\delta\rho')}{\lambda} = \lim_{\lambda\to 0}\frac{\delta F_{\mathrm{LL}}(\rho_v, \lambda\delta\rho_1)}{\lambda} \tag{56}$$

and

$$\lim_{\lambda \to 0} \frac{\delta F_{\mathrm{LL}}(\rho_v, \lambda \delta \rho_1)}{\lambda} = \int \mathrm{d}\mathbf{r} \left(\frac{E_v}{N} - v(\mathbf{r}) \right) \delta \rho_1(\mathbf{r}) \tag{57}$$

This is exactly the definition of the Gâteaux differential (26) in the direction $\delta\rho_1$, and hence we have

$$\boxed{\mathrm{d}F_{\mathrm{LL}}(\rho_v, \delta\rho_1) = \int \mathrm{d}\mathbf{r} \left(\frac{E_v}{N} - v(\mathbf{r}) \right) \delta \rho_1(\mathbf{r})} \tag{58}$$

This relation holds for any direction, which implies that *the functional F_{LL} is Gâteaux differentiable with the Gâteaux derivative*

$$\left(\frac{\delta F_{\mathrm{LL}}[\rho]}{\delta \rho(\mathbf{r})} \right)_{\rho=\rho_v} = \frac{E_v}{N} - v(\mathbf{r}) \tag{59}$$

which is *equivalent to a local multiplicative function.*

Since E_v is the ground-state energy, it follows that the expression (50) is nonnegative. This implies that the functional is *locally convex* in the neighborhood of the density ρ_v. In the standard method for proving the differentiability the convexity of the functional is used [5,4,11]. Since the Levy–Lieb functional is not necessarily convex, this procedure does not work. The reason that in spite of this fact it has been possible to demonstrate the differentiability here could be connected to the fact that the functional is locally convex in the neighborhood of the points of interest.

We have here made no assumption about the normalization of the wavefunction or density. If the density is normalized, the integral over $\delta\rho$ vanishes,

$$\int \mathrm{d}r \delta\rho(\mathbf{r}) = 0$$

and the derivative will be undetermined up to a constant. The constant in equation (59) depends on the particular way the functional is extended into the unnormalized domain and has no physical significance. This constant corresponds to the Lagrange multiplier in the Euler equation (14), when the Euler–Lagrange procedure is used.

In the treatment here we have assumed that Ψ_v is a ground-state wavefunction of a Hamiltonian $\hat{H}_v$ corresponding to the ground-state density ρ_v, but no further assumption has been made. The results hold for nondegenerate as well as degenerate ground states.

We can then conclude that *the Levy–Lieb functional F_{LL} is Gâteaux differentiable at any PS-v-representable density and that the derivative can be represented by a multiplicative local function.*

If the density is *not* that of an eigenstate of a Hamiltonian $\hat{H}_v$—ground or excited state—then the differential cannot be of the form (58), which we conclude will exclude differentiability. On the other hand, we cannot from our analysis exclude the possibility that the functional is differentiable at a density due to an *excited* state of some $\hat{H}_v$. This question, though, requires further study.

Having considered the Gâteaux differentiability of $F_{\mathrm{LL}}[\rho]$ at PS-v-representable densities, we may now turn to the question of possible *Fréchet differentiability* at these densities. The condition (34) is then

$$\lim_{\delta\rho \to 0} \frac{\omega(\rho_v, \delta\rho)}{\|\delta\rho\|} = 0 \tag{60}$$

with $\omega(\rho_v, \delta\rho)$ given by equation (49). As discussed above, this requires that the expression (49) is *bounded* in the neighborhood $\|\delta\rho\| < \varepsilon$ as $\varepsilon \to 0$. The norm could here be $\|\delta\rho\|_1$ or $\|\delta\rho\|_3$ of the spaces L^1 and L^3, respectively.

Since the electrostatic energy is bounded and we can assume that the external potential is such that the potential energy is bounded, it follows that the residual term is bounded, if the kinetic energy is bounded. We have assumed that the kinetic energy is *finite* [equation (6)], but this does not necessarily mean that it is bounded. Generally, we cannot exclude the possibility that the kinetic energy is unbounded, but it should be observed that it is the *infimum* that appears in the expression (49). Therefore, a sufficient condition for the Fréchet differentiability is that for *each* density in any neighborhood of the ground-state density ρ_v there exists *one* wavefunction that generates bounded kinetic energy. It seems clear that all densities in the neighborhood of ρ_v can be generated by functions close to the ground-state function Ψ_v, generating the density ρ_v.[4] On the other hand, it is possible to construct a function, generating a density arbitrary close to ρ_v with arbitrarily high kinetic energy by adding a small rapidly oscillating component to the wavefunction. In such a case the functional would *not* be Fréchet differentiable. From a DFT standpoint, though, it seems that the possible difference between Gâteaux and Fréchet differentiability is of no practical importance.

4.2. The Lieb functional

In the degenerate case we can have a situation, where a linear combination of ground-state densities is not necessarily itself a ground-state density. This has the consequence that the HK [equation (11)] and the Levy–Lieb [equation (38)] functionals are not necessarily *convex*, which for many applications is a disadvantage. A convex functional can be constructed by considering *ensemble-v-representable* (E-v-representable) densities [3,12,11]

$$\rho_{Ev}(\mathbf{r}) = \sum_k \lambda_k \rho_{vk}(\mathbf{r}) \quad \lambda_k \geq 0 \quad \sum_k \lambda_k = 1 \tag{61}$$

---

[4] This problem is closely related to the '*Question 2*', raised by Lieb ([5], p. 247), which Lieb believes has an affirmative answer, although a rigorous proof has not been found.

which is a linear combination of ground-state densities ρ_{vk} of the Hamiltonian $\hat{H}_v$ [equation (1)]. It can be shown that the HK theorems are essentially valid also for such densities. The corresponding *extended Hohenberg–Kohn functional* (EHK) is defined

$$F_{\mathrm{EHK}}[\rho_{Ev}] = E_v - \int \mathrm{d}\mathbf{r}\, v(\mathbf{r})\rho_{Ev}(\mathbf{r}) \tag{62}$$

The ground-state energy then becomes ([11], Theorem 2)

$$E_v = \inf_{\rho \in \mathcal{B}} \left\{ F_{\mathrm{EHK}}[\rho] + \int \mathrm{d}\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r}) \right\} \tag{63}$$

where $\mathcal{B}$ is the space of all E-v-representable densities.

Using the constrained-search procedure, Lieb [5] has in analogy with the Levy–Lieb functional (38) extended the EHK functional (10) to

$$F_{\mathrm{L}}[\rho] = \inf_{\lambda_k, \Psi_k \to \rho} \sum_k \lambda_k \langle \Psi_k | \hat{T} + \hat{W} | \Psi_k \rangle \tag{64}$$

where $\{\Psi_k\}$ is any set of orthonormal eigenfunctions of some $\hat{H}_v$ (not necessarily degenerate) and λ_k has the same restrictions as in equation (61). This is usually referred to as the *Lieb functional*. Both the functionals F_{EHK} and F_{L} in equations (62) and (64) are convex.

The energy functional corresponding to the functional F_{L} is

$$E_{\mathrm{L}}[\rho] = E_{\mathrm{L}}[\rho] + \int \mathrm{d}\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r}) = \inf_{\lambda_k, \Psi_k \to \rho} \sum_k \lambda_k \langle \Psi_k | \hat{T} + \hat{W} + \hat{V} | \Psi_k \rangle$$

which has its minimum, equal to the ground-state energy, when all Ψ_k are ground-state eigenfunctions of $\hat{H}_v$. Therefore,

$$E_v = \min_{\rho \in S} E_{\mathrm{L}}[\rho] = E_{\mathrm{L}}[\rho_{Ev}] \tag{65}$$

where $\rho_{Ev}(\mathbf{r})$ is according to equation (61) composed of any combination of ground-state wavefunctions of the Hamiltonian H_v.

We can now demonstrate the Gâteaux differentiability of the Lieb functional (64) for all E-v densities using the same procedure as in the previous section. We know that the energy functional (65) has its lowest value when all functions belong to the ground state. It then follows that the Lieb functional for an E-v density becomes

$$F_{\mathrm{L}}[\rho_{Ev}] = \sum_k \lambda_k \langle \Psi_{vk} | \hat{T} + \hat{W} | \Psi_{vk} \rangle \quad \lambda_k, \Psi_{vk} \to \rho_{Ev} \tag{66}$$

which can be expressed

$$F_{\mathrm{L}}[\rho_{Ev}] = \sum_k \lambda_k \langle \Psi_{vk} | \hat{H}_v - \hat{V} | \Psi_{vk} \rangle = \int \mathrm{d}\mathbf{r} \left(\frac{E_v}{N} - v(\mathbf{r}) \right) \rho_{Ev}(\mathbf{r}) \tag{67}$$

In exactly the same way as in the previous case, it can then be shown that the differential becomes

$$\begin{aligned}\mathrm{d}F_{\mathrm{L}}(\rho_{Ev},\delta\rho) &= \sum_k \lambda_k\langle\delta\Psi_{vk}|\hat{T}+\hat{W}|\Psi_{vk}\rangle + \text{c.c.}\\ &= \sum_k \lambda_k\langle\delta\Psi_{vk}|\hat{H}_v-\hat{V}|\Psi_{vk}\rangle + \text{c.c.}\\ &= E_v\langle\delta\Psi_{vk}|\Psi_{vk}\rangle + \text{c.c.} - \int \mathrm{d}\mathbf{r}v(\mathbf{r})\delta\rho(\mathbf{r})\\ &= \int \mathrm{d}\mathbf{r}\left(\frac{E_v}{N}-v(\mathbf{r})\right)\delta\rho(\mathbf{r}) \end{aligned} \tag{68}$$

This shows that the functional $F_{\mathrm{L}}[\rho]$ is Gâteaux differentiable at any density generated by an ensemble of ground-state wave functions, i.e., at any E-v-representable density,

$$\boxed{\left(\frac{\delta F_{\mathrm{L}}[\rho]}{\delta\rho(\mathbf{r})}\right)_{\rho=\rho_{Ev}} = \frac{E_v}{N}-v(\mathbf{r})} \tag{69}$$

Using the same arguments as in the previous case, it seems that functionals of physical interest are also Fréchet differentiable at the E-v-representable densities.

If the density in equation (64) is *not* E-v representable, i.e., cannot be expressed as a linear combination of degenerate ground-state densities of any Hamiltonian, H_v, then the minimum cannot be represented by ground-state wavefunctions only—at least one must belong to an excited state. If not all wavefunctions belong to the same energy eigenvalue, then the differential cannot be written in the form (68). Using the same arguments as in the previous case, this means that the functional is *not* differentiable. If, on the other hand, all wavefunctions belong to the same *excited* energy eigenvalue, our analysis does not at present exclude differentiability. As in the previous case, however, this question requires further study.

5. THE KOHN–SHAM MODEL

We shall now show how the formalism examined above can be used to derive the standard Kohn–Sham scheme. We start by considering the Levy–Lieb energy functional (39), which is minimized under the normalization constraint

$$E_v = \min_{\rho\in S} E_{\mathrm{LL}}[\rho] = E_{\mathrm{LL}}[\rho_v] \tag{70}$$

by varying the density in the space $\mathcal{S}$ [equation (7)].

The minimization of $E_{\mathrm{LL}}[\rho]$, using equation (39), leads to

$$\delta E_{\mathrm{LL}}[\rho] = \delta\left\{F_{\mathrm{LL}}[\rho] + \int \mathrm{d}\mathbf{r}\rho(\mathbf{r})v(\mathbf{r})\right\} = 0$$

and staying within the normalization domain to

$$\frac{\delta E_{\mathrm{LL}}[\rho]}{\delta\rho} = \frac{\delta F_{\mathrm{LL}}[\rho]}{\delta\rho} + v(\mathbf{r}) + \text{constant} = 0 \tag{71}$$

The constant is here undetermined, due to the normalization constraint, $\int \mathrm{d}\mathbf{r}\rho(\mathbf{r}) = 0$. If the functional $E_{\mathrm{LL}}[\rho]$ is Gâteaux (Fréchet) differentiable, then its Gâteaux (Fréchet) derivative will vanish at the minimum ([14], p. 460).

In the Kohn–Sham model [2] we consider a system of *noninteracting electrons*, moving in a *local* potential $v_{\mathrm{KS}}(\mathbf{r})$,

$$\hat{H}_{\mathrm{KS}} = \hat{T} + \hat{V}_{\mathrm{KS}} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N} v_{\mathrm{KS}}(\mathbf{r}_i) \tag{72}$$

and the basic idea of the model is to determine the potential $v_{\mathrm{KS}}(\mathbf{r})$ so that the ground-state density of the noninteracting system becomes the same as that of the interacting system we are considering. This requires that the density is *noninteracting v-representable*, i.e., can be reproduced by the ground-state density of a noninteracting system with a local potential. van Leeuwen has shown that this is always possible with arbitrary accuracy [11].

Using the constrained search, the correspondence of the Levy–Lieb functional (38) is for the noninteracting system the minimum of the kinetic energy,

$$T_{\mathrm{KS}}[\rho] = \min_{\Psi\to\rho}\langle\Psi|\hat{T}|\Psi\rangle \tag{73}$$

and the corresponding energy functional becomes

$$E_{\mathrm{KS}}[\rho] = T_{\mathrm{KS}}[\rho] + \int \mathrm{d}\mathbf{r}\rho(\mathbf{r})v_{\mathrm{KS}}(\mathbf{r}) \tag{74}$$

The ground-state energy of the noninteracting system is obtained by minimizing this energy functional under the normalization constraint,

$$E_v = \min_{\rho\in S} E_{\mathrm{KS}}[\rho] \tag{75}$$

where the search is over the same set of densities as in the interacting case. This leads to the equation

$$\frac{\delta E_{\mathrm{KS}}[\rho]}{\delta\rho} = \frac{\delta T_{\mathrm{KS}}[\rho]}{\delta\rho} + v_{\mathrm{KS}}(\mathbf{r}) + \text{constant} = 0 \tag{76}$$

The derivative exists here for densities that are PS-v representable for a non-interacting system.

We now require that the solution of equation (76) should lead to the same ground-state density as equation (71), which yields the condition for the potential v_{KS},

$$\begin{aligned} v_{\mathrm{KS}}(\mathbf{r}) &= \frac{\delta E_{\mathrm{LL}}[\rho]}{\delta\rho} - \frac{\delta T_{\mathrm{KS}}[\rho]}{\delta\rho} \\ &= \frac{\delta F_{\mathrm{LL}}[\rho]}{\delta\rho} - \frac{\delta T_{\mathrm{KS}}[\rho]}{\delta\rho} + v(\mathbf{r}) + \text{constant} \end{aligned} \tag{77}$$

If this potential is inserted in equation (76), we see that equation (71) is automatically satisfied.

We can express F_{LL} as

$$F_{\mathrm{LL}}[\rho] = T_{\mathrm{KS}}[\rho] + E_{\mathrm{Coul}}[\rho] + E_{\mathrm{xc}}[\rho] \tag{78}$$

where the second term on the r.h.s. represents the Coulomb (Hartree) interaction energy and the last term the exchange-correlation energy, including also the (hopefully small) difference between the T_{KS} and the kinetic-energy part of the F_{LL} functional. This leads to the Kohn–Sham potential

$$\boxed{v_{\mathrm{ks}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta E_{\mathrm{Coul}}[\rho]}{\delta\rho} + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho}} \tag{79}$$

leaving out the undetermined constant term.

With the potential (79) the Kohn–Sham model (72) yields the same ground-state density as the original problem, and inserting this density into the HK functional (10) leads, in principle, to the ground-state energy. This is the basic *Kohn–Sham procedure*.

Above we have assumed that the minimization is carried out within the domain of normalized of densities. Alternatively, we can perform the minimization, using the Euler–Lagrange procedure. Then we use the extension of the functionals valid also outside the normalization domain and enforce the normalization constraint by a Lagrange multiplier.[5] For the Levy–Lieb energy functional (70) this leads to

$$\delta\left\{E_{\mathrm{LL}}[\rho] - \mu\int \mathrm{d}\mathbf{r}\,\rho(\mathbf{r})\right\} = 0 \tag{80}$$

and to the Euler equation

$$\frac{\delta F_{\mathrm{LL}}[\rho]}{\delta\rho} + v(\mathbf{r}) = \mu \tag{81}$$

---

[5] As demonstrated in Section 2, the extension of the functionals into the unnormalized domain is nontrivial.

and, similarly, minimization of the KS energy functional to

$$\frac{\delta T_{\mathrm{KS}}[\rho]}{\delta\rho} + v_{\mathrm{KS}}(\mathbf{r}) = \mu' \tag{82}$$

This yields

$$v_{\mathrm{KS}}(\mathbf{r}) = \frac{\delta F_{\mathrm{LL}}[\rho]}{\delta\rho} - \frac{\delta T_{\mathrm{KS}}[\rho]}{\delta\rho} + v(\mathbf{r}) + \text{constant} \tag{83}$$

which is identical to the equation (77).

Instead of basing the treatment on the Levy–Lieb functional (38), the corresponding result can be obtained by using the Lieb functional (64).

6. CONCLUSIONS

We have shown that the Lieb functional (69) is *Gâteaux* differentiable at all E-v-representable densities, which is consistent with the result of Englisch and Englisch [3,4], who demonstrated the differentiability by using the convexity of the functional. The same procedure is used by van Leeuwen [11]. This procedure cannot be used for the Levy–Lieb functional, $F_{\mathrm{LL}}[\rho]$, which is not manifestly convex. According to Englisch and Englisch, the differentiability of this functional is an open question.

The procedure we have applied does not depend on the (global) convexity of the functional, and we have been able to demonstrate the Gâteaux differentiability of the Levy–Lieb functional at all PS-v-representable densities, where this functional is locally convex. It seems plausible that both these functionals are also *Fréchet* differentiable at the same densities, although we have not been able to find a rigorous proof.

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APPENDIX A

A. BASIC TOPOLOGICAL CONCEPTS

In this Appendix we shall define some notations and basic topological concepts, which are needed in treating density functionals in a formal way. (We also refer to the article by van Leeuwen in this volume [11], where some of these concepts are discussed in more detail.)

A.1. Notations

$X, Y, \ldots$ are sets with elements $x, y, \ldots$
$x \in X$ means that x is an element in the set X.
N is the set of nonnegative integers. **R** is the set of real numbers. **C** is the set of complex numbers.
$\mathbf{R}^n$ is the set of real n-dimensional vectors.
$\mathbf{C}^n$ is the set of complex n-dimensional vectors.
$A \subset X$ means that A is a subset of X.
$A \cup B$ is the *union* of A and B. $A \cap B$ is the *intersection* of A and B.
$A = \{x \in X : P\}$ means that A is the set of all elements x in X that satisfy the condition P.
$f : X \longrightarrow Y$ represents a *function* or *operator*, which means that f maps *uniquely* the elements of X onto elements of Y.
A *functional* is a unique mapping $f : X \longrightarrow \mathbf{R}(\mathbf{C})$ of a function space on the space of real (complex) numbers.
The set of arguments $x \in A$ for which the function $f : A \longrightarrow B$ is defined is the *domain*, and the set of results $y \in B$ which can be produced is the *range*.
(a, b) is the *open interval* $\{x \in \mathbf{R} : a < x < b\}$. $[a, b]$ is the *closed interval* $\{x \in \mathbf{R} : a \leq x \leq b\}$.
sup represents the *supremum*, the least upper bound of a set
inf represents the *infimum*, the largest lower bound of a set.

A.2. Vector spaces

A real (complex) *vector space* or function space X is an infinite set of elements, x, referred to as *points* or *vectors*, which is *closed* under addition, $x + y = z \in X$, and under multiplication by a real (complex) number c, $cx = y \in X$. The continuous functions $f(x)$ on the interval $x \in [a, b]$ form a vector space, also with some boundary conditions, like $f(a) = f(b) = 0$.

A subset of X is a *subspace* of X if it fulfills the criteria for a vector space.

A *norm* of a vector space X is a function $p : X \longrightarrow [0, \infty]$ with the properties (1) $p(\lambda x) = |\lambda| p(x)$, (2) $p(x + y) \leq p(x) + p(y)$ for all real $\lambda (\lambda \in \mathbf{R})$ and all $x, y \in X$, and (3) that $p(x) = 0$ always implies $x = 0$. The norm is written $p(x) = \|x\|$. We then have $\|\lambda x\| = |\lambda| \|x\|$ and $\|x + y\| \leq \|x\| + \|y\|$ and $\|x\| = 0 \Rightarrow x = 0$. If the last condition is not fulfilled, it is a *seminorm*.

A vector space with a norm for all its elements is a *normed space*, denoted $(X, \|\cdot\|)$. The continuous functions, $f(x)$, on the interval $[a, b]$ form a normed space by defining a norm, for instance, $\|f\| = [\int_a^b \mathrm{d}t |f(t)|^2]^{1/2}$. By means of the

Cauchy–Schwartz inequality, it can be shown that this satisfies the criteria for a norm ([16], p. 93).

If f is a function $f : A \longrightarrow Y$ and $A \subset X$, then f is defined in the *neighborhood* of $x_0 \in X$, if there is an $\epsilon > 0$ such that the entire sphere $\{x \in X : \|x - x_0\| < \epsilon$ belongs to A ([16], p. 309).

A function/operator $f : X \longrightarrow Y$ is *bounded*, if there exists a number C such that

$$\sup_{0 \neq x \in X} \left[\frac{\|fx\|}{\|x\|} \right] = C < \infty$$

Then $C = \|f\|$ is the *norm* of f. Thus, $\|fx\| \leq \|f\| \, \|x\|$.

A function f is *continuous* at the point $x_0 \in X$, if for every $\delta > 0$ there exists an $\epsilon > 0$ such that for every member of the zset $x : \|x - x_0\| < \epsilon$ we have $\|fx - fx_0\| \leq \delta$ ([16], p. 139). This can also be expressed so that f is continuous at the point x_0, if and only if $fx \longrightarrow fx_0$ whenever $x_n \longrightarrow x_0$, $\{x_n\}$ being a sequence in X, meaning that fx_n converges to fx_0, if x converges to x_0 ([18], p. 70).

A linear function/operator is continuous if and only if it is bounded ([16], p. 197, 213 and [14], p. 22).

A functional $f : X \longrightarrow \mathbf{R}$ is *convex* if

$$f(tx + (t-1)y) \leq tf(x) + (t-1)f(y)$$

for all $x, y \in X$ and $t \in (0, 1)$.

A subset $A \subset X$ is *open*, if for every $x \in A$ there exists an $\epsilon > 0$ such that the entire ball $B_r(x) = \{y \in X| \, \|y - x\| < \epsilon\}$ belongs to A, i.e., $B_r(x) \subset A$ ([13], p. 363; [16], p. 98; [18], p. 57).

A *sequence* $\{x_n\}$, where n is an integer ($n \in \mathbf{N}$), is an infinite numbered list of elements in a set or a space. A *subsequence* is a sequence, which is a part of a sequence.

A sequence $\{x_n \in A\}$ is (strongly) *convergent* towards $x \in A$, if and only if for every $\epsilon > 0$ there exists an N such that $\|x_n - x\| < \epsilon$ for all $n > N$ ([16], p. 95, 348).

A sequence is called a *Cauchy sequence* if and only if for every $\epsilon > 0$ there exists an N such that $\|x_n - x_m\| < \epsilon$ for all $m, n > N$. If a sequence $\{x_n\}$ is convergent, then it follows that for $n, m > N$

$$\|x_m - x_n\| = \|(x_n - x) + (x - x_m)\| \leq \|x_n - x\| + \|x_m - x\| < 2\epsilon$$

which means that a convergent sequence is always a Cauchy sequence. The opposite is not necessarily true, since the point of convergence need not be an element of X ([19], p. 44).

A normed space in which every Cauchy sequence converges (to a point in the space) is said to be complete and termed a Banach space.

A subset A of a normed space is termed *compact*, if every infinite sequence of elements in A has a subsequence, which converges to an element in A. The closed interval $[0, 1]$ is an example of a compact set, while the open interval $(0, 1)$

is noncompact, since the sequence 1, 1/2, 1/3... and all of its subsequences converge to 0, which lies outside the set ([18], p. 149). This sequence satisfies the Cauchy convergence criteria but not the (strong) convergence criteria.

L^p represents the Banach space with the norm $\|f(x)\| = \left[\int dx|f(x)|^p\right]^{1/p} < \infty$ [13].

A *dual space* or *adjoint space* of a vector space X, denoted X^*, is the space of all functions on X.

An *inner or scalar product* in a vector space X is a function $\langle\cdot,\cdot\rangle : X \times X \rightarrow \mathbf{R}$ with the properties (1)

$$\langle x, \lambda_1 y_1 + \lambda_2 y_2\rangle = \lambda_1\langle x, y_1\rangle + \lambda_2\langle x, y_2\rangle, \qquad \langle x, y\rangle = \langle y, x\rangle$$

for all $x, y, y_1, y_2 \in X$ and all $\lambda_j \in \mathbf{R}$, and (2) $\langle x, x\rangle = 0$ only if $x = 0$. A Banach space with the norm $x \rightarrow \|x\| = +\sqrt{\langle x, x\rangle}$ is called a *Hilbert space* ([13], p. 364).

A *Sobolev space* $H^{(m)}(\mathbf{R}^{3N})$ is the space of all functions which together with their partial derivatives up to order m are square integrable in the space $\mathbf{R}^{3N}$, i.e., belong to the space L^2 ([14], p. 97).

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Electronic Structure and Chemical Reactivity: Density Functional and Information-Theoretic Perspectives

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Abstract

A general theme of this survey is the electronic density as a source and carrier of the information about molecular structure and reactivity. First, the classical rules of the electronic structure and chemical reactivity are reexamined, stressing the continuity of ideas in chemistry and exposing the interrelations between their original, mostly intuitive basis, and more rigorous foundations within the Density Functional Theory (DFT). The conceptual advantages of the DFT approach are stressed and a distinction is made between changes in the ground-state density ('horizontal' displacements) and in a division of the fixed molecular density ('vertical' displacements). The molecular charge sensitivities for the *global equilibrium* (of the mutually open subsystems) and the *constrained equilibrium* (of the mutually closed subsystems) are summarized and expressed in terms of the principal second derivatives of the system energy. The DFT treatment of a wide variety of molecular responses, to be eventually used as reactivity indices, is briefly surveyed. A wealth of reactivity concepts originating from the DFT rooted charge sensitivity analysis is reviewed, including both the electronic and external potential related quantities. This overview also covers general criteria for the equilibrium distribution of electrons in molecular systems and their fragments, explicit relations between alternative sets of the conjugate state-parameters, reflecting the transformations between displacements (*perturbations*) of the controlled state variables into the equilibrium linear *responses* of their respective energy conjugates, and the DFT characterization of the embedded molecular fragments, e.g., atoms-in-molecules, reactants, etc. Recent developments in a 'thermodynamic'-like approach to molecules and their constituent fragments are then summarized, with the *entropic* representation description provided by the information theory, and the elements of the 'communication' system approach to the chemical bond multiplicities. In particular, the Hirshfeld partitioning of molecular one-electron densities (probabilities) is summarized and its minimum entropy deficiency basis is stressed. The same entropic principle can be used to derive the 'stockholder' rule of dividing the joint many-electron probabilities and the local softness (Fukui function) characteristics of the electronic gas in the molecular/reactive systems and their constituent fragments. For example, the proportionality relations between the charge responses of subsystems in the molecular/reactive system and their 'promolecular' reference, respectively, directly follow from the relevant minimum entropy deficiency principles formulated in terms of the local softness or Fukui function descriptors of molecular fragments.

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The charge sensitivities of the Hirshfeld fragments are examined and the surprisal analysis of molecular densities is advocated as an attractive interpretative tool, supplementary to the familiar density difference diagrams. The local equalization rules of the subsystem information-distance densities at the corresponding global value, which are satisfied by the Hirshfeld molecular fragments, are then emphasized. These local measures of the information distance with respect to the separated subsystems of the relevant promolecular reference are semi-quantitatively related to the molecular density difference function. The entropy representation 'forces' driving the charge transfer (CT) between reactants in the donor–acceptor systems are defined. These CT *affinities* combine the familiar Fukui functions of the subsystems with the information-distance densities, i.e., the entropy representation 'intensive' conjugates of the subsystem electron densities ('extensive' local state variables), and exactly vanish for the 'stockholder' densities of reactants.

Contents

1. INTRODUCTION

The prediction of chemical reactivity presents a constant challenge to the chemist, who desires to define optimum conditions for performing specific reactions. The basic aim of the *theories* of reactivity is to find an *explanation* of the experimentally or computationally determined course of a chemical reaction. Such theories have to provide means of systematization, recognition of regularities, and rationalization of the myriads of established facts, thereby disclosing the fundamental rules governing chemical reactivity. The most general of them are formulated in terms of the appropriate *variational principles* or the most favorable *matching rules* for the crucial physical properties of reactants (global or regional) uncovering a deeper level of causality in a variety of reactivity phenomena. Investigations into the factors responsible for the chemical behavior of molecules cover both the thermodynamic/statistical and quantum–mechanical laws of a chemical change. For example, the concept of activation energy in a bimolecular reaction is statistical in character, but the actual value of this critical energy of reactants, required for the reactive outcome of their collision, cannot be understood without the quantum–mechanical description of changes in the electronic structure of reacting species.

The ultimate goal of theoretical chemistry is to predict and understand the electronic structure of chemical compounds and their reactions, using the concepts and techniques of both the molecular static and dynamical approaches. The basic objective of the dynamical approach is to calculate the rates of chemical reactions from first principles. Given a specific interaction potential for the nuclear motion in a given system of reactants, one should in principle be able to obtain the probabilities, cross sections, and rate constants for fundamental elementary reaction processes by solving the quantum–mechanical equation of motion for the system. This dynamical goal has so far been realized only for a very few, simple reactions involving three or four atoms, due to the computationally immense task in the complete determination of the electronically adiabatic Born–Oppenheimer (BO) potential energy surface (PES) and in solving the Schrödinger equation for the nuclear motion. Therefore, much of the understanding of chemical reaction dynamics at a molecular level has come about by using a limited information about the multidimensional PES, e.g., model PES reproducing the network of selected *ab initio* points, approximate dynamical methods, e.g., the classical dynamics or various statistical assumptions, as in the *transition-state theory*, where only the information about geometries and frequencies at the transition-state complex is needed to convert this limited information about the reactant interaction into the measurable rate quantities.

In this review, we shall omit completely this very active research area, where the experimental and theoretical techniques for probing reactive systems are becoming more refined, mutually stimulating our deeper understanding of the detailed *state-to-state dynamics* of elementary reactive collisions. We shall also leave aside all the dynamical aspects of reactions in solutions, such as the influence of the diffusion processes, frictional effects, and dielectric relaxation. Instead, we shall focus on novel *static principles* governing the preferred course of a chemical reaction, and models leading to predictions of relative rates of admissible reactions, which have been established within the Density Functional Theory (DFT) of Kohn, Hohenberg, and Sham ([1,2]; see also Ref. [3]), and related physical models, e.g., the charge sensitivity analysis (CSA) of both molecular and reactive systems [4–13].

The present survey will examine selected elements of a conceptual basis of the modern theory of electronic structure and chemical reactivity, originating from the DFT and the *Information Theory* [14–19]. It will be argued that these two theoretic approaches allow one to tackle more completely the main goals of a *chemical* theory of the electronic structure of molecules and their fragments, and to predict and/or rationalize behavior of reactants in different chemical environments. It has been recently shown [20–30] that the information-theoretic development is capable of describing the results of rigorous calculations in terms of qualitative and semi-quantitative models, which are close to chemical thinking and intuition, which uses the concept of the infinite, overlapping atoms-in-molecules (AIM), embedded in the intra- and inter-molecular potentials, which resemble the most their free (separated) atom analogs. It appears that molecules have a good 'memory' about the constituent separated atoms. Indeed, to a large extent they resemble free atoms which took part in their formation. In other words, the chemical (bonded) atoms retain much of the free atom individuality.

We shall also briefly elaborate on how to characterize the equilibrium states of electrons in molecular and reactive systems subject to different constraints (fixed state variables), and how to determine changes following displacements of the relevant state parameters, modifying the intra-molecular or external environments. An overview of the principal charge sensitivities, defining the alternative second-order Taylor expansions of the system electronic energy and its relevant Legendre transforms, will also be given. It demonstrates how naturally known aspects of a chemical behavior appear in these DFT rooted expansions. The main objective of this CSA development is to emphasize that the density-functional concepts are especially suitable for chemistry. In particular, the advantages of DFT approach when dealing with reactive systems will be demonstrated within the subsystem resolved description. The recent successful applications of the CSA include the classical problems of explicit transformations between molecular perturbations and responses and the coupling between electronic and geometrical structure parameters [4,5,7,8,12,31,32], as well as the charge sensitivities for open and closed molecular systems [7,9,12] of demonstrated applicability in diagnosing trends of chemical reactivity.

It has recently been demonstrated [20,26,33] that the information theory can be successfully used to tackle the definition of AIM, at different stages of their reconstruction in a molecular environment, exhibiting the least *information distance* (entropy deficiency, missing information) relative to the corresponding free atoms of the periodic table of elements, which determine the so called 'promolecule' of the familiar density difference diagrams. The optimum information-theoretic AIM were shown to be identical with the 'stockholder' *atoms* [34]. Such infinite (overlapping) atoms immersed in the chemical environment of the molecule are natural constituents and basic building units of molecules. This entropic definition complements the rigorously defined concept of the 'zero-flux' (non-overlapping) topological AIM of Bader [35], defined by the appropriate partitioning of the molecular density in the *physical* space. The information-theoretic molecular fragments have been shown to be independent of the specific measure of the Shannon-entropy related information distance, e.g., Kullback–Leibler *directed divergence* or Kullback's *divergence*, and they exhibit attractive, 'thermodynamic' properties [22–24,33]. This development also includes the entropic measures of the bond-orders [27,28], the surprisal and entropy displacement analyses of molecular electron densities [29,30], entropic 'forces' driving the charge redistribution in subsystems [30], the analysis of the information principles in the Lodge Theory, including a proposition of the 'stockholder' loges [25], and related entropic principles in a general theory of electronic structure [26], a thermodynamic-like theory of the non-equilibrium processes and density fluctuations in molecular subsystems [23], and a use of the minimum entropy deficiency principle in deriving relations between charge responses [softnesses and Fukui functions (FF)] of the Hirshfeld (H) molecular subsystems and the relevant separated molecular fragments determining the promolecular reference, respectively [30].

It is the main purpose of this review to summarize all these novel developments in the combined DFT-Information-Theoretic approach to molecular and reactive systems. We shall begin, however, with a short survey of the key ideas in the theory of chemical reactivity, emphasizing a need for the truly two-reactant description. The conceptual advantages of the DFT and information theory in making a connection to the classical ideas and concepts of chemistry are elucidated throughout.

2. UNDERSTANDING CHEMICAL REACTIVITY

A use of the concept of *conservation of orbital symmetry* in organic chemistry [36] has proved to be a major advance in the theory of chemical reactivity. It has succeeded in bringing together and rationalizing diverse areas of the subject. It has also provided a basis for a unified mechanistic approach to the cycloadditions and molecular rearrangements. Nowadays the criteria of *orbital symmetry conservation* and *correlation diagrams* are the standard part of the organic mechanistic vocabulary [37–42]. The *Woodward–Hoffmann rules* have correlated a great number of existing chemical facts and stimulated further widespread experimentation. Similar ways of comprehending the geometry and reactivity of inorganic molecules have also been proposed [43] thus demonstrating that the frontier orbital ideas and simple concepts of symmetry and bonding are applicable to the understanding of all molecules. General *symmetry rules of chemical reactions* have also been formulated by considering the symmetry restrictions on the excited-state contributions to the perturbed ground-state wave functions of reactants, which describe the polarization and charge transfer (CT) due to the perturbation created by a given normal-mode displacement of the nuclei [44,45].

The accurate calculation of the energy profiles along the minimum-energy path on molecular PES by the established numerical methods cannot be itself regarded as a *theory*, but rather as a computer *experiment*. In fact, most of the activity of theoretical chemists has been directed not towards an understanding of chemistry, if that term is to imply the *rules* governing reactions, but towards an understanding of physical properties of static molecular systems. In the past, the use of simplified models or principles, which permit a useful chemical information, e.g., relative rates of admissible reaction channels, to be derived without such an elaborate calculation, has provided a valuable insight into our understanding of molecular reactivity preferences, and a way to analyze molecules and calculations on molecules in theoretically consistent framework that allows a chemist to understand the results of calculations in terms of the *language* of chemistry.

The molecular orbital (MO) theory has enabled us to understand a wide range of physical properties of molecules, their relative reactivity trends, and in particular, the preferred pathways taken by chemical reactions. For chemical community it therefore provides a natural framework to understand in a qualitative or semi-quantitative sense what happens to the electronic structure, when a molecule distorts in a changed environment, e.g., when it undergoes a chemical reaction. Such a theory also warrants predictions of changes in the molecular geometry accompanying a given, real or hypothetical change in the electronic structure. These theories are useful to the chemical community, since the experimentalist must have an understanding of *why* molecules react the way they do, as well as of what determines their electronic structure and how this influences reactivity. In other words, they provide a rationale for understanding the development of reactions along specific routes, without the assistance of rather complex computer routines. Such simple models are based on concepts such as symmetry, overlap, and electronegativity; they deliberately de-emphasize the computational aspect, aiming at a more qualitative understanding of electronic structure and chemical reactions.

The MO theory has been quite successful in interpreting and predicting the orientation and stereoselection in a large variety of chemical reactions [46–51]. However, the characterization of a reaction as *allowed* or *forbidden* provides no quantitative information. In many cases, there are several allowed reaction paths, and it becomes necessary to distinguish between them in order to determine which one is the most probable and, ideally, to estimate yield ratios and relative reaction rates. A number of perturbative methods have emerged for this very purpose. Early work on organic reactivity concentrated on the conjugated π-electron systems, and as a result of this analysis various reactivity indices were proposed, e.g., the π-electron density, free valence or the self-polarizability of atoms in a conjugated system, with the high value of either index assumed to imply high reactivity. The localization energy method assumes a model for the transition-state, the Wheland intermediate, in which both the attacking reagent and the atom to be substituted are bonded to the roughly tetrahedral carbon, which is thus isolated from the remainder of the original π-electron system. The associated change in the π-electron energy, the so-called localization energy, is then taken as the reactivity index, on the basis of the assumption that other contributions to the activation energy are likely to be approximately constant for a given reagent. Dewar has developed a general perturbational molecular orbital (PMO) theory of organic chemistry and shown, how it can be used to obtain an approximate value for the localization energy, called the reactivity number.

Of similar character is the frontier electron density index of Fukui and co-workers [5,47,48,52] and the related superdelocalizability index of reactivity. It has been observed, that the electrophilic aromatic substitutions take place predominantly at the carbon position, where the partial electron density in the highest occupied molecular orbital (HOMO) exhibits the largest value; similarly, the positions of the largest value of the electron density in the lowest unoccupied molecular orbital (LUMO) were usually confirmed as the preferred locations for the nucleophilic aromatic substitution. These two particular MOs were termed the frontier orbitals. Taking into account the hyperconjugation in the transition-state of an aromatic substitution, between the aromatic π-electron system of the attacked molecule and the pseudo π-orbital of the subsystem consisting of the reagent and the hydrogen to be replaced, another reactivity index called the superdelocalizability was derived.

The PMO methods were also widely invoked after the formulation of Woodward–Hoffmann rules, to treat chemical reactions more comprehensively [49]. In these approaches the reactivity trends are not linked to a single term in the corresponding Taylor expansion of the interaction energy, but rather to the combined sum of contributions due to the steric interactions, electrostatic, polarization and electron-transfer effects, solvation energy, etc. All these more elaborate treatments within the semi-empirical MO approaches take account of the charge distribution and the overlap between the reactant orbitals. In the familiar Klopman–Salem energy expression [53–57] a domination of the electrostatic interaction between the substrates marks the ‘charge control’ of the reaction, when reactants are both highly charged and relatively difficult to polarize. This is characteristic of the ‘hard’ species in the Pearson’s terminology [58]. When the CT stabilization, due to the mixing of the filled orbitals on one molecule with the empty orbitals on the other molecule, dominates the interaction energy, when both reactants are uncharged and highly polarizable (‘soft’), the reaction is ‘frontier orbital controlled’. Klopman was able to rationalize the Pearson’s *Hard and Soft Acids and Basis* (HSAB) principle [58], that hard acids form stable complexes with hard bases, and soft acids with soft bases, whereas the complexes of hard acids with soft bases (or of soft acids with hard bases) remain relatively less stable. He was also able to take into account the nature of the attacking reagent in the electrophilic or nucleophilic aromatic substitution, and to show that the ratios of yields of the *ortho*, *meta*, and *para* products of the substitution of the benzene derivatives depend on the competition between the charge and frontier orbital controls.

This perturbation theory of chemical reactivity is based upon an early stage of the reactant mutual approach, when the molecules are still distinct though close enough for the MO description of the combined reactive system to be valid, say separated by a distance of the order of 5–10 a.u. The implicit assumption is that the reaction profiles for the compared reaction paths are of similar shape, so that the trend of the predicted energy differences at an early point on the reaction coordinate is expected to reflect the difference in the activation energy.

The frontier orbital approximation recognizes the interaction between the HOMO and LUMO on both reactants as the crucial effect controlling the course of a chemical reaction. In many cases a further approximation is made by taking a single HOMO–LUMO pair of both reactants, for which the orbital energy separation is the smallest, e.g., the *donor* HOMO and the *acceptor* LUMO, in the acid–base interactions. The argument against such a drastic approximation is that it neglects many contributions to the Klopman–Salem equation from other MOs, which may outweigh the frontier orbital contribution. Further uncertainties arise in the unique determination of the orbital energies. To remedy this shortcoming the orbital energies have been substituted by the ionization potentials and electron affinities, by virtue of the familiar Koopmans' theorem. Nevertheless, the frontier orbital theory undoubtedly works, though it is not as universally successful as the Woodward–Hoffmann rules.

In order to further justify the frontier electron model, Fukui has formulated the three supplementary principles [47]: of the 'positional parallelism between the charge-transfer (CT) and bond-interchange', of 'narrowing the frontier orbital separation', and of 'growing the frontier electron density' along the reaction path. Although these principles have been subject to some criticism by other theoreticians [39], they correctly recognize the need to include the relaxation effects, of both the electronic and geometrical structures of reactants, with the progress along the reaction path. Indeed, a chemical reaction always involves a subtle coupling between the equilibrium electron (chemical bond) distribution on one side and the nuclear configuration on the other side, with the latter determining the external potential for the fast movements of electrons within the familiar BO approximation.

The changes in the distribution of electrons create extra forces acting on the nuclei. This Hellmann–Feynman, 'electron-preceding' perspective [59–61] is indeed very close to the intuitive chemical thinking, in which manipulations of the electronic structure are considered as preceding and ultimately accelerating the subsequent changes in the molecular geometry. The BO, 'electron-following' perspective provides the complementary description, in which displacements in the nuclear positions precede the concomitant electronic relaxation [5,7,8,32]. Clearly, the complete understanding of a molecular mechanism of a chemical reaction must ultimately involve reactivity criteria relating to both these outlooks. In the former, the displacements in the reactant electron densities or the associated electron populations (or net charges) of bonded AIM are considered as the independent degrees-of-freedom of the reactive system under consideration; in the latter, the displacements in the nuclear coordinates, or the associated changes in the reactant external potentials, are viewed as the independent coordinates determining the course of a chemical change.

The geometrical relaxations, in response to displacements in the electronic structure of the acid–base (acceptor–donor) reactive system, are also the subject of the intuitive, structural bond-variation rules of Gutmann [62]. They also follow the above Hellmann–Feynman (electron-preceding) perspective of Nakatsuji, who obtained interesting interrelations between changes in the electron density and nuclear configuration in a variety of contexts associated with chemical reactions. He has shown, for example, that the centroid of a given change in the electron density tends to lag the change in the nuclear coordinates in a movement away from a stable configuration, and it tends to lead the geometrical change in a movement away from an unstable geometrical structure towards the equilibrium one.

The interaction between the frontier orbitals is the strongest, when the mutual orientation of both reactants at a given inter-molecular separation gives the maximum overlap. Thus, the frontier electron theory identifies such a maximum overlap direction as the preferred one. Therefore, the theory represents the overlap *matching* rule of chemical reactivity, valid for the frontier-controlled reactions in the Klopman classification. The corresponding rule for the charge-controlled reactions follows from the corresponding matching of the molecular electrostatic potentials (EP) of both reactants, with the largest stabilization resulting when the electron-stabilizing regions of the acceptor (acidic) reactant are overlapping the most with the proton-stabilizing regions of the donor (basic) reactant [63,64]. The EP analysis has now become firmly established as an effective guide to molecular interactions. It is being applied to a variety of important chemical and biological systems, covering the preferred sites for the nucleophilic and electrophilic attacks, solvent effects, catalysis, as well as the molecular cluster and crystal behavior. The EP is a unique functional of the molecular electron density and it exhibits interesting topological characteristics reflecting the opposing contributions from the nuclei and electrons.

Investigation of the local features of the electron density distribution and the associated Laplace field [35] leads to the unique topological definition and description of AIM, chemical bonds, molecular structure, and structural changes. It can also be used to gain a valuable insight into the bonding mechanism, to identify the sites that are prone to the electrophilic or nucleophilic attacks, and the bonds that can be easily broken in a molecule [35,65]. The maps of local features of the laplasjan of the molecular density can be also used to predict the best matching of the electron-depleted region of the acidic reactant with the electron-concentrated region of the basic reactant, which should roughly determine their preferred mutual orientation in the course of a chemical reaction.

3. COMPUTATIONAL AND CONCEPTUAL QUANTUM CHEMISTRY

The rates and mechanisms of chemical reactions can be predicted, in principle, by the standard methods of statistical thermodynamics, in terms of the partition functions of reactants and the transition-state complex. However, the range of applicability of this transition-state (absolute rate) theory is severely limited by the fact, that an evaluation of the vibrational partition function for the transition state requires a detailed consideration of the whole PES for the reaction. Thus, a calculation of the absolute rate constants is possible only for relatively simple systems. This indicates a need for more approximate, empirical methods of treating chemical reactions and formulating the reactivity theory, which would allow chemists to go further in their prediction of properties and chemical interactions of new compounds and reactions of ever increasing complexity. Because of the extreme electronic complexity of molecules and reactions, e.g., those of interest to organic chemists, crude assumptions have to be made in most theoretical treatments and empirical factors are introduced into theoretical expressions. Therefore, one must realize that from the purist point of view such ‘theories’ should be more appropriately classified as theoretical *models* of reactivity. An example of such a heuristic approach is the celebrated Hammond postulate of a relative similarity of the transition-state complex to reactants (products) in the exothermic (endothermic) reactions [66,67].

The last decades have witnessed a dramatic growth of quantum chemistry, both conceptual and computational, with the latter providing very accurate *ab initio* results of admirable accuracy, obtained by using both the wave-function and DFT methods, and the former generating means for understanding. Moreover, the modern quantitative results are often synergetically combined with laboratory techniques, verifying experimental data and guiding the researchers in their planning of future experiments. However, the wavefunctions resulting from the modern high-level methods of computational quantum chemistry are so immensely complex that they cannot be immediately understood in simple and physically meaningful terms. The categorization and interpretation objectives in chemistry call for the well founded general principles and conceptual models, which are both transparent, intuitively appealing and useful for both qualitative and semi-quantitative applications to large systems of interests in chemistry.

On one hand, such general conceptual tools *a posteriori* reduce the overwhelming level of the information embodied in the *ab initio* wavefunctions to a more manageable, qualitative level by extracting common roots of seemingly unrelated data. On the other hand, they provide a valuable understanding of the molecular structure and behavior, thus enabling a better prediction of reactivities of chemical compounds, a planning and a more precise characterization of experiments. Adequate theoretical models offer a rationale for *trends* within families of related compounds and they bridge a gap between the rigorous quantum mechanics and empirical concepts of the phenomenological chemistry.

The qualitative and quantitative theories/models of the electronic structure and chemical reactivity are thus inevitable and necessary ingredients of the scientific method of chemistry; only the presence of both marks its harmonious development. The qualitative concepts determine the scientific vocabulary of interpretative chemistry, while the approximate model relations allow for a semi-quantitative prediction of trends implied by changing structural and experimental conditions.

Chemistry is concerned with the properties and reactions of an enormous number of different compounds, which for the purpose of expediency are classified into similarity groups, e.g., those with the same functional group(s), so that the physical and chemical properties of a particular compound may be inferred from the behavior of any other member. A number of qualitative and quantitative relations have been formulated to relate properties of members belonging to the same and different similarity groups. Representative examples in the area of chemical reactivity are provided by the familiar directing influences of the *electron-withdrawing* and *electron-donating* substituents in benzene systems, and the related experimental correlation of Hammett [68–70]. The latter and other 'free-energy' relationships [71,72] have been extremely valuable to chemists in helping them to predict the reactivity of chemical compounds and to understand a subtle interrelationship between *reactivity* and *selectivity* in chemical reactions.

As we have already mentioned, the first task confronting a chemist is to identify the reactive sites as a function of the molecular structure, and to determine their relative reactivity trends. Owing to the complexity of organic molecules, a particular reagent may contain several alternative *nucleophilic*, *electrophilic*, or *radical* centers, and hence the competition for these reaction sites is a very important general problem. To meet this challenge one has to understand how the molecular structure affects the reactivity of various active centers of the molecule. The relative reactivity of an active site may vary with the nature of the attacking agent (*ambident reactivity*). Ambidency may also be exhibited as a result of changing experimental conditions. Obviously, its explanation must also be included in a satisfactory theory of chemical reactivity. The differentiation between the *thermodynamic* and *kinetic* controls of competing reactions is essential for explaining such processes. Clearly, a description and, ultimately, an understanding of such phenomena call for the truly *two-reactant* theoretical treatment, since only such an approach provides an adequate framework for describing a changing reactivity of one reactant (site) with the changing character of the other reactant (site). When two large species orient themselves relative to one another, at an early stage of a chemical reaction, an even more subtle challenge for the reactivity theory emerges. It is related to the fact, that the very classification of sites as susceptible of undergoing an attack by the electrophilic (electron-deficient, acceptor, acidic) or nucleophilic (electron rich, donor, basic) sites of the other reactant, is only relative. In other words, a molecular site may act as a base towards one (relatively acidic) site of the reaction partner, while it can also act as an acid towards another (relatively basic) site of the other reactant. Moreover, the reaction at one site is not without an influence on the simultaneous reactivity of the other site.

Molecular structure, defined in terms of chemical atoms and bonds which connect them in a molecule, is the central and most fruitful theme in chemistry. The knowledge of the molecular electronic and geometric structural parameters gives important clues for understanding the behavior of molecules in different reactive environments and it is a starting point for the subsequent more detailed, perturbative studies of molecular interactions, in which the separated reactant limit (SRL) defines the convenient reference state at the early stage of the reactant mutual approach. Often the structure of reactants already reveals the expected main features of the preferred minimum energy path (MEP), thus determining gross features of the easiest ascent route from reactants towards the transition-state complex, which determines the activation barrier.

As we have already argued above, a satisfactory reactivity theory has to take into account the subtle coupling between the electronic and geometrical coordinates of the reactive system in question. The so called ‘mapping’ transformations between these two aspects of the molecular structure [4,5,7,8,31, 32,73–75] provide the direct and unifying concepts for both qualitative understanding and semi-quantitative characterization of such couplings. Both the *electron-preceding* and *electron-following* transformations involving local, normal and the *minimum energy* nuclear displacements of the *compliant approach* to nuclear motions [76–79], can be studied in this way, thus decisively extending the range of applications in comparison to the empirical structural rules [62]. The electron-following mapping relations (of the BO perspective) in principle allow one to predict trends in the electron redistribution following a given (hypothetical or real) displacement of the system geometry. The inverse, electron-preceding relations (of the Hellmann–Feynman perspective), closer to an intuitive chemical thinking, are required to solve another typical reactivity problem: how to manipulate the electronic structure parameters, such as the charge distribution in the *fine-grained*, local description or the effective oxidation states (net charges) of AIM in the *coarse-grained*, atomic resolution, in order to achieve a desired change in the system geometry, e.g., breaking of the specific bond(s). Through the mapping relations any shift in the nuclear position space can be ‘translated’ into the conjugate displacement in the electron distribution, and *vice versa*. This feature greatly enhances the diagnostic and interpretative tools of chemistry and provides a quantitative characterization of a coupling between the nuclear and electronic aspects of the molecular structure in chemical processes.

4. TWO-REACTANT APPROACH

When considering a behavior of a single molecule or a family of chemically similar molecules in a given type of a chemical reaction, e.g., during the electrophilic, nucleophilic, or radical attack by a small agent, various *single-reactant* reactivity concepts have proven their utility in predicting the most reactive site [46–48,51]. Such criteria are based upon the underlying notion of an inherent chemical reactivity of a molecule, or a hierarchy of relative reactivities of its parts, for the fixed reaction *stimulus* determined by the perturbation created by the same attacking agent at each of the compared locations. Clearly, this notion implying that the way the molecule reacts is somehow predetermined by its own structure, is approximate one, since it neglects the mutual influence of both reactants. A more subtle, *two-reactant* description of chemical reactivity is required to probe alternative arrangements of two large molecules, e.g., in cyclization reactions, when more than one chemical bond is being formed. To account for the mutual influence of both molecular subsystems of a given bimolecular reactive system the relevant reactivity criteria have to include also the *embedding* energy terms, consisting of the *reaction stimulus* due to a given reactant, at a given, early stage of the mutual approach of reactants, and the *response* quantity of the complementary reactant to this perturbation, determined by the relevant generalized ‘polarizability’ of the perturbed subsystem.

In general, the electronic energy E of a given molecular or reactive system is a function of the global equilibrium state-parameters $\mathbf{a} = (a, b, \ldots)$, referring to the system as a whole, and a functional of the local state-variables $\mathbf{x}(\mathbf{r}) = [x_1(\mathbf{r}), x_2(\mathbf{r}'), \ldots]$. The 1st-order energy change $\Delta^1 E[\mathbf{a}, \mathbf{x}] \equiv \Delta^1 E[\Delta\mathbf{a}, \Delta\mathbf{x}]$, linear in displacements $\Delta\mathbf{a}$ and $\Delta\mathbf{x}$ of these independent *degrees-of-freedom* of the system under consideration, is determined by the *potentials* $\mathbf{E}_\mathbf{a} = \{E_a = \partial E/\partial a\}$ and $\mathbf{E}_\mathbf{x}(\mathbf{r}) = \{E_i(\mathbf{r}) = [\partial E/\partial x_i(\mathbf{r})]_{j \neq i}\}$, i.e., the energy conjugates of the state variables $\{\mathbf{a},\ \mathbf{x}\}$ defined by the relevant partial derivatives calculated for the fixed values of the remaining state parameters. For example, for a pair of a single global and local state parameters $[a, x(\mathbf{r})]$:

$$\Delta^1 E[a, x] = E_a \Delta a + \int E_x(\mathbf{r}) \Delta x(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{1}$$

This equation shows, that the single-reactant indices are the 1st-order criteria. Indeed, for the fixed perturbations $[\Delta a, \Delta x(\mathbf{r}_1)]$ and $[\Delta a, \Delta x(\mathbf{r}_2)]$ due to the same agent attacking the two alternative locations $\mathbf{r}_1$ and $\mathbf{r}_2$ in a molecule, the trends in $\Delta^1 E[a, x(\mathbf{r}_1)]$ and $\Delta^1 E[a, x(\mathbf{r}_2)]$ are reflected by those in $E_x(\mathbf{r}_1)$ and $E_x(\mathbf{r}_2)$, so that the local potential constitute a valid single-reactant reactivity criterion. The embedding energy contributions are of the 2nd-order in such a perturbational approach.

In order to determine the 2nd-order energy $\Delta^2 E[\mathbf{a}, \mathbf{x}]$ the knowledge of the system response quantities (generalized polarizabilities) is needed [3–8,12,80–84]. In what follows the response of the potential E_a or $E_i(\mathbf{r})$, per unit value of the displacement in the stimulus b or $x_j(\mathbf{r}')$, for the fixed values of the remaining state-parameters, will be called the molecular charge sensitivity (CS). Such quantities are defined by the relevant second partial derivatives of the system electronic energy:

$$\text{global}: \quad y(b, a) = \partial E_a/\partial b = \partial^2 E/\partial b\, \partial a = y(a, b) = \partial E_b/\partial a = \partial^2 E/\partial a\, \partial b,$$

$$\begin{aligned} \text{local}: \quad y[a, x_i(\mathbf{r})] &\equiv \partial E_i(\mathbf{r})/\partial a = \partial/\partial a[\partial E/\partial x_i(\mathbf{r})] = y[x_i(\mathbf{r}), a] \\ &\equiv [\partial E_a/\partial x_i(\mathbf{r})]_{j \neq i} = [\partial/\partial x_i(\mathbf{r})(\partial E/\partial a)]_{j \neq i} \end{aligned}$$

$$\begin{aligned} \text{two-point derivatives}: \quad y[x_i(\mathbf{r}), x_j(\mathbf{r}')] &= [\partial E_j(\mathbf{r}')/\partial x_i(\mathbf{r})]_{k \neq i} \\ &\equiv \partial^2 E/\partial x_i(\mathbf{r}) \partial x_j(\mathbf{r}') = y[x_j(\mathbf{r}'), x_i(\mathbf{r})] \\ &= [\partial E_i(\mathbf{r})/\partial x_j(\mathbf{r}')]_{k \neq j} \equiv \partial^2 E/\partial x_j(\mathbf{r}') \partial x_i(\mathbf{r}), \end{aligned} \tag{2}$$

where we have also listed the relevant Maxwell relations (cross differentiation identities).

These ‘normalized’ response quantities determine the corresponding embedding energy contributions, the quadratic functions of the reaction stimuli $\Delta\mathbf{a}$ and $\Delta\mathbf{x}(\mathbf{r})$.

For example, in the case of a single global (a) and local (x) state-variables the 2nd-order energy includes the following terms:

$$\Delta^2 E[a,x] = \tfrac{1}{2}\{[y(a,a)(\Delta a)^2 + 2\Delta a \int y[a,x(\mathbf{r})]\Delta x(\mathbf{r})d\mathbf{r} + \int\int \Delta x(\mathbf{r}')y[x(\mathbf{r}'),x(\mathbf{r})]\Delta x(\mathbf{r})d\mathbf{r}'\,d\mathbf{r}\} \quad (3)$$

Such embedding energy contributions are included in all 2nd-order perturbational approaches to chemical reactivity [3–13,47,51,52,57,73,75,80,83,85–89].

The response contributions to the reactive system energy can be both ‘diagonal’ (intra-reactant), when both stimuli in the relevant second derivative refer to the same subsystem (reactant), or ‘off-diagonal’ (inter-reactant), when the two stimuli in the derivative correspond to different subsystems. For example the ‘diagonal’ terms originating from the two-point CS reflect the influence of an attack on one location in a given reactant on its reactivity at other location, while the ‘off-diagonal’ energies similarly account for the influence of one reactant on the reactivity of the other reactant. In a consistent two-reactant approach, all such contributions have to be included at the same level of approximation. This coupling between the reactive system state-variables indicates that in the *reactant resolution* changes in the system energy, due to the specified (fixed) reaction stimuli, have to be indexed by *vectors* of potentials and *matrices* of charge sensitivities, since no single parameter can fully account for trends in the interaction energy relative to the separated reactant limit. The above energy changes also demonstrate a dependence of the overall BO interaction energy, $\Delta W[a,x] \equiv \Delta V_{\mathrm{nn}} + \Delta E[a,x]$, where ΔV_{nn} denotes the inter-reactant repulsion energy between the reactant nuclei and $\Delta E[a,x] \cong \Delta^1 E[a,x] + \Delta^2 E[a,x]$ approximates a change in the electronic energy, on the current geometry of the reactive system determining the shifted external potential due to the presence of the other reactant. It has to be taken into account also in the approximate treatment using the separated reactant molecular potentials and charge sensitivities to approximate the Taylor expansion of the electronic energy at finite inter-reactant separations.

For a series of similar reactions, e.g., attacks at alternative sites of the same molecule by atomic agents of a similar chemical character, one may assume that at comparable stages of the reactant approach the sum of the 1st-order electronic energy and ΔV_{nn} remains approximately constant for the all compared locations, so that the 2nd-order (embedding) energy determines the preferred reaction path. For comparable values of the reaction stimuli at all such positions the trends in the embedding energy are then reflected by the relevant charge sensitivities themselves [3,80]. Notice, however, that such a simplified treatment cannot be used in a general reactive system involving two large reactants, the size and reactivity of which changes in a series of compared mutual orientations, often leading to different reaction paths. This is because each orientation implies different matching between the site reaction stimuli and the corresponding potentials on one hand, and the site response quantities on the other hand. In such a general case the whole set of molecular potentials and CS has to be combined with the appropriate reaction stimuli to produce the overall interaction energy, to be eventually compared for a series of the probed geometries of the reactive system. This is often crucial for predicting the direction of the energetically preferred approach of reactants at an early stage of the reactant approach, expected to adequately represent the least activation energy course of the reaction also for the close approach geometries.

A remarkable progress in DFT [1–3,90,91] has provided an attractive framework for formulating novel concepts and rules describing behavior of molecular systems in different chemical environments [3–13,82,83,87–89,92–97], besides producing new efficient schemes for the electronic structure computation. In chemistry, and particularly in the reactivity theory, this conceptual development had a distinctly unifying character. For example, some of the originally intuitive, but remarkably successful tools of chemistry, such as the electronegativity [98–103] and hardness [58,81], which have long been part of the chemical vocabulary, have been shown to be fundamental and well defined [104,105].

According to the Hohenberg–Kohn (HK) theorem of DFT [1] and its shape-function reformulation for Coulomb systems [106] the ground-state electron density $\rho(\mathbf{r})$, or the density per electron $\sigma(\mathbf{r}) = \rho(\mathbf{r})/N$ (*shape function*, one-electron probability distribution), carries all the information about the molecular system, uniquely identifying the shape of its external potential and the overall number of electrons and, hence, the coulombic molecular hamiltonian. This exact result has given a new impetus towards using DFT and the Information Theory [14–19, 107–110] in the density-based chemical interpretation of the electronic structure of molecular systems in terms of AIM and bond multiplicities, which connect them in a given molecular or reactive system [13,20–28,30,33,111,112]. In DFT this approach leads to the *information theoretic* 'thermodynamics' of molecular systems and their fragments [23,33], a description in the spirit of the earlier DFT approaches [113–115]. In this review we shall explore various density-based descriptors of electronic structure and chemical reactivity, recently established in the DFT and Information Theory.

5. WAVEFUNCTION AND DENSITY FUNCTIONAL THEORIES

In the BO approximation of the Schrödinger wave mechanics the state function of the N-electron molecular system, $\Psi = \Psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N; \mathbf{X}_1, \mathbf{X}_2, \ldots \mathbf{X}_m) \equiv \Psi(\mathbf{q}; \mathbf{X}) \equiv \Psi[(\mathbf{r}, \boldsymbol{\sigma}); (\mathbf{R}, \boldsymbol{\Sigma})] \equiv \Psi(\mathbf{q})$, determines all of the information that can be known about a molecular system for a given geometry specified by the nuclear positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_m)$. It depends on the spin $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \ldots, \sigma_N)$ and position $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ coordinates of electrons and, parametrically, on the set of nuclear spin ($\mathbf{\Sigma}$) and position ($\mathbf{R}$) coordinates, $\mathbf{X} = (\mathbf{R}, \mathbf{\Sigma})$, with the latter determining the external potential generated by the nuclear charges $\mathbf{Z} = (Z_1, Z_2, \ldots, Z_m)$,

$$v(\mathbf{r}_i) = -\sum_{\alpha} Z_\alpha / \mathbf{r}_{i\alpha}, \qquad r_{i\alpha} = |\mathbf{r}_i - \mathbf{R}_\alpha| \tag{4}$$

acting on ith electron at position $\mathbf{r}_i$; the atomic units are used throughout.

The stationary states of electrons in molecular systems satisfy the time-independent Schrödinger equation:

$$H\Psi = E\Psi \tag{5}$$

where H denotes the molecular electronic hamiltonian:

$$\begin{aligned} H(N, v) &= \sum_i v(\mathbf{r}_i) - \tfrac{1}{2}\sum_i \Delta_i + \sum_{i<j}\sum 1/r_{ij} \equiv H(\mathbf{q}; \mathbf{R}) \\ &= V_{\mathrm{ne}}(N, v) + [T_{\mathrm{e}}(N) + V_{\mathrm{ee}}(N)] \equiv V_{\mathrm{ne}}(N, v) + F(N), \\ r_{ij} &= |\mathbf{r}_i - \mathbf{r}_j| \end{aligned} \tag{6}$$

here T_{e} is the electronic kinetic energy operator, with Δ_i standing for the laplasjan acting on the Cartesian coordinates of the ith electron, V_{ne} is the operator for electron–nucleus attraction energy, V_{ee} stands for the electron repulsion energy operator, and F denotes the universal (v-independent) part of $H(N, v)$. The basic variational principle of the wavefunction quantum mechanics, which yields the electronic Schödinger equation (5) for the 'frozen' external potential $v(\mathbf{r})$, involves the minimization of the system electronic energy, the expectation value of the electronic Hamiltonian,

$$E_v[\Psi] = \int \Psi^* H \Psi \, \mathrm{d}\mathbf{q} \equiv \langle \Psi | H | \Psi \rangle, \tag{7}$$

subject to the wave function normalization constraint $\langle \Psi | \Psi \rangle = 1$. At the stationary value of the electronic energy, for the ground-state $\Psi_0 = \Psi[N, v]$,

$$\delta(E_v[\Psi] - E[N, v]\langle \Psi | \Psi \rangle)_{\Psi[N,v]} = 0, \tag{8}$$

when the expectation value, $E_v[\Psi[N, v]] = \min_{\Psi}\{E_v[\Psi]\}_{\langle \Psi | \Psi \rangle = 1} \equiv E[N, v] \equiv E_0$, reaches the ground-state eigenvalue of equation (5): $H\Psi_{0.} = E_0\Psi_0$. Notice, that in the energy minimum principle of equation (8) the ground-state energy is the Lagrange multiplier associated with the wavefunction normalization constraint.

The stationary-state Schrödinger equation also implies that the *local* energy $E[\mathbf{q}] \equiv \mathrm{H}(\mathbf{q})\Psi(\mathbf{q})/\Psi(\mathbf{q})$, is equalized for the exact eigenfunction of the hamiltonian, throughout the whole (spin-position) configuration space $\mathbf{q}$ of N electrons, at the exact eigenvalue, e.g.,

$$E_0[\mathbf{q}] = H(\mathbf{q})\Psi_0(\mathbf{q})/\Psi_0(\mathbf{q}) = E[N, v] \tag{9}$$

As demonstrated by Hohenberg–Kohn [1], the external potential is uniquely determined, up to an additive constant, by the ground-state electron density:

$$\rho_0(\mathbf{r}) = \langle \Psi_0 | \sum_i \delta(\mathbf{r}_i - \mathbf{r}) | \Psi_0 \rangle. \equiv \rho[\Psi_{0.}; \mathbf{r}] \equiv \rho[N, v] \tag{10}$$

$v(\mathbf{r}) = v[\rho_0; \mathbf{r}]$. Therefore, since $N = \int \rho_0(\mathbf{r})\mathrm{d}\mathbf{r} \equiv N[\rho_0]$ is also uniquely determined by the density, the system Hamiltonian is the unique functional of the ground-state density, $H(N[\rho_0], v[\rho_0]) = H[\rho_0]$, and so are the physical properties of its eigenstates. For example, the ground-state energy is the functional of the electron density:

$$\begin{aligned} E[N, v] &= E_v[\rho_0[N, v]] = \langle \Psi[\rho_0[N, v]] | H(N, v) | \Psi_0[\rho_0[N, v]] \rangle \\ &\equiv \int v(\mathbf{r})\rho_0(\mathbf{r})\mathrm{d}\mathbf{r} + \langle \Psi_0[\rho_0[N, v]] | F(N) | \Psi_0[\rho_0[N, v]] \rangle \\ &\equiv V_{\mathrm{ne}}[\rho_0] + F[\rho_0], \end{aligned} \tag{11}$$

where the universal density functional $F[\rho_0] = T_{\mathrm{e}}[\rho_0] + V_{\mathrm{ee}}[\rho_0] \equiv F[N, v]$ generates the sum of the electronic kinetic and repulsion energies:

$$T_{\mathrm{e}}[\rho_0] = \langle \Psi_0[\rho_0[N, v]] | T_{\mathrm{e}}(N) | \Psi_0[\rho_0[N, v]] \rangle \equiv T_{\mathrm{e}}[N, v], \tag{12}$$

$$V_{\mathrm{ee}}[\rho_0[N, v]] = \langle \Psi_0[\rho_0[N, v]] | V_{\mathrm{ee}}(N) | \Psi_0[\rho_0[N, v]] \rangle \equiv V_{\mathrm{ee}}[N, v]. \tag{13}$$

It follows from the first HK theorem that the non-degenerate ground-state is also uniquely determined by its electron density: $\Psi_0 = \Psi_0[\rho_0]$. Thus, $\rho_0(\mathbf{r})$ represents the alternative, exact specification of the molecular quantum-mechanical ground-state. In other words, there is a unique mapping between Ψ_0 and ρ_0, $\Psi_0 \leftrightarrow \rho_0$, so that both functions carry exactly all the information about the quantum-mechanical state of the N electron system.

The fact that ρ_0 identifies the molecular Hamiltonian should not come as a surprise. Indeed, the nuclear cusps [116] of the electron density in an atom, molecule or solid, in the neighborhood of the atomic nuclei, necessary to avoid divergences in $H\Psi$ of the Schrödinger equation for $\{\mathbf{r} \rightarrow \mathbf{R}_\alpha\}$, i.e., $r_\alpha = |\mathbf{r} - \mathbf{R}_\alpha| \equiv |\mathbf{r}_\alpha| \rightarrow 0$,

$$\partial \rho_{\mathrm{av}}(r_\alpha)/\partial r_\alpha|_0 = -2Z_\alpha \rho_{\mathrm{av}}(0), \tag{14}$$

where the derivative of $\rho_{\mathrm{av}}(r_\alpha)$, the spherical average of $\rho(\mathbf{r}_\alpha) \equiv \rho(r_\alpha, \theta_\alpha, \varphi_\alpha)$,

$$\rho_{\mathrm{av}}(r_\alpha) \equiv (1/4\pi) \int\int \rho(r_\alpha, \theta_\alpha, \varphi_\alpha) \sin\theta_\alpha \,\mathrm{d}\theta_\alpha \,\mathrm{d}\varphi_\alpha, \tag{15}$$

is calculated for $r_\alpha = 0$, identify both the nuclear positions $\mathbf{R}$ and charges $\mathbf{Z}$, thus providing sufficient information to generate the external potential of equation (4).

The second HK theorem [1] represents the DFT variational principle:

$$\delta\{E_v[\rho] - \mu[N, v]N[\rho]\}_{\rho[N,v]} = 0, \tag{16}$$

where the Lagrange multiplier μ associated with the density normalization constraint, $N[\rho] = N$, is the ground-state *chemical potential* of electrons [3,5,104]:

$$\begin{aligned}\mu_0 &= \mu[N, v] = \mu[\rho[N, v]] \equiv (\partial E[N, v]/\partial N)_v = \{\delta E_v[\rho]/\delta \rho(\mathbf{r})\}_{\rho[N,v]} \\ &\equiv \mu[N, v; \mathbf{r}] \end{aligned} \tag{17}$$

Therefore, for the fixed external potential the ground-state density minimizes the energy density functional subject to the constraint of the density normalization. The last equation also demonstrates, that the local chemical potential $\mu[N, v; \mathbf{r}]$ is equalized throughout the physical space at the global chemical potential level $\mu[N, v]$. Moreover, since the net electric charge of the system under consideration $Q = (\sum_\alpha Z_\alpha) - N$, the chemical potential equalization principle of equation (17) can be also interpreted as the equalization of the local electronegativity $\chi[N, v; \mathbf{r}]$ at the corresponding global level [99,100]:

$$\begin{aligned}\chi_0 &= \chi[N, v] = \chi[\rho[N, v]] \equiv (\partial \bar{E}[Q, v]/\partial Q)_v = -\mu[N, v] \\ &= -\{\delta E_v[\rho]/\delta \rho(\mathbf{r})\}_{\rho[N,v]} \equiv \chi[N, v; \mathbf{r}] = -\mu[N, v; \mathbf{r}] \end{aligned} \tag{18}$$

where $\bar{E}[Q, v] = E[N, v]$.

To summarize, the ground-state wavefunction, defined in the 4N-dimensional configuration space, and the electron density, defined in the 3-dimensional physical space, constitute exactly equivalent definitions of the quantum–mechanical state of the N-electron molecular system. They both carry the complete physical information about the system under consideration. The theory of electronic structure of matter can thus be rigorously based on the electronic density and this offers both computational and conceptual/interpretative advantages.

6. CONCEPTUAL ADVANTAGES OF DENSITY FUNCTIONAL THEORY

The modern DFT ([1,2]; see also Refs. [3,90,91]) provides a convenient theoretical framework for formulating new approaches to classical problems in chemistry: the origins of the chemical bonding, equilibrium identity of AIM and molecular subsystems, determining factors and relative importance of alternative reaction sites and pathways in large reactive and catalytic systems, stability of molecular charge distribution, etc. [3–6,12,81,82]. The theory represents an alternative viewpoint, from which one can approach a description of the molecular or reactive systems, in the spirit of the classical Sanderson's *electronegativity equalization* principle [99,100] for the molecular ground-state equilibrium. In DFT the ground-state distribution of electrons is regarded as that of a *fluid*, which is fully characterized by it's equilibrium density $\rho_0(\mathbf{r})$ for a given external potential of the BO approximation.

This new perspective has enriched the theory of electronic structure and chemical reactivity by both rationalizing and quantifying basic, classical ideas and rules of chemistry, e.g., the electronegativity/chemical potential equalization of Sanderson [104] or the hard–soft acids and bases (HSAB) principle of Pearson [95,105], bringing about a deeper understanding of the nature of chemical bonds and variety of reactivity preferences [3–5,11,117].

In DFT the frontier electron theory has also been given a more rigorous foundation in terms of the new reactivity index for open molecular systems, called the electronic FF [3–5,84,92,118–122], the CS measuring a response in the local electron density per unit displacement in the system global number of electrons N:

$$f(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial N]_v = [\partial\mu/\partial v(\mathbf{r})]_N \tag{19}$$

As we have indicated above, it can be also interpreted, by the Maxwell relation, as the response in the system global chemical potential to a unit local displacement in the external potential.

The corresponding *nuclear FF* [7,8,82] has also been introduced,

$$\varphi_\alpha = (\partial\mathbf{F}_\alpha/\partial N)_v = -(\partial\mu/\partial\mathbf{R}_\alpha)_N = (\partial\chi/\partial\mathbf{R}_\alpha)_N \tag{20}$$

monitoring the normalized response of the force acting on nucleus α, $\mathbf{F}_\alpha = -\partial W/\partial\mathbf{R}_\alpha$, per unit displacement in the global number of electrons; here $W(\mathbf{R}) = E(\mathbf{R}) + V_{\mathrm{n,n}}(\mathbf{R})$ is the ground-state PES including the electronic energy $E(\mathbf{R})$ and the nuclear repulsion energy $V_{\mathrm{n,n}}(\mathbf{R}) = \sum_\alpha \sum_{\beta\alpha} Z_\alpha Z_\beta/R_{\alpha\beta}$, where $R_{\alpha\beta} = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$. In equation (20) we have also listed the alternative derivative interpretation of the nuclear FF index implied by the corresponding Maxwell relation, as the response of the system global electronegativity to a unit shift in the position of nucleus α.

The electronic ground-state energy $E[N, v]$ for a given average number of electrons N and the external potential v of the BO approximation is also the functional of the grand-canonical ensemble density [123]:

$$E[N, v] = E_v[\rho] \equiv \int v(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} + F[\rho] \tag{21}$$

where in the last expression we have separated the attraction energy between electrons and nuclei from the remaining, v-independent (universal) part of the electronic energy, $F[\rho]$, which groups the electronic kinetic and repulsion energies [124]. The first partial derivatives of the ground-state energy surface $E[N, v]$ with respect to the BO state-parameters $\mathbf{X} = (N, v)$, calculated for the specified (reference) ground-state molecular system, determine the corresponding BO *principal* (canonical) ‘potentials’, $\mathbf{Y} = \partial E/\partial\mathbf{X} \equiv \mathbf{E}_{\mathbf{X}} = (\mu_0, \rho_0(\mathbf{r})]$, including the electronic *chemical potential* $\mu_0 = \mu[N, v]$ [equation (17)], negative of the system global electronegativity $\chi_0 = \chi[N, v]$ [equation (18)], and the ground-state density itself (Hellmann–Feynman theorem):

$$\rho_0(\mathbf{r}) = \rho[N, v; \mathbf{r}] = [\partial E[N, v]/\partial v(\mathbf{r})]_N \tag{22}$$

The corresponding second partials of the system electronic energy, $\mathbf{P} = \partial^2E/\partial\mathbf{X}\partial\mathbf{X} = \partial\mathbf{Y}/\partial\mathbf{X} \equiv \mathbf{y}(\mathbf{X})$, group the system conjugate principal BO *charge sensitivities*. These canonical derivatives include:

the global hardness [105]:

$$\eta = (\partial^2E[N, v]/\partial N^2)_v = (\partial\mu/\partial N)_v \tag{23}$$

the inverse of the global softness:

$$S = (\partial N/\partial\mu)_v = 1/\eta \tag{24}$$

the *electronic FF* [3,92] [see equation (19)]:

$$f(\mathbf{r}) = [\partial/\partial N\{\partial E[N, v]/\partial v(\mathbf{r})\}_N]_v = \{\partial/\partial v(\mathbf{r})[\partial E/\partial N]_v\}_N \tag{25}$$

the linear response function (LRF) [93,94]:

$$\beta(\mathbf{r}, \mathbf{r}') = [\partial^2E[N, v]/\partial v(\mathbf{r})\partial v(\mathbf{r}')]_N = [\partial\rho(\mathbf{r}')/\partial v(\mathbf{r})]_N \tag{26}$$

The corresponding quantities for reactants, i.e., molecular subsystems in the overall reactive system, have also been defined [4,5,7,8,12,13,83,84,118–120], also in the case of the simultaneously (externally) open reactants, e.g., molecules adsorbed on the surface of a catalyst [7,9].

These quantities determine the associated quadratic Taylor expansion of the system electronic energy, around the ground-state reference system value, e.g., for the molecular or reactive system as a whole:

$$\begin{aligned}\Delta^{1+2}E[N, v] = \mu\Delta N + \int\rho(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} + \tfrac{1}{2}[\eta(\Delta N)^2 + 2\Delta N\int f(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r}\\ + \int\int\Delta v(\mathbf{r})\beta(\mathbf{r}, \mathbf{r}')\Delta v(\mathbf{r}')d\mathbf{r}\, d\mathbf{r}']\end{aligned} \tag{27}$$

Its generalization for the subsystem resolution constitutes a basis for most of the DFT, linear-response treatments of the embedded reactants, perturbed by the presence of the reaction partner (or a catalyst) [4,5,7,12,13,73,75,83,85–89,95,119, 122]. More specifically, for the fixed geometry of the reactive system each reactant subsystem α undergoes displacements in its effective state-parameters N_α^{eff} and V_α^{eff}, relative to the corresponding reference values in the separated reactant limit: $\Delta N_\alpha = N_\alpha^{\mathrm{eff}} - N_\alpha^0$ (the inter-reactant CT) and $\Delta v_\alpha(\mathbf{r}) = v_\alpha^{\mathrm{eff}}(\mathbf{r}) - v_\alpha(\mathbf{r})$ (the displacement in the subsystem effective external potential). These perturbations generate the reorganization of the electronic structure of both these embedded reactants, which modifies the forces on nuclei, acting in the direction of the equilibrium configuration of nuclei of the whole bimolecular reactive system. The direction of such a geometry relaxation can then be probed using either the nuclear FF [equation (20)] [82] or it can be determined semi-quantitatively using the explicit electron-preceding mapping transformations of the CSA [4,5,8,32,73] or electronegativity equalization method (EEM) [31,75,86].

The (N, v)-perturbational expansion of equation (27), for the electronic energy of a reactive system [3–5,7,82–84,97,122] then provides a natural basis for the complete (electron-following) two-reactant theory of chemical reactivity, covering both its electronic (N) and nuclear [$v(\mathbf{R})$ or $\mathbf{R}$] degrees-of-freedom [5,8]. In this description the promoted state of the mutually closed reactants, at the intermediate, polarization (P) stage of a chemical reaction, and the equilibrium state of the mutually open reactants, at the final CT stage, can be treated adequately and consistently. This expansion connects naturally to the conventional stages, in which the reaction mechanism is described in chemistry: the initial (Δv-driven) *polarization* of reactants, followed by the ($\mathbf{\Delta}N$-driven) CT between the already polarized reactants, which is needed to restore the global equilibrium, i.e., the electronegativity equalization throughout the whole reactive system. It should be stressed at this point, that the inter-reactant CT itself induces a further polarization inside each subsystem [5,12,13].

A modified expansion for the reactants in contact with the external electron reservoirs provides an adequate description of the adsorbed species in catalytic reactions [7,9,11,12]. The charge sensitivities defining the quadratic Taylor expansions of the relevant molecular 'thermodynamic' *potentials* for alternative specifications of the molecular equilibrium states, represented by the corresponding Legendre transforms of the system electronic energy, have also been formulated [8,9,12,13,93,125], to provide a more complete theory of chemical reactivity. The *transition* reactivity indices, i.e., the derivatives of the energy differences for the two geometrical structures of the system under consideration, e.g., of the activation or reaction energies, have also been explored [7]. In particular, the *transition FF* has been introduced to transform the displacement of the overall number of electrons into the associated change in the energy difference of the two isoelectronic molecular systems corresponding to different external potentials.

Density functional theory also offers an attractive computational scheme, the Kohn–Sham (KS) theory [2], similar to the Hartree–Fock (HF) approach, which in principle takes into account both the electron exchange and correlation effects. The canonical KS orbitals thus offer certain interpretative advantages over the widely used HF orbitals, especially for describing the bond dissociation and the open system characteristics, when the electrons are added or removed from the system [3,82,126–130]. For this reason, a determined effort has been made to calculate the reactivity indices from the KS DFT calculations [3,82,83,112,118,119,121, 131–136].

7. HORIZONTAL AND VERTICAL DISPLACEMENTS OF THE ELECTRONIC STRUCTURE

In the 'thermodynamic' treatment of molecular systems [23,33,113–115] one aims at describing changes in the electronic structure accompanying the displacement of the molecule under consideration from one equilibrium (ground-state) density,

$\rho_1(\mathbf{r}) = \rho[N_1, v_1; \mathbf{r}]$, to another, $\rho_2(\mathbf{r}) = \rho[N_2, v_2; \mathbf{r}]$, both uniquely determined by the two state parameters determining the current electronic hamiltonian: the overall number of electrons N_i and the external potential due to the nuclei $v_i(\mathbf{r})$, $i = 1, 2$. We call such shifts in the system electronic structure the 'horizontal' displacements [7,33] on the ground-state density 'surface', $\rho[N, v; \mathbf{r}] \equiv \rho_0(\mathbf{r})$. A displacement from one v-representable electronic density to another gives rise to the associated change in the generalized density functional for the ground-state energy:

$$E[\rho_0] \equiv \int v[\rho_0; \mathbf{r}]\rho_0(\mathbf{r})\mathrm{d}\mathbf{r} + F[\rho_0] \equiv E[N[\rho_0],\ v[\rho_0]] \tag{28}$$

in which the external potential changes with the electron density in such a way, that always the current $\rho_0(\mathbf{r})$ matches $v(\mathbf{r}) = v[\rho_0; \mathbf{r}]$, for which it is the ground-state (equilibrium) density.

It should be emphasized, that this density functional for the *ground-state* energy differs from the (HK) functional for the energy, $E_v[\rho]$, in which the external potential is fixed (not related to the trial density ρ). Only for the exact ground-state density $E_v[\rho_0] = E[\rho_0]$. The variational principle of equation (16), also defined for the fixed $v(\mathbf{r})$, determines the minimum of $E_v[\rho]$ subject to the density normalization constraint $N[\rho] = \int \rho(\mathbf{r})\mathrm{d}\mathbf{r} = N$. The associated Euler equation for the optimum (ground-state) density $\rho(\mathbf{r}) = \rho[N_0, v; \mathbf{r}] = \rho_0(\mathbf{r})$ reads:

$$\mu[N, v; \mathbf{r}] \equiv \{\delta E_v[\rho]/\delta\rho(\mathbf{r})\}_v = v(\mathbf{r}) + \delta F/\delta\rho(\mathbf{r}) = \mu[N, v] \tag{29}$$

where the functional derivatives with respect to the electronic density are calculated for $\rho = \rho_0$; to simplify notation in what follows we shall omit the subscript 0 identifying the exact ground-state density. The Euler equation implies that the external potential relative to the global chemical potential represents the unique functional of the ground-state density:

$$u(\mathbf{r}) \equiv v(\mathbf{r}) - \mu \equiv u[\rho; \mathbf{r}] = -\delta F/\delta\rho(\mathbf{r}) \tag{30}$$

and *vice versa*: $\rho(\mathbf{r}) = \rho[u; \mathbf{r}]$. However, the external potential itself is determined by ρ only up to a constant μ, which can be related to the chemical potential of an external *electron reservoir* $\mathcal{R}$: $\mu = \mu^{\mathcal{R}}$. Therefore, the unique specification of the external potential as the functional of ρ additionally requires the knowledge of this 'intensive' (global) state-parameter:

$$v(\mathbf{r}) = u(\mathbf{r}) + \mu = \mu - \delta F/\delta\rho(\mathbf{r}) \equiv v[\mu, \rho; \mathbf{r}] \tag{31}$$

The 'horizontal' character of changes in the ground-state electronic structure is in contrast to a search for the equilibrium *partitioning* of the fixed molecular ground-state density $\rho(\mathbf{r})$ into the subsystem densities $\boldsymbol{\rho}(\mathbf{r}) \equiv \{\rho_\alpha(\mathbf{r}) = \rho_\alpha[\rho; \mathbf{r}]\}$ (a row vector), e.g., those of m constituent AIM or two reactants, which sum up to this given density, $\rho(\mathbf{r}) = \sum_\alpha \rho_\alpha(\mathbf{r})$. The latter is 'vertical' in character, i.e., performed for the fixed molecular density [20–24,33], as is also the case in the Levy constrained search construction of $F[\rho]$ [124]. As argued elsewhere [33], such a division problem involves a search for the *effective* external potentials of subsystems $\mathbf{v}^{eff} = \{v_\alpha^{\mathrm{eff}}\}$:

$$v_\alpha^{\mathrm{eff}}(\mathbf{r}) = v_\alpha^{\mathrm{eff}}[\rho;\mathbf{r}] = v(\mathbf{r}) + \{\partial F^n[\boldsymbol{\rho}]/\partial \rho_\alpha(\mathbf{r})\}_{\beta\neq\alpha}, \qquad \alpha = 1,2,\ldots,m \qquad (32)$$

where the partial functional differentiation with respect to ρ_α of the *non-additive* part $F^n[\boldsymbol{\rho}]$ of the universal Hohenberg–Kohn–Levy functional $F[\rho] = F[\boldsymbol{\rho}]$,

$$F^n[\boldsymbol{\rho}] \equiv F[\boldsymbol{\rho}] - \sum_\gamma F[\rho_\gamma] \equiv F[\boldsymbol{\rho}] - F^a[\boldsymbol{\rho}] \qquad (33)$$

with $F^a[\boldsymbol{\rho}]$ denoting the *additive* part, is carried out for the fixed densities of the remaining subsystems $\{\rho_{\beta\neq\alpha}\}$. These effective external potentials of the embedded subsystems in a molecule are then related to their respective densities through the global-like ground-state Euler equation of DFT [see equations (17) and (29)]:

$$\mu_\alpha(\mathbf{r}) = \mu_\alpha[\boldsymbol{\rho}[\rho];\mathbf{r}] \equiv v_\alpha^{\mathrm{eff}}(\mathbf{r}) + \delta F[\rho_\alpha]/\delta\rho_\alpha(\mathbf{r}) = \mu[\rho] \qquad (34)$$

where we have indicated that the local chemical potentials of the mutually open subsystems,

$$\boldsymbol{\mu}(\mathbf{r}) \equiv \{\mu_\alpha(\mathbf{r}) \equiv \{\partial\varepsilon_\alpha[\boldsymbol{\rho}, v]/\partial\rho_\alpha(\mathbf{r})\}_{v,\beta\neq\alpha}\} = \{\mu_\alpha \equiv (\partial\epsilon[\boldsymbol{N}, v]/\partial N_\alpha)_v\} \equiv \boldsymbol{\mu}$$

$$= \mu\mathbf{1} \text{ (row vector)} \qquad (35)$$

where the unit vector $\mathbf{1} = (1,1,\ldots)$, $E[N,v] \equiv \epsilon[\boldsymbol{N},v]$, and the row vector $\boldsymbol{N} \equiv \{N_\gamma = \int \rho_\gamma(\mathbf{r})d\mathbf{r} \equiv N[\rho_\gamma]\}$ groups the effective overall numbers of electrons in subsystems, are equalized at the corresponding global chemical potential levels $\{\mu_\alpha\}$, all equal to the global chemical potential μ of the system as whole. The partial derivatives in equations (34) and (35) are also calculated for the fixed external potential v, due to the nuclei of all subsystems. The density functional for the energy of the embedded molecular fragment α is defined as follows:

$$\varepsilon_\alpha[\boldsymbol{\rho}, v] = \left\{\int v(\mathbf{r})\rho_\alpha(\mathbf{r})d\mathbf{r} + F[\rho_\alpha]\right\} + F^n[\boldsymbol{\rho}] \equiv E_v[\rho_\alpha] + F^n[\boldsymbol{\rho}], \qquad (36)$$

where $E_v[\rho_\alpha]$ stands for the electronic energy contribution due to the ρ_α alone, and $F^n[\rho]$ represents the embedding energy term due to the presence of the electrons in the remaining subsystems [33].

8. LEGENDRE TRANSFORMS OF THE ELECTRONIC ENERGY AND THEIR DERIVATIVES

It has been discussed elsewhere [5,7,8,12,13,93,137,138] that there are four alternative Legendre-transformed representations of a molecular (single component) system, corresponding to the following sets of the ground-state parameters $\{a, x(\mathbf{r})\}$:

$$\{N, v(\mathbf{r})\}, \qquad \{\mu, v(\mathbf{r})\} = \{u(\mathbf{r})\}, \qquad \{N, \rho(\mathbf{r})\} = \{\rho(\mathbf{r})\}, \qquad \{\mu, \rho(\mathbf{r})\}, \tag{37}$$

including one global (N or μ) and one local [$v(\mathbf{r})$ or $\rho(\mathbf{r})$] state-parameters, which uniquely specify the equilibrium states of the externally closed or open molecular systems in question. The ground-state energy functional $E[N, v]$ for the integer values of N is defined by the Schrödinger or Hohenberg–Kohn–Levy variational principles (equations (8) and (16)), while the energy for a fractional (ensemble average) value of the global number of electrons corresponds to the grand canonical average over such integer-N eigenvalues of the system energy operator, with the ensemble probabilities being determined by the externally imposed thermodynamic state parameters: $\mu^{\mathcal{R}}$—the chemical potential of the *electron reservoir*, and T—the absolute temperature of the *heat bath*.

Such an ensemble generalized ground-state energy functional, $E = E[N, v] = E[\rho[N, v]]$, represents the ‘thermodynamic’ potential of the $\{N, v\}$-representation, with the corresponding generalized Hellmann–Feynman expression for its differential (see equations (17), (22) and (27)):

$$\mathrm{d}E[N, v] = \mu[N, v]\mathrm{d}N + \int \rho[N, v; \mathbf{r}]\mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r} \tag{38}$$

The corresponding ‘potentials’ for the three remaining specifications of the system equilibrium state are given by the relevant Legendre transforms of the electronic energy:

$$Q[\mu, v] = E - (\partial E/\partial N)_v N = E[\rho[u]] - \mu[\rho[u]]N[\rho[u]] \equiv Q[u] \tag{39}$$

$$F[\rho \to N] = E - \int [\partial E/\partial v(\mathbf{r})]_N v(\mathbf{r})\mathrm{d}\mathbf{r} = E - \int \rho(\mathbf{r})v(\mathbf{r})\mathrm{d}\mathbf{r} = F[\rho] \tag{40}$$

$$R[\mu, \rho] = E - (\partial E/\partial N)_v N - \int [\partial E/\partial v(\mathbf{r})]_N v(\mathbf{r})\mathrm{d}\mathbf{r} = F[\rho] - \mu N[\rho] \tag{41}$$

where in equation (40) the symbol $\rho \to N$ denotes the density integrating to N electrons. These functionals give rise to the following differentials:

$$\begin{aligned} \mathrm{d}Q[\mu, v] &= \mathrm{d}E - \mu\,\mathrm{d}N - N\mathrm{d}\mu = -N[\mu, v]\mathrm{d}\mu + \int \rho[\mu, v; \mathbf{r}]\mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r} \\ &= \int \rho[u; \mathbf{r}]\mathrm{d}u(\mathbf{r})\mathrm{d}\mathbf{r} = \mathrm{d}Q[u] \end{aligned} \tag{42}$$

$$\begin{aligned} \mathrm{d}F[\rho] &= \mathrm{d}E - \int \rho(\mathbf{r})\mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r} - \int v(\mathbf{r})\mathrm{d}\rho(\mathbf{r})\mathrm{d}\mathbf{r} = \mu[\rho]\mathrm{d}N - \int v(\mathbf{r})\mathrm{d}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \\ &= -\int u[\rho; \mathbf{r}]\mathrm{d}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \end{aligned} \tag{43}$$

$$\mathrm{d}R[\mu,\rho] = \mathrm{d}E - \mu\mathrm{d}N - N\mathrm{d}\mu - \int \rho(\mathbf{r})\mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r} - \int v(\mathbf{r})\mathrm{d}\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

$$= -N[\mu,\rho]\mathrm{d}\mu - \int v[\mu,\rho;\mathbf{r}]\mathrm{d}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \tag{44}$$

which identify the parameters conjugate to those defining the representation:

$$\mu = (\partial E[N,v]/\partial N)_v, \qquad \rho(\mathbf{r}) = \{\partial E[N,v]/\partial v(\mathbf{r})\}_N \tag{45}$$

$$-N = (\partial Q[\mu,v]/\partial\mu)_v, \quad \rho(\mathbf{r}) = \{\partial Q[\mu,v]/\partial v(\mathbf{r})\}_\mu = \delta Q[u]/\delta u(\mathbf{r}) \tag{46}$$

$$-u(\mathbf{r}) = \mu - v(\mathbf{r}) = \delta F[\rho]/\delta\rho(\mathbf{r}) \tag{47}$$

$$-N = (\partial R[\mu,\rho]/\partial\mu)_\rho, \quad -v(\mathbf{r}) = \{\partial R[\mu,\rho]/\partial\rho(\mathbf{r})\}_\mu \tag{48}$$

The energy functional defines the second derivatives of equations (23)–(26), called the principal *charge sensitivities*, which determine the associated second differential of the Taylor expansion of equation (27):

$$\mathrm{d}^2E[N,v] = \tfrac{1}{2}\{\eta(\mathrm{d}N)^2 + 2\mathrm{d}N\int f(\mathbf{r})\mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r}$$

$$+ \int\int \mathrm{d}v(\mathbf{r})\beta(\mathbf{r},\mathbf{r}')\mathrm{d}v(\mathbf{r}')\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\} \tag{49}$$

The linear response kernel $\beta(\mathbf{r},\mathbf{r}')$ is linked to the softness kernel

$$\sigma(\mathbf{r},\mathbf{r}') = -\partial\rho(\mathbf{r}')/\delta u(\mathbf{r}) = -[\partial\rho(\mathbf{r}')/\partial v(\mathbf{r})]_\mu = \eta^{-1}(\mathbf{r}',\mathbf{r}) \tag{50}$$

the inverse of the hardness kernel,

$$\eta(\mathbf{r},\mathbf{r}') = \delta^2F/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') = -\delta u(\mathbf{r}')/\delta\rho(\mathbf{r}) = -[\partial v(\mathbf{r}')/\partial\rho(\mathbf{r})]_\mu \tag{51}$$

through the relation [94]:

$$\beta(\mathbf{r},\mathbf{r}') = -\sigma(\mathbf{r},\mathbf{r}') + f(\mathbf{r})Sf(\mathbf{r}') \tag{52}$$

One also defines the local softnesses [4,5,87,94],

$$s(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial\mu]_v = f(\mathbf{r})S = \int \sigma(\mathbf{r}',\mathbf{r})\mathrm{d}\mathbf{r}' = -\delta N/\delta u(\mathbf{r}) = -[\partial N/\partial v(\mathbf{r})]_\mu \tag{53}$$

additive contributions to the global softness of equation (24):

$$S = (\partial N/\partial\mu)_v = \int s(\mathbf{r})\mathrm{d}\mathbf{r} \tag{54}$$

It should be observed that equation (52) directly follows from the following transformation of the derivative defining the softness kernel [equation (50)]:

$$\sigma(\mathbf{r},\mathbf{r}') = -[\partial\rho(\mathbf{r}')/\partial v(\mathbf{r})]_\mu = -[\partial\rho(\mathbf{r}')/\partial v(\mathbf{r})]_N - [\partial N/\partial v(\mathbf{r})]_\mu[\partial\rho(\mathbf{r}')/\partial N]_v$$

$$= -\beta(\mathbf{r},\mathbf{r}') + s(\mathbf{r})f(\mathbf{r}') = -\beta(\mathbf{r},\mathbf{r}') + f(\mathbf{r})Sf(\mathbf{r}') \tag{55}$$

A similar functional chain-rule transformation gives the expression for the global hardness in terms of the hardness kernel:

$$\eta = \int\int [\partial\rho(\mathbf{r})/\partial N]_v [\delta^2 E_v[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')]_v [\partial\rho(\mathbf{r}')/\partial N]_v \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'$$
$$= \int\int f(\mathbf{r})\eta(\mathbf{r},\mathbf{r}')f(\mathbf{r}')\mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}', \tag{56}$$

including the product of the Fukui functions determining the weighting factor. The same result follows from the corresponding one-point weighted expression defining the local derivative

$$\eta(\mathbf{r}) = [\partial\mu(\mathbf{r})/\partial N]_v = \int [\delta^2 E_v[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')]_v [\partial\rho(\mathbf{r}')/\partial N]_v d\mathbf{r}'$$
$$= \int \eta(\mathbf{r},\mathbf{r}')f(\mathbf{r}')\mathrm{d}\mathbf{r}' = [\partial\mu/\partial N]_v = \eta \tag{57}$$

since $\mu(\mathbf{r}) = \mu$, by the local chemical potential equalization for the ground-state density [equation (17)]. The last equation marks the local hardness equalization [5]. It does not contradict equation (56), since the Fukui function normalization requires $\int f(\mathbf{r})\mathrm{d}\mathbf{r} = 1$.

9. CONSTRAINED EQUILIBRIA IN SUBSYSTEMS

The AIM chemical potentials defined by the partial functional derivatives of equation (35), calculated for the fixed external potential and the 'frozen' embedding densities $\{\rho_{\beta\neq\alpha}(\mathbf{r})\}$ of the remaining subsystems, are equalized only when the subsystems are mutually *open* [4,5]. This is the case in the *global equilibrium* state considered in the preceding section. In what follows we shall denote such open subsystem condition by the vertical *broken* lines in the symbolic representation of the molecular system as a whole, $M_g = (\alpha\,\vdots\,\beta\,\vdots\,\gamma\,\vdots\,...)$, in the *global* (g, inter-subsystem) *equilibrium* of the ground-state of an externally open system:

$$\mu_\alpha(\mathbf{r}) = \{\partial E_V[\rho]/\partial\rho_\alpha(\mathbf{r})\}_{V,\beta\neq\alpha} = \mu_\alpha = \mu, \qquad \alpha = 1,2,...,m; \tag{58}$$

here the row vector of the subsystem densities $\boldsymbol{\rho} = (\rho_\alpha, \rho_\beta, \rho_\gamma, ...)$ gives rise to the overall density $\rho = \sum_\gamma \rho_\gamma = \mathbf{1}\boldsymbol{\rho}^{\mathrm{T}}$ and the row vector of the subsystem external potentials $V(\mathbf{r}) = v(\mathbf{r})\mathbf{1}$. This equalization of the subsystem chemical potentials, $\boldsymbol{\mu} = (\mu_\alpha, \mu_\beta, \mu_\gamma, ...) = \mu\mathbf{1}$, can be attributed to a *common* external *reservoir* ($\mathcal{R}$) of electrons, exhibiting the chemical potential

$$\mu^{\mathcal{R}} = \mu_\alpha = \mu, \qquad \alpha = 1,2,...,m \tag{59}$$

to which all molecular subsystems are coupled in the combined system $\mathcal{M}[M_g] \equiv (\mathcal{R}\,\vdots\,\alpha\,\vdots\,\beta\,\vdots\,\gamma\,\vdots\,...)$.

In the subsystem resolution one also considers the *constrained* (intra-subsystem) *equilibrium* states [4,5,7,9,12,83], when all subsystems are mutually *closed*, which is symbolized by the vertical *solid* lines in the symbolic representation of a collection of AIM in $M_c = (\alpha|\beta|\gamma|...)$. In order to probe the open subsystem characteristics in M_c, when each AIM is characterized by the intra-subsystem equalized, generally different levels of the AIM chemical potentials,

$$\mu_\alpha(\mathbf{r}) = \mu_\alpha \neq \mu_\beta(\mathbf{r}) = \mu_\beta \neq \mu_\gamma(\mathbf{r}) = \mu_\gamma \neq ... \neq \mu \tag{60}$$

one envisages the *separate* external reservoirs $\{\mathcal{R}_\alpha\}$ for each subsystem, characterized by the independently controlled chemical potentials $\{\mu_\alpha^{\mathcal{R}}\}$, in the combined system $\mathcal{M}[M_c] \equiv (\mathcal{R}_\alpha \mathrel{\vdots} \alpha|\mathcal{R}_\beta \mathrel{\vdots} \beta|\mathcal{R}_\gamma \mathrel{\vdots} \gamma|...)$. Notice, that only for the global equilibrium, when $\mathcal{R}_\alpha = \mathcal{R}_\beta = \mathcal{R}_\gamma = ... = \mathcal{R}$, $\boldsymbol{\mu} = \mu\mathbf{1}$ [equation (59)]. Similarly, when only a single subsystem or a subset of molecular fragments is considered externally open, while the remaining subsystems are held externally closed, one envisages a coupling of a specified selection of subsystems to their corresponding reservoirs, e.g., in $\mathcal{M}[M_\alpha] \equiv (\mathcal{R}_\alpha \mathrel{\vdots} \alpha|\beta|\gamma|...)$.

The equilibrium state of the subsystem α in contact with $\mathcal{R}_\alpha$ is characterized by the equalization of the subsystem chemical potential with that of its reservoir: $\mu_\alpha^{\mathcal{R}} = \mu_\alpha$. Therefore, in this thermodynamic description the hypothetical, independent displacements of the subsystem chemical potentials reflect those of the corresponding subsystem reservoirs: $d\mu_\alpha^{\mathcal{R}} = d\mu_\alpha$.

In such a subsystem resolution one defines the row vector of the AIM relative external potentials,

$$\mathbf{u}(\mathbf{r}) \equiv -\partial F[\boldsymbol{\rho}]/\partial \boldsymbol{\rho}(\mathbf{r}) = v(\mathbf{r})\mathbf{1} - \boldsymbol{\mu} \equiv V(\mathbf{r}) - \boldsymbol{\mu} = \{u_\alpha(\mathbf{r}) \equiv v(\mathbf{r}) - \mu_\alpha$$

$$= -[\partial F[\boldsymbol{\rho}]/\partial \rho_\alpha(\mathbf{r})]_{\beta\neq\alpha}\} \tag{61}$$

The quantities of the preceding equation represent the negative partial derivatives of the universal part [see equation (33)],

$$F[\boldsymbol{\rho}] = F^n[\boldsymbol{\rho}] + F^a[\boldsymbol{\rho}] \tag{62}$$

of the energy density functional $E_V[\rho]$ in the subsystem resolution:

$$E_V[\boldsymbol{\rho}] = \int V(\mathbf{r})\boldsymbol{\rho}(\mathbf{r})^{\mathrm{T}} d\mathbf{r} + F[\boldsymbol{\rho}] \tag{63}$$

This conclusion directly follows from the corresponding Euler equations determining the optimum subsystem densities in the constrained equilibrium state:

$$\delta\{E_V[\boldsymbol{\rho}] - \sum_\gamma \mu_\gamma N[\rho_\gamma]\} = 0, \qquad \text{or}$$

$$\{\partial E_V[\boldsymbol{\rho}]/\partial \rho_\alpha(\mathbf{r})\}_{\beta\neq\alpha} \equiv \mu_\alpha(\mathbf{r}) = v(\mathbf{r}) + \{\partial F[\boldsymbol{\rho}]/\partial \rho_\alpha(\mathbf{r})\}_{\beta\neq\alpha} = \mu_\alpha,$$
$$\alpha = 1, 2, ..., m \tag{64}$$

It follows from the last equation, that the equilibrium densities of the mutually closed, but externally open subsystems are unique functionals of the molecular external potential and the reservoir chemical potentials, $\boldsymbol{\rho} = \boldsymbol{\rho}[\mathbf{u}[\boldsymbol{\mu}, V]] = \boldsymbol{\rho}[\boldsymbol{\mu}, V]$, and so is the row vector of the average numbers of electrons: $N[\boldsymbol{\rho}] = \int \boldsymbol{\rho}[\boldsymbol{\mu}, V; \mathbf{r}]\mathrm{d}\mathbf{r}$. Similarly, when all subsystems are both mutually and externally closed in $M \equiv (\alpha|\beta|\gamma|\ldots)$, the external potential and the numbers of electrons in subsystems uniquely determine the equilibrium densities $\boldsymbol{\rho} = \boldsymbol{\rho}[N, V]$, the system energy, $E_V[\boldsymbol{\rho}[N, V]] = E[N, V]$, and all its physical properties, e.g., the subsystem chemical potentials $\boldsymbol{\mu} = \boldsymbol{\mu}[N, V]$.

Following the global equilibrium development of the preceding section one defines the 'thermodynamic' potentials corresponding to the four alternative sets of the constrained-equilibrium states, for the alternative sets of the state parameters,

$$\{N, V\}, \qquad \{\boldsymbol{\mu}, V\} = \{\mathbf{u}\}, \qquad \{N, \boldsymbol{\rho}\} = \{\boldsymbol{\rho}\}, \qquad \{\boldsymbol{\mu}, \boldsymbol{\rho}\} \tag{65}$$

as the corresponding Legendre transforms of the electronic energy $E[N, V]$:

$$Q[\boldsymbol{\mu}, V] = E - N(\partial E/\partial N)_V^{\mathrm{T}} = E[\boldsymbol{\rho}[\mathbf{u}]] - N[\boldsymbol{\rho}[\mathbf{u}]]\,\boldsymbol{\mu}[\boldsymbol{\rho}[\mathbf{u}]]^{\mathrm{T}} = Q[\mathbf{u}] \tag{66}$$

$$F[\boldsymbol{\rho} \rightarrow N] = E - \int V(\mathbf{r})\{\partial E/\partial V(\mathbf{r})\}_N^{\mathrm{T}}\mathrm{d}\mathbf{r} = E - \int V(\mathbf{r})\boldsymbol{\rho}(\mathbf{r})^T\mathrm{d}\mathbf{r} = F[\boldsymbol{\rho}] \tag{67}$$

$$\begin{aligned} R[\boldsymbol{\mu}, \boldsymbol{\rho}] &= E - N(\partial E/\partial N)_V^{\mathrm{T}} - \int V(\mathbf{r})\{\partial E/\partial V(\mathbf{r})\}_N^{\mathrm{T}}\mathrm{d}\mathbf{r} \\ &= F[\boldsymbol{\rho}] - N[\boldsymbol{\rho}]\,\boldsymbol{\mu}[\boldsymbol{\rho}]^{\mathrm{T}} \end{aligned} \tag{68}$$

Clearly, in the subsystem resolution one could also consider all intermediate specifications of the molecular (constrained) equilibria, when only a part of the subsystems remains externally open (characterized by the fixed chemical potentials of a common reservoir) with the remaining, complementary set of subsystems being closed (characterized by the fixed subsystem numbers of electrons) [4,5]. Such mixed representations can be also naturally defined in the CSA approach. We would like to observe, that in the theory of chemical reactivity these partially opened situations do indeed arise, e.g., in the surface reactions, when one adsorbate is opened (*chemisorbed*) while the other reactant remains externally closed (*physisorbed*) on the catalyst surface, which acts as the electron reservoir for the reaction.

The corresponding differentials of the system electronic energy in the subsystem resolution and its Legendre transforms of equations (66)–(68) are:

$$\mathrm{d}E[N, V] = \boldsymbol{\mu}[N, V]\,\mathrm{d}N^T + \int \boldsymbol{\rho}[N, V; \mathbf{r}]\,\mathrm{d}\mathbf{V}(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} \tag{69}$$

$$\begin{aligned} \mathrm{d}Q[\boldsymbol{\mu}, V] &= -N\mathrm{d}\boldsymbol{\mu}^{\mathrm{T}} + \int \boldsymbol{\rho}[N, V, \mathbf{r}]\,\mathrm{d}V(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} \\ &= \int \boldsymbol{\rho}[\mathbf{u}; \mathbf{r}]\,\mathrm{d}\mathbf{u}(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} = \mathrm{d}Q[\mathbf{u}] \end{aligned} \tag{70}$$

$$\mathrm{d}F[\boldsymbol{\rho}] = \boldsymbol{\mu}\, dN^{\mathrm{T}} - \int V(\mathbf{r})\,\mathrm{d}\boldsymbol{\rho}(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} = -\int \mathbf{u}[\boldsymbol{\rho};\mathbf{r}]\,\mathrm{d}\boldsymbol{\rho}(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} \tag{71}$$

$$\mathrm{d}R[\boldsymbol{\mu},\boldsymbol{\rho}] = -N\,\mathrm{d}\boldsymbol{\mu}^{\mathrm{T}} - \int V(\mathbf{r})\,\mathrm{d}\boldsymbol{\rho}(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} \tag{72}$$

It should be observed, that the displacements $\mathrm{d}V(\mathbf{r})$ also allow for the independent changes of the external potential of each subsystem, due to external sources.

The differential expressions of equations (69)–(72) identify the parameters conjugate to those defining the representation:

$$\boldsymbol{\mu} = (\partial E[N,V]/\partial N)_V, \qquad \boldsymbol{\rho}(\mathbf{r}) = \{\partial E[N,V]/\partial V(\mathbf{r})\}_N; \tag{73}$$

$$N = -(\partial Q[\boldsymbol{\mu},V]/\partial\boldsymbol{\mu})_V, \quad \boldsymbol{\rho}(\mathbf{r}) = \{\partial Q[\boldsymbol{\mu},V]/\partial V(\mathbf{r})\}_{\mu} = \delta Q[\mathbf{u}]/\delta\mathbf{u}(\mathbf{r}); \tag{74}$$

$$-\mathbf{u}(\mathbf{r}) = \boldsymbol{\mu} - V(\mathbf{r}) = \delta F[\boldsymbol{\rho}]/\delta\boldsymbol{\rho}(\mathbf{r}); \tag{75}$$

$$-N = (\partial R[\boldsymbol{\mu},\boldsymbol{\rho}]/\partial\boldsymbol{\mu})_{\rho}, \qquad -V(\mathbf{r}) = \{\partial R[\boldsymbol{\mu},\boldsymbol{\rho}]/\partial\boldsymbol{\rho}(\mathbf{r})\}_{\mu} \tag{76}$$

The relevant second-order Taylor expansion of the molecular electronic energy in powers of displacements of the canonical state parameters, $[\mathrm{d}N,\mathrm{d}V(\mathbf{r})]$, is determined by the relevant principal derivatives of the energy representation:

$$\begin{aligned}
\mathrm{d}^{1+2}E[N,V] = {} & \mathrm{d}N(\partial E[N,V]/\partial N)_V^{\mathrm{T}} + \int \{\partial E[N,V]/\partial V(\mathbf{r})\}_N\,\mathrm{d}V(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r}\\
& + \tfrac{1}{2}\{\mathrm{d}N(\partial^2 E[N,V]/\partial N\partial N)_V\mathrm{d}N^{\mathrm{T}}\\
& + 2\,\mathrm{d}N[\partial/\partial N\int \{\partial E[N,V]/\partial V(\mathbf{r})\}_N]_V\mathrm{d}V(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r}\}\\
& + \int\!\!\int \mathrm{d}V(\mathbf{r})\{\partial^2 E[N,V]/\partial V(\mathbf{r})\partial V(\mathbf{r}')\}_N\mathrm{d}V(\mathbf{r}')^{\mathrm{T}}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\\
\equiv {} & \mathrm{d}N\,\boldsymbol{\mu}^{\mathrm{T}} + \int \boldsymbol{\rho}(\mathbf{r})\,\mathrm{d}V(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r} + \tfrac{1}{2}\{\mathrm{d}N\,\mathbf{H}\,\mathrm{d}N^{\mathrm{T}}\\
& + 2\,\mathrm{d}N\int \mathbf{F}(\mathbf{r})\,\mathrm{d}V(\mathbf{r})^{\mathrm{T}}\mathrm{d}\mathbf{r}\\
& + \int\!\!\int \mathrm{d}V(\mathbf{r})\,\mathbf{B}(\mathbf{r},\mathbf{r}')\,\mathrm{d}V(\mathbf{r}')^{\mathrm{T}}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\}
\end{aligned} \tag{77}$$

with the second differential defined by the corresponding principal charge sensitivities in the subsystem resolution. They include:

the *subsystem hardness matrix*:

$$\mathbf{H} = (\partial\boldsymbol{\mu}/\partial N)_V = \{H_{\alpha,\beta} = (\partial\boldsymbol{\mu}_{\beta}/\partial N_{\alpha})_V\} \tag{78a}$$

the *matrix of subsystem Fukui functions*:

$$\begin{aligned}
\mathbf{F}(\mathbf{r}) = [\partial\boldsymbol{\rho}(\mathbf{r})/\partial N]_V = [\partial\boldsymbol{\mu}/\partial V(\mathbf{r})]_N^{T} = \{F_{\alpha,\beta}(\mathbf{r}) \equiv [\partial\rho_{\beta}(\mathbf{r})/\partial N_{\alpha}]_V\\
= F_{\beta,\alpha}(\mathbf{r}) \equiv [\partial\mu_{\alpha}/\partial v_{\beta}(\mathbf{r})]_N\}
\end{aligned} \tag{78b}$$

the *matrix of linear response kernels of subsystems*:

$$\mathbf{B}(\mathbf{r},\mathbf{r}') = [\partial \boldsymbol{\rho}(\mathbf{r}')/\partial \boldsymbol{V}(\mathbf{r})]_N = \{B_{\alpha,\beta}(\mathbf{r},\mathbf{r}') = [\partial \rho_\beta(\mathbf{r}')/\partial v_\alpha(\mathbf{r})]_N\} \quad (78c)$$

One also defines the corresponding *matrices of softness quantities* in the subsystem resolution:

the *softness matrix*:

$$\mathbf{S} = (\partial \boldsymbol{N}/\partial \boldsymbol{\mu})_V = \mathbf{H}^{-1} = \{S_{\alpha,\beta} = (\partial N_\beta/\partial \mu_\alpha)_V\} = \int \mathbf{s}(\mathbf{r})\mathrm{d}\mathbf{r} \quad (79a)$$

the *matrix of local softnesses*:

$$\begin{aligned}\mathbf{s}(\mathbf{r}) &= -\partial \boldsymbol{N}/\partial \mathbf{u}(\mathbf{r}) = [\partial \boldsymbol{\rho}(\mathbf{r})/\partial \boldsymbol{\mu}]_V \\ &= \{s_{\alpha,\beta}(\mathbf{r}) = -\partial N_\beta/\partial u_\alpha(\mathbf{r}) = [\partial \rho_\beta(\mathbf{r})/\partial \boldsymbol{\mu}_\alpha]_V\} \quad (79b)\end{aligned}$$

the *matrix of softness kernels*:

$$\begin{aligned}\boldsymbol{\sigma}(\mathbf{r},\mathbf{r}') &= -\partial \boldsymbol{\rho}(\mathbf{r}')/\partial \mathbf{u}(\mathbf{r}) = -[\partial \boldsymbol{\rho}(\mathbf{r}')/\partial \boldsymbol{V}(\mathbf{r})]_{\boldsymbol{\mu}} \\ &= \{\sigma_{\alpha,\beta}(\mathbf{r},\mathbf{r}') = [\partial \rho_\beta(\mathbf{r}')/\partial v_\alpha(\mathbf{r})]_{\boldsymbol{\mu}}\} \quad (79c)\end{aligned}$$

Again, a straightforward chain rule transformation gives the following expression for $\mathbf{s}(\mathbf{r})$ in terms of $\boldsymbol{\sigma}(\mathbf{r},\mathbf{r}')$:

$$\mathbf{s}(\mathbf{r}) = \int [\partial \mathbf{u}(\mathbf{r}')/\partial \boldsymbol{\mu}]_V [\partial \boldsymbol{\rho}(\mathbf{r})/\partial \mathbf{u}(\mathbf{r}')]\mathrm{d}\mathbf{r}' = \int \mathbf{I}\boldsymbol{\sigma}(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' \quad (79d)$$

where the identity matrix $\mathbf{I} = \{\delta_{\alpha,\beta}\}$. A similar transformation gives the expression for the Fukui function matrix [equation (78b)] in terms of the local softnesses [equation (79b)]:

$$\begin{aligned}\mathbf{F}(\mathbf{r}) &= \int [\partial \mathbf{u}(\mathbf{r}')/\partial \boldsymbol{N}]_V [\partial \boldsymbol{\rho}(\mathbf{r})/\partial \mathbf{u}(\mathbf{r}')]\mathrm{d}\mathbf{r}' = [\partial \boldsymbol{\mu}/\partial \boldsymbol{N}]_V \int \boldsymbol{\sigma}(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' \\ &= \mathbf{H}\mathbf{s}(\mathbf{r}) = \mathbf{S}^{-1}\mathbf{s}(\mathbf{r}) \quad (79e)\end{aligned}$$

Multiplying both sides of the last equation by $\mathbf{S} = \mathbf{H}^{-1}$ also gives

$$\mathbf{s}(\mathbf{r}) = \mathbf{S}\mathbf{F}(\mathbf{r}) \quad (79f)$$

The matrix of softness kernels is the inverse of the corresponding hardness kernel matrix:

$$\begin{aligned}\boldsymbol{\eta}(\mathbf{r},\mathbf{r}') &= \{\partial^2 E_V[\boldsymbol{\rho}]/\partial \boldsymbol{\rho}(\mathbf{r})\partial \boldsymbol{\rho}(\mathbf{r}')\}_V = \partial^2 F[\boldsymbol{\rho}]/\partial \boldsymbol{\rho}(\mathbf{r})\partial \boldsymbol{\rho}(\mathbf{r}') = -\partial \mathbf{u}(\mathbf{r}')/\partial \boldsymbol{\rho}(\mathbf{r}) \\ &= \boldsymbol{\sigma}^{-1}(\mathbf{r}',\mathbf{r}) = -[\partial \boldsymbol{V}(\mathbf{r}')/\partial \boldsymbol{\rho}(\mathbf{r})]_{\boldsymbol{\mu}} = \{\eta_{\alpha,\beta}(\mathbf{r},\mathbf{r}') = -\partial u_\beta(\mathbf{r}')/\partial \rho_\alpha(\mathbf{r}) \\ &= [\partial v_\beta(\mathbf{r}')/\partial \rho_\alpha(\mathbf{r})]_\mu\} \quad (80)\end{aligned}$$

These two sets of kernels satisfy the following reciprocity relation:

$$\int \boldsymbol{\eta}(\mathbf{r}', \mathbf{r})\boldsymbol{\sigma}(\mathbf{r}, \mathbf{r}'')\mathrm{d}\mathbf{r}$$

$$= \left\{ \sum_{\gamma} \int \eta_{\alpha\gamma}(\mathbf{r}', \mathbf{r})\sigma_{\gamma,\beta}(\mathbf{r}, \mathbf{r}'')\mathrm{d}\mathbf{r} = \partial\rho_{\beta}(\mathbf{r}'')/\partial\rho_{\alpha}(\mathbf{r}') = \delta_{\alpha,\beta}\, \delta(\mathbf{r}' - \mathbf{r}'') \right\} \quad (81)$$

since in the subsystem resolution the AIM densities are the independent state-variables.

The hardness matrix of equation (78a) can be expressed in terms of the subsystem hardness kernels using the following chain-rule transformation:

$$\mathbf{H} = (\partial\boldsymbol{\mu}/\partial N)_V = \int\int [\partial\boldsymbol{\rho}(\mathbf{r})/\partial N]_V [\partial^2 E_V[\rho]/\partial\boldsymbol{\rho}(\mathbf{r})\partial\boldsymbol{\rho}(\mathbf{r}')]_V$$

$$\times [\partial\boldsymbol{\rho}(\mathbf{r}')/\partial N]_V^{\mathrm{T}} \mathrm{d}\mathbf{r}\, \mathbf{d}\mathbf{r}' = \int\int \mathbf{F}(\mathbf{r})\boldsymbol{\eta}(\mathbf{r}, \mathbf{r}')\mathbf{F}(\mathbf{r}')^{\mathrm{T}} \mathrm{d}\mathbf{r}\, \mathbf{d}\mathbf{r}' \quad (82a)$$

The subsystem resolved analog of the local hardness equalization principle now reads:

$$\boldsymbol{\eta}(\mathbf{r}) = [\partial\boldsymbol{\mu}(\mathbf{r})/\partial N]_V = \int [\partial^2 E_V[\boldsymbol{\rho}]/\partial\boldsymbol{\rho}(\mathbf{r})\partial\boldsymbol{\rho}')]_V [\partial\boldsymbol{\rho}(\mathbf{r}')/\partial N]_V^{\mathrm{T}} \mathrm{d}\mathbf{r}'$$

$$= \int \boldsymbol{\eta}(\mathbf{r}, \mathbf{r}')\mathbf{F}(\mathbf{r}')^{\mathrm{T}} \mathrm{d}\mathbf{r}' = [\partial\boldsymbol{\mu}/\partial N]_V = \mathbf{H} \quad (82b)$$

where we have used the intra-subsystem chemical potential equalization of equation (60).

10. TRANSFORMATIONS OF PERTURBATIONS INTO RESPONSES

In the global equilibrium state, when all constituent subsystems are mutually open, the transformations of infinitesimal displacements (*perturbations*) of the global and local parameters of state, which determine the Legendre transformed representation under consideration, into differentials of the respective conjugate state-variables (*responses*) can be summarized in terms of the following matrix integral equations [4,5,8,12,13]:

In the $\{N, v\}$-representation :

$$[\mathrm{d}\mu, \mathrm{d}\rho(\mathbf{r})] = [\mathrm{d}N, \int \mathrm{d}\mathbf{r}'\, \mathrm{d}v(r')] \begin{bmatrix} \eta & f(\mathbf{r}) \\ f(\mathbf{r}') & \beta(\mathbf{r}', \mathbf{r}) \end{bmatrix}$$

$$\equiv [\mathrm{d}N, \mathrm{d}v]\, \mathbf{T}[\{N, v\} \to \{\mu, \rho\}] \quad (83)$$

The inverse, $\{\mu, \rho\}$-representation gives rise to the following transformation:

$$[\mathrm{d}N, \mathrm{d}v(\mathbf{r})] = [\mathrm{d}\mu, \int \mathrm{d}\mathbf{r}'\ \mathrm{d}\rho(\mathbf{r}')] \begin{bmatrix} 0 & 1 \\ 1 & -\eta(\mathbf{r}', \mathbf{r}) \end{bmatrix}$$
$$\equiv [\mathrm{d}\mu, \mathrm{d}\rho]\ \mathbf{T}[\{\mu, \rho\} \rightarrow \{N, v\}] \tag{84}$$

with $\mathbf{T}[\{\mu, \rho\} \rightarrow \{N, v\}] = \mathbf{T}[\{N, v\} \rightarrow \{\mu, \rho\}]^{-1}$.

In the case of the $\{N \rightarrow \rho\} = \{\rho\}$-representation the perturbations → responses transformation similarly reads:

$$\mathrm{d}u(\mathbf{r}) = -\int \mathrm{d}\boldsymbol{\rho}(\mathbf{r}')\eta(\mathrm{r}', \mathbf{r})\mathrm{d}\mathbf{r}' \equiv \mathrm{d}\rho\ \mathbf{T}[\rho \rightarrow u] \tag{85}$$

It has been demonstrated recently [12,13], that this transformation can be further resolved into the corresponding matrix relation linking the independent displacements of N (*external CT*) and the N-conserving changes in the *internal density* $\rho^i(\mathbf{r})$ [*internal polarization* (P)] with the responses in the conjugate state-variables μ and $v(\mathbf{r})$, respectively. This (P, CT)-separation of displacements in molecular electronic structure is achieved by using the appropriately defined Hilbert space of the P and CT vectors. This separation leads to the corresponding partition of charge sensitivities and the associated transformation: $[\mathrm{d}\mu, \mathrm{d}v(\mathbf{r})] = [\mathrm{d}N, \mathrm{d}\rho^i]\ \mathbf{T}[\{N, \rho^i\} \rightarrow \{\mu, v\}]$.

Finally, within the $\{\mu, v\}$- or $\{u\}$-representation, the softness kernel defines the transformation:

$$\mathrm{d}\rho(\mathbf{r}) = -\int \mathrm{d}u(\mathbf{r}')\sigma(\mathbf{r}', \mathbf{r})\mathrm{d}\mathbf{r}' \equiv \mathrm{d}u\ \mathbf{T}[u \rightarrow \rho], \qquad \mathrm{d}N[\rho] = \int \mathrm{d}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \tag{86}$$

where $\mathbf{T}[u \rightarrow \rho] = \mathbf{T}[\rho \rightarrow u]^{-1}$ [see equation (85)]. It can be also resolved [12,13] into the equivalent form corresponding to the transformation of perturbations $[\mathrm{d}\mu, \mathrm{d}v(\mathbf{r}')]$ into responses $[\mathrm{d}N, \mathrm{d}\rho^i(\mathbf{r})]$, $\mathbf{T}[\{\mu, v\} \rightarrow \{N, \rho^i\}] = \mathbf{T}[\{N, \rho^i\} \rightarrow \{\mu, v\}]^{-1}$.

When the constituent subsystems are mutually closed (in molecular fragment resolution), the corresponding matrices of charge sensitivities replace the global quantities in the corresponding four *perturbation* → *response* transformations:

In the $\{\mathsf{N}, \mathsf{V}\}$-representation:

$$[\mathrm{d}\boldsymbol{\mu}, \mathrm{d}\boldsymbol{\rho}(\mathbf{r})] = [\mathrm{d}\mathsf{N}, \int \mathrm{d}\mathbf{r}'\ \mathrm{d}\mathsf{V}(\mathbf{r}')] \begin{bmatrix} \mathbf{H} & \mathbf{F}(\mathbf{r}) \\ \mathbf{F}(\mathbf{r}')^{\mathrm{T}} & \mathbf{B}(\mathbf{r}', \mathbf{r}) \end{bmatrix}$$
$$\equiv [\mathrm{d}\mathsf{N}, \mathrm{d}\mathsf{V}]\ \mathbf{T}[(\mathsf{N}, \mathsf{V}\} \rightarrow \{\boldsymbol{\mu}, \boldsymbol{\rho}\}] \tag{87}$$

In the $\{\boldsymbol{\mu}, \boldsymbol{\rho}\}$-representation:

$$[\mathrm{d}N, \mathrm{d}V(\mathbf{r})] = [\mathrm{d}\boldsymbol{\mu}, \int \mathrm{d}\mathbf{r}' \, \mathrm{d}\boldsymbol{\rho}(\mathbf{r}')] \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ \mathbf{I} & -\boldsymbol{\eta}(\mathbf{r}', \mathbf{r}) \end{bmatrix}$$

$$\equiv [\mathrm{d}\boldsymbol{\mu}, \mathrm{d}\boldsymbol{\rho}] \, \mathbf{T}[\{\boldsymbol{\mu}, \boldsymbol{\rho}\} \to \{N, V\}] \tag{88}$$

with $\mathbf{T}[\{\boldsymbol{\mu}, \boldsymbol{\rho}\} \to \{N, V\}] = \mathbf{T}[\{N, V\} \to \{\boldsymbol{\mu}, \boldsymbol{\rho}\}]^{-1}$.

In the $\{N, \boldsymbol{\rho}\}$- or $\{\boldsymbol{\rho}\}$-representation:

$$\mathrm{d}\mathbf{u}(\mathbf{r}) = -\int \mathrm{d}\boldsymbol{\rho}(\mathbf{r}')\boldsymbol{\eta}(\mathbf{r}', \mathbf{r})\mathrm{d}\mathbf{r}' \equiv \mathrm{d}\boldsymbol{\rho} \, \mathbf{T}[\boldsymbol{\rho} \to \mathbf{u}] \tag{89}$$

or the equivalent transformation $[\mathrm{d}\boldsymbol{\mu}, \mathrm{d}V] = [\mathrm{d}N, \mathrm{d}\boldsymbol{\rho}^i] \, \mathbf{T}[\{N, \boldsymbol{\rho}^i\} \to \{\boldsymbol{\mu}, V\}]$, where the internal densities of subsystems $\boldsymbol{\rho}^i$ conserve the overall numbers of electrons N [12,13].

In the $\{\boldsymbol{\mu}, V\} = \{\mathbf{u}\}$-representation:

$$\boldsymbol{\rho}(\mathbf{r}) = -\int \mathrm{d}\mathbf{u}(\mathbf{r}')\boldsymbol{\sigma}(\mathbf{r}', \mathbf{r})\mathrm{d}\mathbf{r}' \equiv \mathrm{d}\mathbf{u} \, \mathbf{T}[\mathbf{u} \to \boldsymbol{\rho}], \qquad \mathrm{d}N[\boldsymbol{\rho}] = \int \mathrm{d}\boldsymbol{\rho}[\mathbf{r}]\mathrm{d}\mathbf{r} \tag{90}$$

where $\mathbf{T}[\mathbf{u} \to \boldsymbol{\rho}] = \mathbf{T}[\boldsymbol{\rho} \to \mathbf{u}]^{-1}$, or equivalently the transformation $\mathbf{T}[\{\boldsymbol{\mu}, V\} \to \{N, \boldsymbol{\rho}^i\}] = \mathbf{T}[\{N, \boldsymbol{\rho}^i\} \to \{\boldsymbol{\mu}, V\}]^{-1}$ [12,13].

11. HIRSHFELD DIVISION OF THE MOLECULAR GROUND-STATE DENSITY

There has been a renewed interest in the Hirshfeld (‘stockholder’) partitioning [34] of the molecular electronic density into fragment densities, e.g., those of bonded atoms [20–26,28,29,33], created by the recent demonstration [20,26,33] of the information-theoretic basis of this division scheme. It was shown, that the Hirshfeld densities minimize the so called *missing information* [107] contained in the fragment densities relative to the separated atoms defining the ‘promolecule’ of the familiar density difference diagrams. The information-theoretic outlook on molecular fragments has also given rise to a new, thermodynamic-like, entropic description of molecular subsystems [23,33].

This entropic approach to bonded fragments in a molecule has created a new impetus to a search for novel, information-distance measures of the chemical bond multiplicities [27,28]. The resulting entropic ‘bond-orders’ reflect upon the molecular ‘communication’ system involving the ‘promolecular’ *input* probability scheme and the molecular *output* probability scheme, of finding electrons on specified AIM. Clearly, the promolecule probabilities of atomic assignments are modified in a molecule as a result of the communication ‘noise’ created by the electron delocalization throughout the molecular system, via a network of the chemical bonds. Specific entropy differences have been found to reflect both the global and localized covalent and ionic bond components; they have been successfully tested against accepted chemical intuition on several model systems [27,28]. A similar approach to problems of molecular similarity has also been suggested [20] and the intermediate, polarized AIM densities, before the inter-atomic CT, have been defined [21] using the minimum entropy deficiency principle of Kullback and Leibler. These entropy differences measure various information distances between the 'promolecular' and molecular probability schemes. They involve both the one-electron probabilities in atomic resolution and the simultaneous probabilities of finding two (or three) electrons on specified AIM.

Clearly, the atomic assignments of electrons depend on the specific atomic discretization scheme used. In this respect, the Hirshfeld partitioning appears to be particularly promising, since the 'stockholder' atoms represent well behaving, equilibrium densities (see Fig. 1), which conserve the most of the information contained in the isolated constituent atoms of the 'promolecule'. It has been shown [33], that they may be assigned within the subsystem-resolved DFT the effective external potentials [see equation (32)], for which they are the ground-state densities. In other words, they represent the *v-representable* subsystem densities. This important feature also implies that the familiar causal outlook on the electronic structure of bonded atoms, of the subsystem density representing the equilibrium distribution in the effective external potential due to a changing chemical environment in the molecule, can be rigorously invoked within such

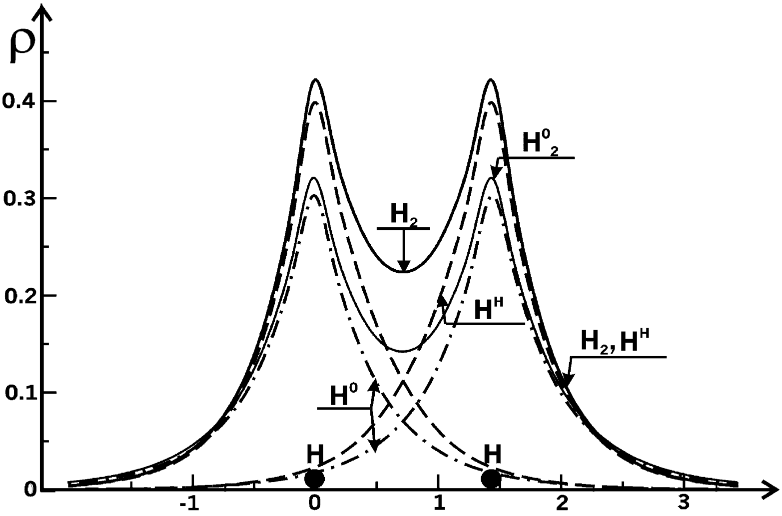

Fig. 1. The Hirshfeld electron densities (H^H) of bonded hydrogen atoms obtained from the molecular density (H_2). The free hydrogen densities (H^0) and the resulting electron density of the promolecule (H_2^0) are also shown for comparison. The density values and inter-nuclear distances are in a.u. The zero cusp at nuclear positions is the artifact of the Gaussian basis set used in DFT calculations.

a ‘thermodynamic’ description, in close analogy the ordinary thermodynamics. Such thermodynamic analogies can be also extended into the realm of non-equilibrium processes, including instantaneous density fluctuations and irreversible flows electrons between molecular subsystems [23].

Obviously, a given division of the molecular electron density into atomic contributions also implies the associated partitioning of the molecular one-electron probability distribution (*shape function*), since a straightforward renormalization of the Hirshfeld subsystem electron densities gives the associated subsystem shape functions. However, the entropic measures of the bond multiplicities also involve the simultaneous and conditional two-electron probabilities in atomic resolution [27,28]. An extension of the ‘stockholder’ principle to many-electron probabilities has also been tackled [22] using the minimum entropy deficiency principle appropriately reformulated in terms of the many-electron densities (or shape functions), referenced to the corresponding quantities of the separated-fragments defining the relevant promolecule system (see Section 12).

Let us begin a survey of this development with a brief reminder of the Hirshfeld (H) partition scheme and its information-theoretic justification. The ‘stockholder’ division [34] of the molecular electron density $\rho(\mathbf{r})$, experimental or theoretical, into the AIM densities, $\rho(\mathbf{r}) = \sum_\alpha \rho_\alpha^H(\mathbf{r})$,

$$\boldsymbol{\rho}^{H}(\mathbf{r}) \equiv \{\rho_\alpha^H(\mathbf{r}) = [\rho_\alpha^0(\mathbf{r})/\rho^0(\mathbf{r})]\rho(\mathbf{r}) \equiv D_\alpha^0(\mathbf{r})\rho(\mathbf{r}) \equiv \rho_\alpha^H(\rho;\mathbf{r}) \equiv w(\mathbf{r})\rho_\alpha^0(\mathbf{r})\} \qquad (91a)$$

where $\boldsymbol{\rho}^0(\mathbf{r}) \equiv \{\rho_\alpha^0(\mathbf{r})\}$ and $\rho^0(\mathbf{r}) = \sum_\alpha \rho_\alpha^0(\mathbf{r})$ stand for the isolated atom and the so called ‘promolecule’ densities, respectively. Let us recall, that the promolecule reference density of the familiar density difference function, $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho^0(\mathbf{r})$, consists of the isolated atom densities shifted to the atomic position in the molecule.

The original justification for this exhaustive division of $\rho(\mathbf{r})$ was the ‘stockholder’ principle, that the AIM should participate in the local molecular ‘profit’, $\rho(\mathbf{r})$, in proportion to the their ‘shares’ $\{D_\alpha^0(\mathbf{r})\}$ in the overall promolecular ‘investment’, $\rho^0(\mathbf{r})$:

$$D_\alpha^0(\mathbf{r}) \equiv \rho_\alpha^0(\mathbf{r})/\rho^0(\mathbf{r}) = D_\alpha(\mathbf{r}) \equiv \rho_\alpha^H(\mathbf{r})/\rho(\mathbf{r}) \qquad (91b)$$

It has been shown [20], that this partitioning minimizes the information distance (missing information, entropy deficiency, directed divergence) [107],

$$\Delta\mathcal{H}[\boldsymbol{\rho} \to \rho|\boldsymbol{\rho}^0 \to \rho^0] \equiv \Delta\mathcal{H}[\boldsymbol{\rho}|\boldsymbol{\rho}^0] = \sum_\alpha \int \rho_\alpha(\mathbf{r})\ln[\rho_\alpha(\mathbf{r})/\rho_\alpha^0(\mathbf{r})]d\mathbf{r}$$

$$\equiv \sum_\alpha \Delta\mathcal{H}_\alpha[\rho_\alpha|\rho_\alpha^0] \equiv \sum_\alpha \int \Delta h_\alpha(\mathbf{r})d\mathbf{r} \equiv \int \Delta h(\mathbf{r})d\mathbf{r} \qquad (92)$$

between the AIM densities yielding a given molecular density, $\boldsymbol{\rho}(\mathbf{r}) \to \rho(\mathbf{r})$, and the reference, free atom densities, which give rise to the ‘promolecule’ density, $\boldsymbol{\rho}^0(\mathbf{r}) \to \rho^0(\mathbf{r})$. More specifically, the Hirshfeld pieces of molecular density satisfy the variational principle of the maximum information similarity to the free atom densities subject to the local side condition of the exhaustive partitioning:

$$\delta\{\Delta\mathcal{H}[\boldsymbol{\rho}|\boldsymbol{\rho}^0] - \int \lambda(\mathbf{r})\sum_{\alpha}\rho_\alpha(\mathbf{r})d\mathbf{r}\} = 0 \quad \Rightarrow \quad \boldsymbol{\rho} = \boldsymbol{\rho}^{\mathrm{H}}, \quad \text{or}$$

$$\min \Delta\mathcal{H}[\boldsymbol{\rho} \to \rho|\boldsymbol{\rho}^0 \to \rho^0] = \Delta\mathcal{H}[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^0] = \int \rho(\mathbf{r})\ln[\rho(\mathbf{r})/\rho^0(\mathbf{r})]d\mathbf{r}$$

$$\equiv \Delta\mathcal{H}[\rho|\rho^0] = \int \Delta h(\mathbf{r})d\mathbf{r} \qquad (93a)$$

where $\lambda(\mathbf{r})$ stands for the Lagrange multiplier function associated with the local constraint: $\sum_\alpha \rho_\alpha(\mathbf{r}) = \rho(\mathbf{r})$. The same result is obtained when other, Shannon entropy related measure of the information distance, e.g., the symmetrized entropy deficiency (divergence, [17]) is adopted ([24,30]). Therefore, the stockholder atoms, by preserving as much as possible of the information contained in the densities of the free atoms, have a solid theoretical basis in the information theory. A reference to Fig. 1 also shows that they exhibit a single cusp at the atomic nucleus and decay exponentially with increasing distance from it. It has also been demonstrated [21] that they are very weakly dependent on alternative choices of the 'promolecule' reference, with the *atomic* 'promolecule' being uniquely identified as the preferred one in chemical interpretations, by both the accepted chemical convention and by the truly non-bonded status of the atomic fragments in such a reference state.

It has also been shown [33] that only for the Hirshfeld partitioning the local measures of the information contained in atomic components, e.g., local entropies, surprisals, or the information 'temperatures', of such mutually open subsystems equalize. We shall discuss this subject in a more detail in Section 16. This local information-distance equalization principles represent a novel, entropic criterion of the *equilibrium* between the molecular subsystems. This condition is complementary to the energetic criterion of the subsystem chemical potential (electronegativity) equalization of Sanderson [see equation (59)]. The latter is satisfied for any exhaustive division of the ground-state density among the mutually open subsystems, thus failing to distinguish one partition from another. The entropic *stability* of the stockholder partitioning have also been demonstrated [33].

It has recently been observed [22,26] that the 'stockholder' principle of equation (91b) in fact states the equality between the local *conditional* probabilities: $\{D_\alpha^0(\mathbf{r}) \equiv p^0(\alpha|\mathbf{r})\} \equiv \mathbf{p}^0(\mathbf{r})$ and $D_\alpha(\mathbf{r}) \equiv p(\alpha|\mathbf{r})\} \equiv \mathbf{p}(\mathbf{r})$, that an electron found at a given location in space originates from the specified free or bonded subsystem. Thus, a restatement of the information principle, more appropriate to justify the 'stockholder' rule, should be in terms of these conditional probabilities. Indeed, for a given location in space the following local variational principle is satisfied [26]:

$$\delta\{\Delta\mathcal{H}[\mathbf{p}(\mathbf{r})|\mathbf{p}^0(\mathbf{r})] - \xi\sum_{\alpha} p(\alpha|\mathbf{r})\} = 0, \quad \Rightarrow \quad \mathbf{p}(\mathbf{r}) = \mathbf{p}^0(\mathbf{r}) \equiv \mathbf{p}^{\mathrm{H}}(\mathbf{r}) \qquad (93b)$$

where $\Delta\mathcal{H}[\mathbf{p}(\mathbf{r})|\mathbf{p}^0(\mathbf{r})] = \sum_\alpha p(\alpha|\mathbf{r})\ln[p(\alpha|\mathbf{r})/p^0(\alpha|\mathbf{r})]$ and ξ is the Lagrange multiplier enforcing the normalization of conditional probabilities: $\sum_\alpha p(\alpha|\mathbf{r}) = 1$.

It is also of interest to compare the densities $\Delta\mathfrak{H}(\mathbf{r})$ of the Shannon entropy displacements for the molecule as a whole,

$$\Delta\mathcal{H}=\mathcal{H}[\rho]-\mathcal{H}[\rho^0]\equiv\int\Delta\mathfrak{H}(\mathbf{r})d\mathbf{r},\quad \mathcal{H}[\rho]=-\int\rho(\mathbf{r})\ \ln\rho(\mathbf{r})d\mathbf{r},\ \text{etc.}\tag{94}$$

with the familiar density difference function, $\Delta\rho(\mathbf{r})=\rho(\mathbf{r})-\rho^0(\mathbf{r})$. This is the subject of Fig. 2 reporting the relevant contour diagrams and profiles for selected diatomics and triatomics.

The corresponding plots for the atomic density and the integrands of the entropy displacements of the Hirshfeld AIM,

$$\Delta\rho_\alpha^{\mathrm{H}}(\mathbf{r})=\rho_\alpha^{\mathrm{H}}(\mathbf{r})-\rho_\alpha^0(\mathbf{r}),\ \ \Delta\mathcal{H}_\alpha^{\mathrm{H}}=\mathcal{H}[\rho_\alpha^{\mathrm{H}}]-\mathcal{H}[\rho_\alpha^0]\equiv\int\Delta\mathfrak{H}_\alpha^{\mathrm{H}}(\mathbf{r})d\mathbf{r}\tag{95}$$

are shown in Fig. 3.

A reference to Figs 2 and 3 shows that qualitatively the density and entropy displacement functions are very similar, with the latter providing a somewhat more resolved picture of entropy/information changes in the valence shell. These plots demonstrate that both functions can be used to probe changes in the electronic structure due to bond formation in molecules, reflecting the ‘promotion’ (polarization) of bonded atoms in the molecular *valence state*, as a result of the electron excitation and orbital hybridization, and the inter-atomic electron CT effects.

12. MINIMUM ENTROPY DEFICIENCY PARTITIONING OF MANY-ELECTRON DENSITIES

Consider the k-electron molecular density [22], $\Theta_k(\mathbf{r}_1=\mathbf{r},\mathbf{r}_2=\mathbf{r}',\ldots,\mathbf{r}_k=\mathbf{r}'')\equiv\Theta_k(\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'')$, $1<k\le N$, of simultaneously finding one electron at $\mathbf{r}$, another at $\mathbf{r}'$, etc.,

$$\Theta_k(\mathbf{r},\ldots,\mathbf{r}'')=\langle\Psi|\rho_k(\mathbf{r},\ldots,\mathbf{r}'')|\Psi\rangle\tag{96}$$

defined by the expectation value for a given molecular state $\Psi(\mathbf{q})=\Psi(1,2,\ldots,N)$ of the corresponding k-electron density operator,

$$\rho_k(\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'')=\sum_i\sum_{j\neq i}\cdots\sum_{l\neq\cdots\neq j\neq i}\delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j-\mathbf{r}')\cdots\delta(\mathbf{r}_l-\mathbf{r}'')\tag{97}$$

Let $\Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'')$ denotes the corresponding ‘promolecule’ k-electron density:

$$\Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'')=\langle\Psi^0|\rho_k(\mathbf{r},\ldots,\mathbf{r}'')|\Psi^0\rangle\tag{98}$$

where $\Psi^0(\mathbf{q})=\Psi^0(1,2,\ldots,N)$ denotes the corresponding (isoelectronic) state of the m free constituent atoms, given by the product of the (antisymmetric) atomic states $\{\Phi_\alpha^0(1,\ldots,N_\alpha^0)\}$,

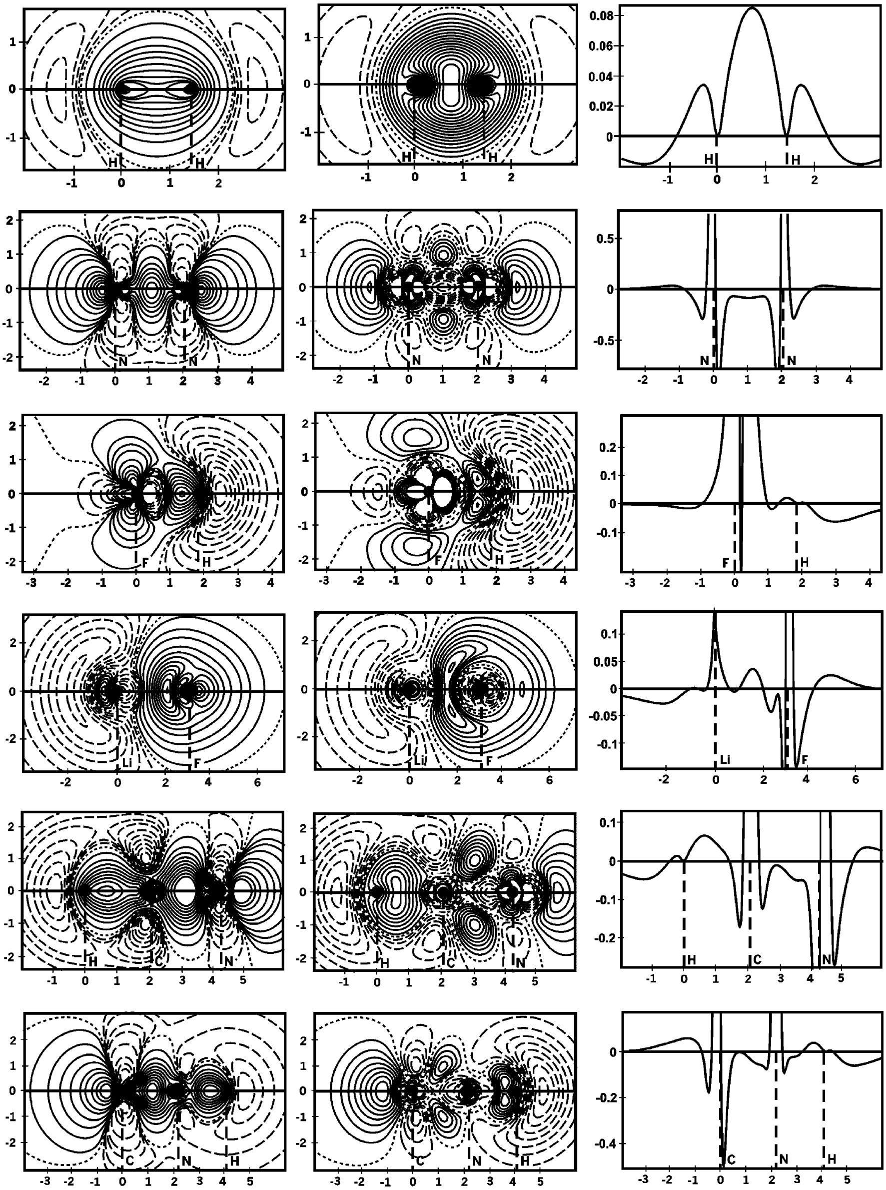

Fig. 2. A comparison between contour diagrams of the density difference $\Delta\rho(\mathbf{r})$ (first column) and entropy difference $\Delta\mathfrak{S}(\mathbf{r})$ (second column) functions for representative diatomics (H_2, N_2, HF, LiF) and linear triatomics (HCN and HNC). In view of the qualitative nature of this comparison, to show more dramatically the overall similarity of the two surfaces not equidistant contour values have been selected. The corresponding profiles of $\Delta\mathfrak{S}(\mathbf{r})$, for the cuts along the bond axis, are shown in the third column of the figure ([29]).

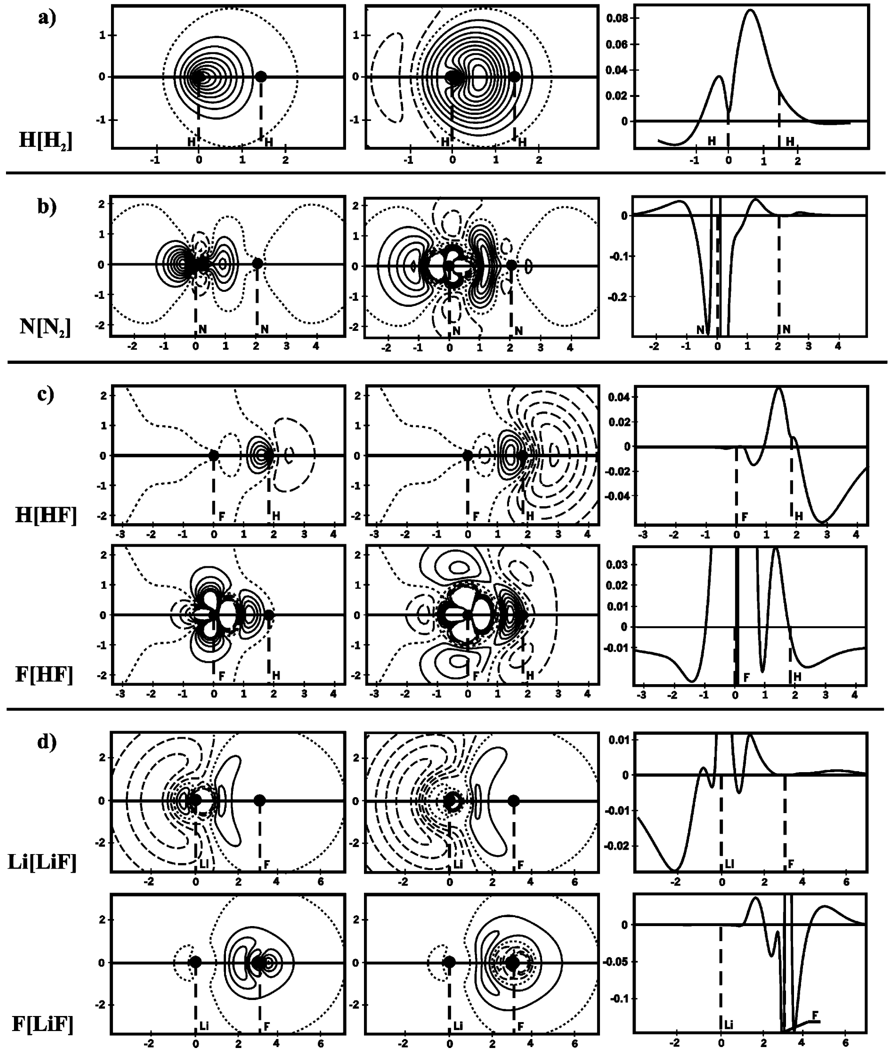

Fig. 3. Representative (equidistant) contour maps of $\Delta\rho_X^{\mathrm{H}}(\mathbf{r})$ (first panel), $\Delta\mathfrak{H}_\alpha^{\mathrm{H}}(\mathbf{r})$ (second panel) and the $\Delta\mathfrak{H}_\alpha^{\mathrm{H}}(\mathbf{r})$ profile of the cut along the bond axis (third panel), for the constituent atoms of typical diatomics: H_2 (a), N_2 (b), HF (c), and LiF (d) ([29]).

$$\begin{aligned}\Psi^0(1,2,\ldots,N) = &\Phi_1^0(1,\ldots,N_1^0)\Phi_2^0(N_1^0+1,\ldots,N_1^0+N_2^0)\cdots\\ &\times\Phi_m^0(N-N_m^0+1,\ldots,N)\end{aligned} \qquad (99)$$

This reference function describes the *distinguishable* groups of electrons on independent, free atoms, with the electrons of a given group being mutually *indistinguishable*. This reference assignment of electrons to the corresponding atoms uniquely partitions the density operator of equation (97) the into atomically resolved contributions:

$$\rho_k(\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'') = \sum_\alpha \sum_{i\in\alpha} \sum_\beta \sum_{j\in\beta} \cdots \sum_\gamma \sum_{l\in\gamma} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}')\ldots,\delta(\mathbf{r}_l - \mathbf{r}'')$$

$$\equiv \sum_\alpha \sum_\beta \cdots \sum_\gamma \rho_k(\alpha,\beta,\ldots,\gamma|\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'') \tag{100}$$

which define the associated atomic partitioning of $\Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'')$:

$$\Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'') = \sum_\alpha \sum_\beta \cdots \sum_\gamma \langle \Psi^0 | \rho_k(\alpha,\beta,\ldots,\gamma|\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'')|\Psi^0\rangle$$

$$\equiv \sum_\alpha \sum_\beta \cdots \sum_\gamma \Theta_k^0(\alpha,\beta,\ldots,\gamma|\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'') \tag{101}$$

into the separated AIM contributions $\{\Theta_k^0(\alpha,\beta,\ldots,\gamma|\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'')\}$, corresponding to clusters of k atomic labels $(\alpha,\beta,\ldots,\gamma)$ assigned to k electrons at indicated positions in space.

We are interested in the optimum partition of the known k-electrom density in a molecule in the AIM (or subsystem) resolution satisfying the exhaustive division constraint:

$$\Theta_k(\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'') = \sum_\alpha \sum_\beta \cdots \sum_\gamma \Theta_k(\alpha,\beta,\ldots,\gamma|\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}'') \tag{102}$$

The k-electron generalized information-theoretic criterion of equation (93) now reads [22]:

$$\begin{aligned}
&\min \Delta\mathcal{H}[\{\Theta_k(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')\} \to \Theta_k(\mathbf{r},\ldots,\mathbf{r}'')|\{\Theta_k^0(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')\}\\
&\qquad\qquad\qquad\qquad \to \Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'')]\\
&= \Delta\mathcal{H}[\{\Theta_k^S(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')\}|\{\Theta_k^0(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')\}]\\
&= \int\cdots\int \Theta_k(\mathbf{r},\ldots,\mathbf{r}'')\ln[\Theta_k(\mathbf{r},\ldots,\mathbf{r}'')/\Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'')]d\mathbf{r},\ldots,d\mathbf{r}''\\
&\equiv \Delta\mathcal{H}[\Theta_k|\Theta_k^0]
\end{aligned} \tag{103}$$

The optimum ('stockholder') k-electron fragments $\{\Theta_k^S(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')\}$ are then uniquely determined by the molecular and 'promolecular' k-electron densities [22]:

$$\begin{aligned}
\Theta_k^S(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'') &= [\Theta_k^0(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')/\Theta_k^0(\mathbf{r},\ldots,\mathbf{r}'')]\Theta_k(\mathbf{r},\ldots,\mathbf{r}'')\\
&\equiv D_{\alpha,\ldots,\gamma}(\mathbf{r},\ldots,\mathbf{r}'')\Theta_k(\mathbf{r},\ldots,\mathbf{r}'') \equiv w^{(k)}(\mathbf{r},\ldots,\mathbf{r}'')\Theta_k^0(\alpha,\ldots,\gamma|\mathbf{r},\ldots,\mathbf{r}'')
\end{aligned} \tag{104}$$

Therefore (see equation (103)), these Hirshfeld-type k-electron density pieces in the AIM resolution minimize the information distance, from the corresponding promolecule (free atom) distributions, to the lowest level possible, i.e., to the missing information between the global molecular and 'promolecular' k-electron densities. Again, as in the one-electron case, they are the entropy equilibrium, stable, infinitely extending fragments of the molecular k-electron distribution, of simultaneously finding k electrons ascribed to the specified cluster of AIM, at specified locations in space. The corresponding derivation of this principle from the entropy deficiency principle in terms of the local conditional k-electron probabilities is straightforward.

The same 'stockholder' division principle applies to the associated k-electron probability distribution (k-electron shape function):

$$\begin{aligned}
&\theta_k(\mathbf{r},...,\mathbf{r}'') = \Theta_k(\mathbf{r},...,\mathbf{r}'')/[N(N-1)\cdots,(N-k+1)],\\
&\int\cdots\int \theta_k(\mathbf{r},...,\mathbf{r}'')\mathrm{d}\mathbf{r}\cdots\mathrm{d}\mathbf{r}'' = 1\\
&\theta_k(\mathbf{r},...,\mathbf{r}'') = \sum_{\alpha}\cdots\sum_{\gamma} \theta_k^{\mathrm{S}}(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}''),\\
&\theta_k^{\mathrm{S}}(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}'') = [\theta_k^0(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}'')/\theta_k^0(\mathbf{r},...,\mathbf{r}'')]\theta_k(\mathbf{r},...,\mathbf{r}'')\\
&\quad = \Theta_k^{\mathrm{S}}(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}'')/N(N-1)\cdots(N-k+1)] \qquad (105)
\end{aligned}$$

where the AIM division of the known 'promolecular' shape function

$$\theta_k^0(\mathbf{r},...,\mathbf{r}'') = \Theta_k^0(\mathbf{r},...,\mathbf{r}'')/[N(N-1)...,(N-k+1)] \qquad (106)$$

reads:

$$\begin{aligned}
&\theta_k^0(\mathbf{r},...,\mathbf{r}'') = \sum_{\alpha}\cdots\sum_{\gamma} \theta_k^0(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}''), \quad \int\cdots,\int \theta_k^0(\mathbf{r},...,\mathbf{r}'')\mathrm{d}\mathbf{r}\cdots\mathrm{d}\mathbf{r}'' = 1\\
&\theta_k^0(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}'') = \Theta_k^0(\alpha,...,\gamma|\mathbf{r},...,\mathbf{r}'')/[N(N-1)\cdots(N-k+1)] \qquad (107)
\end{aligned}$$

The 'stockholder' principle thus provides the unique scheme for partitioning the simultaneous probabilities of $1 < k \leq N$ electrons among the clusters of constituent AIM, when the natural free-atom reference is applied. By an appropriate integration, each k-electron AIM probability components, generate slightly different, *effective* one-electron probability distributions of constituent atoms. These 'stockholder' k-electron probabilities of the AIM clusters can then be used to define the so called 'stockholder' AIM *loges*, in the spirit of Daudel's theory [139–141], and in solving the problem of a truly unbiased effective one-electron distributions of molecular fragments [25], given by an appropriate weighted average of the effective one-electron densities derived from partitioning the k-electron distributions, where $1 < k \leq N$.

It should be finally recalled, that the Loge Theory has made a vital connection between the Information Theory and the theory of electronic structure [142], i.e., a link between the entropy/information concept and the electron distributions in atomic and molecular systems. The latter have been previously exploited mainly in the context of the energy representation. The very fact that the electron densities lend themselves to the information-theoretic analysis has prompted further research into the entropy/information treatments of atomic and molecular systems.

13. CHARGE SENSITIVITIES OF THE STOCKHOLDER ATOMS

Equation (91a) implies the following relation between the local displacement of the overall (molecular) ground-state density and the corresponding changes in densities of the Hirshfeld AIM:

$$\mathrm{d}\rho_\alpha^{\mathrm{H}}(\mathbf{r}) = D_\alpha(\mathbf{r})\,\mathrm{d}\rho(\mathbf{r}), \qquad \alpha = 1, 2, \ldots, m \tag{108}$$

This gives the following relations between the Hirshfeld AIM density response properties and those of the molecular density as a whole [22]:

$$\begin{gathered}
[\delta\rho_\alpha^{\mathrm{H}}(\mathbf{r}')/\delta v(\mathbf{r})]_N \equiv \beta_\alpha^{\mathrm{H}}(\mathbf{r},\mathbf{r}') = \beta(\mathbf{r},\mathbf{r}')D_\alpha(\mathbf{r}'),\\
[\partial\rho_\alpha^{\mathrm{H}}(\mathbf{r})/\partial\mu]_v \equiv s_\alpha^{\mathrm{H}}(\mathbf{r}) = s(\mathbf{r})D_\alpha(\mathbf{r}),\\
-\delta\rho_\alpha^{\mathrm{H}}(\mathbf{r}')/\delta u(\mathbf{r}) = -[\delta\rho_\alpha^{\mathrm{H}}(\mathbf{r}')/\delta v(\mathbf{r})]_\mu \equiv \sigma_\alpha^{\mathrm{H}}(\mathbf{r},\mathbf{r}') = \sigma(\mathbf{r},\mathbf{r}')D_\alpha(\mathbf{r}'),\\
[\partial\rho_\alpha^{\mathrm{H}}(\mathbf{r})/\partial N]_v \equiv f_\alpha^{\mathrm{H}}(\mathbf{r}) = f(\mathbf{r})D_\alpha(\mathbf{r})
\end{gathered} \tag{109}$$

By integrating the preceding equation one finds the 'normalized' response in $N_\alpha^{\mathrm{H}} = \int \rho_\alpha^{\mathrm{H}}(\mathbf{r})\mathrm{d}\mathbf{r}$, per unit shift in the global number of electrons:

$$[\partial N_\alpha^{\mathrm{H}}/\partial N]_v = \int f_\alpha^{\mathrm{H}}(\mathbf{r})\mathrm{d}\mathbf{r} = \int f(\mathbf{r})D_\alpha(\mathbf{r})\mathrm{d}\mathbf{r} \tag{110}$$

Also, by the Hellmann–Feynman theorem,

$$\rho_\alpha^{\mathrm{H}}(\mathbf{r}) = \{\partial\varepsilon_\alpha[\boldsymbol{\rho}^{\mathrm{H}}, v]/\partial v(\mathbf{r})\}_{\boldsymbol{\rho}} \tag{111}$$

where the partial differentiation is carried out for the 'frozen' subsystem densities and the differential of the energy in the Hirshfeld AIM resolution reads:

$$\begin{aligned}
\mathrm{d}E_v[\boldsymbol{\rho}^{\mathrm{H}}] &= \sum_\alpha \int \{\partial E_v[\boldsymbol{\rho}^{\mathrm{H}}]/\partial\rho_\alpha^{\mathrm{H}}(\mathbf{r})\}_v\,\mathrm{d}\rho_\alpha^{\mathrm{H}}(\mathbf{r})\mathrm{d}\mathbf{r} + \int \{\partial E_v[\rho]/\partial v(\mathbf{r})\}_v \mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r}\\
&\equiv \sum_\alpha \int \mu_\alpha^{\mathrm{H}}(\mathbf{r})\mathrm{d}\rho_\alpha^{\mathrm{H}}(\mathbf{r})\mathrm{d}\mathbf{r} + \int \rho(\mathbf{r})\mathrm{d}v(\mathbf{r})\mathrm{d}\mathbf{r}
\end{aligned} \tag{112}$$

where the row vector of the Hirshfeld subsystem densities $\boldsymbol{\rho}^{\mathrm{H}}[\rho] = (\rho_\alpha^{\mathrm{H}}[\rho], \rho_\beta^{\mathrm{H}}[\rho], \ldots,)$. One also derives from the global equilibrium chemical potential/electronegativity equalization principle of equation (58) the corresponding relations for the functional derivatives with respect to the Hirshfeld AIM densities, defined in the preceding equation, in terms of the associated derivatives with respect to the overall molecular density. In particular, one finds [33] that the so called *Hirshfeld potentials* of equation (112),

$$\boldsymbol{\mu}^{\mathrm{H}}(\mathbf{r}) \equiv \{\partial E_v[\boldsymbol{\rho}^{\mathrm{H}}]/\partial \boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})\}_v = \{[\partial E_v[\boldsymbol{\rho}^{\mathrm{H}}]/\partial \rho_\alpha^{\mathrm{H}}(\mathbf{r})]_v$$
$$= [\partial E_v[\rho]/\partial \rho(\mathbf{r})]_v[\mathrm{d}\rho(\mathbf{r})/\mathrm{d}\rho_\alpha^{\mathrm{H}}(\mathbf{r})] = \mu/D_\alpha(\mathbf{r}) \equiv \mu_\alpha^{\mathrm{H}}(\mathbf{r})\} \qquad (113)$$

are not equalized, both between themselves and throughout the space, due to the local AIM share factor (conditional probability) $D_\alpha(\mathbf{r})$ of equation (91a). Indeed, the global equilibrium condition, when expressed in terms of the Hirshfeld potentials, reads:

$$\mu_\alpha^{\mathrm{H}}(\mathbf{r})D_\alpha(\mathbf{r}) = \mu_\beta^{\mathrm{H}}(\mathbf{r})D_\beta(\mathbf{r}) = \cdots = \mu \qquad (114)$$

It also follows from equations (30), (61) and (108) that

$$\mathrm{d}u_\alpha^{\mathrm{H}}(\mathbf{r}) = D_\alpha(\mathbf{r})^{-1}\,\mathrm{d}u(\mathbf{r}) \qquad (115)$$

Hence, using equations (80) and (115) one finds the following relations between the hardness and softness kernels in the Hirshfeld resolution, and the corresponding global kernels for the system as a whole:

$$\eta^{\mathrm{H}}(\mathbf{r},\mathbf{r}')_{\alpha,\beta} = -\delta u_\beta^{\mathrm{H}}(\mathbf{r}')/\delta\rho_\alpha^{\mathrm{H}}(\mathbf{r}) = D_\alpha(\mathbf{r})^{-1}\eta(\mathbf{r},\mathbf{r}')D_\beta(\mathbf{r}')^{-1} \qquad (116)$$

$$\sigma^{\mathrm{H}}(\mathbf{r},\mathbf{r}')_{\alpha,\beta} = -\delta\rho_\beta^{\mathrm{H}}(\mathbf{r}')/\delta u_\alpha^{\mathrm{H}}(\mathbf{r}) = D_\alpha(\mathbf{r})\sigma(\mathbf{r},\mathbf{r}')D_\beta(\mathbf{r}') \qquad (117)$$

14. ELEMENTS OF INFORMATION-THEORETIC ‘THERMODYNAMICS’ OF MOLECULES AND THEIR FRAGMENTS

As we have already mentioned, the Hirshfeld fragments constitute the equilibrium pieces of the molecular electronic density, satisfying the corresponding stability condition [see equation (93)] for the entropy deficiency of equation (92). This implies that any hypothetical CT between the ‘stockholder’ fragments, marking a deviation from the Hirshfeld division, will increase the missing information (entropy deficiency) with respect to the global value between the molecular and ‘promolecular’ densities. The chemical potential equalization principle, the attribute of an arbitrary set of the mutually open subsystems, does not discriminate between alternative divisions of a given molecular density. As such it cannot be used as the criterion for distinguishing the optimum partitioning of the electronic density from a multitude of alternative divisions. The information-theoretic justification of the Hirshfeld scheme emphasizes the need for an independent, *entropy/information* criterion, complementary to the familiar *energy* criterion of the subsystem chemical potential equalization. Only the energy and information entropy representations combined provide a complete theory of the electronic structure [33].

The optimum information-theoretic (Hirshfeld) fragments were shown to exhibit several unique features [33]. They are independent of the Shannon-type information-distance measure applied to assimilate the reference atomic information in the molecular subsystem densities and they reduce to zero the non-additivity of the missing information relative to the 'promolecular' (isolated subsystem) reference. The entropy/information equilibrium criteria, in terms of the *local* entropy deficiencies of subsystems or the associated information *temperatures* defined by the partial derivatives of the embedded subsystem energies (equation (36)) with respect to the subsystem entropy densities, give an attractive interpretation of the optimum partitioning. More specifically, one finds that only for the Hirshfeld partitioning a given type of the local entropy deficiency parameters of subsystems equalize for all mutually open subsystem components (see Section 16). Therefore, these local information-entropy ('temperature') transcriptions of the inter-subsystem equilibrium criterion can be thought of as a local 'thermodynamic' supplement ('vertical', for the fixed ρ, see Section 7) of the familiar chemical potential equalization principle. While the latter fails to identify the equilibrium partitioning, the local entropy/information criteria uniquely select the Hirshfeld division scheme as the equilibrium partition. According to this entropy principle one reaches the equilibrium pieces of the molecular density, when the local information distances of all open subsystem component locally equalize at the corresponding global value [23,33].

The ultimate goal of a 'thermodynamic' description of molecular systems, however, is to determine the 'horizontal' displacements of the electronic structure (see Section 7), i.e., transitions from one v-representable molecular density to another. In order to relate the information entropy $\mathcal{H}[\rho]$, possibly involving also the reference densities (equation (92)), to the system energetic parameters one uses the generalized variational principle in the entropy representation [108]:

$$\delta\{\mathcal{H}[\rho] - \sum_k \lambda_k I_k[\rho]\} = 0 \quad \text{or} \quad \delta\{\Delta\mathcal{H}[\rho|\rho^0] - \sum_k \lambda_k I_k[\rho]\} = 0 \qquad (118)$$

where λ_k is the Lagrange multiplier associated with kth constraint, $I_k[\rho] = I_k^0$, with the set of constraints including energetic quantities. Indeed, an example of such an application of the information theory in determining the exchange-correlation part of the effective one-body potential [2] has recently been reported [143]. This procedure constitutes the information-theoretic variant of the Zhao–Morrison–Parr (ZMP) procedure [144,145]. The entropy term in equation (118) represents a 'device', which allows one to assimilate, in the most unbiased manner possible, in the optimum density ρ the physical information contained in the constraints and the reference densities.

Consider as an illustrative example a single component case. As in the ordinary thermodynamics of open systems [146] the entropy extremum principle of equation (118) requires the constraint of the fixed number of electrons, $N[\rho] = N^0$. Moreover, in order to introduce a temperature parameter T, associated with the constraint of the fixed average energy as the inverse of the condition Lagrange multiplier, one also requires $E[\rho] = E^0$ [see equation (28)]. The corresponding extreme entropy principle then reads:

$$\delta\{\mathcal{H}[\rho] - \tau^{-1}E[\rho] + \omega\tau^{-1}N[\rho]\} = 0 \tag{119}$$

where, by analogy with ordinary thermodynamics,

$$\tau^{-1} = (\partial\mathcal{H}/\partial E)_N \quad \text{and} \quad -\omega\tau^{-1} = (\partial\mathcal{H}/\partial N)_E \tag{120}$$

It should be stressed, that the above information-theoretic, thermodynamic 'chemical potential' ω differs from the chemical potential of equations (17) and (29).

The corresponding variational principle in the energy representation for the fixed information entropy $\mathcal{H}[\rho] = \mathcal{H}^0$,

$$\delta\{E[\rho] - \tau\mathcal{H}[\rho] - \omega N[\rho]\} = 0 \tag{121}$$

identifies the two Lagrange multipliers as:

$$\tau = (\partial E/\partial\mathcal{H})_N \quad \text{and} \quad \omega = (\partial E/\partial N)_{\mathcal{H}} \tag{122}$$

Following the ordinary thermodynamics [146] one can summarize the above information-theoretic thermodynamic-like description in terms of the three basic postulates [33]:

Postulate I. Among all possible partitions of the molecular ground-state density ρ into densities of molecular fragments $\{\rho_\alpha\}$, for the fixed 'promolecule' (free atom) reference, a natural choice in chemistry, there exists the *equilibrium* division into the 'stockholder' fragments, that are characterized completely by ρ and by the reference densities alone.

Postulate II. There exists a functional $\Delta\mathcal{H}[\rho|\rho^0]$, called the *entropy deficiency* (directed divergence or divergence), of the extensive subsystem parameters $\{\rho_\alpha\}$ of a composite molecular system, defined for all equilibrium (Hirshfeld) divisions of ρ and having the following property. The values assumed by $\{\rho_\alpha\}$ in the absence of the internal constraints are those that minimize $\Delta\mathcal{H}[\rho|\rho^0]$ over the manifold of constrained equilibrium states, the latter being defined by the effective subsystem external potentials $\{v_\alpha^{\text{eff}}(\mathbf{r}) = v_\alpha^{\text{eff}}[\{\rho_\alpha\}; \mathbf{r}]\}$.

Postulate III. The information-entropy deficiency of a composite system and its density are *additive* over the constituent components.

Molecular fragments are the mutually open subsystems, which exhibit fluctuations in their electron densities and overall numbers of electrons. In chemistry one is interested in both the *equilibrium* distributions of electrons and *non-equilibrium* processes characterized by *rates*. Recently, it has been demonstrated [23] that the information theory provides all necessary tools for the local *dynamical* description of the density fluctuations and electron flows between molecular subsystems, which closely follows the thermodynamic theory of irreversible processes [146].

The conceptual structure of the irreversible thermodynamics calls for two types of quantities: *affinities*, to describe the 'forces' that drive a process, and *fluxes*, to describe responses to these forces. Their identification is not unique: it depends on both the selected state-parameters and the adopted measure of the information distance relative to the 'promolecule' reference. The local reciprocity rules, the information-theoretic analogs of the familiar Onsager relations of the ordinary irreversible thermodynamics, have been derived through fluctuations and the distribution average fluctuation of the entropy deficiency have been linked to the electronic densities of subsystems. This analysis has amply demonstrated, that the previously identified thermodynamic analogies observed for the Hirshfeld equilibria in the local ('vertical') entropic description of molecular subsystems can indeed be extended to non-equilibrium electron distributions and irreversible processes. In this development the entropy-determined subsystems-in-molecules, previously viewed as *static* pieces of the molecular electron density, are treated as *dynamical* entities, with the distribution of local fluctuations in the instantaneous parameters of state being related in the thermodynamic-like fashion to the local value of the relevant Legendre transform of the missing information density.

Clearly, the 'vertical' reality of molecular subsystems, so important for interpretations in chemistry, cannot be verified or validated experimentally. However, the information-theoretic entropy representation gives rise to a consistent local 'thermodynamic' description of the submolecular equilibria and processes of reaching them. The causality of a subtle interplay between the affinities and fluxes of the ordinary thermodynamics has been extended to the molecular world, thus offering a novel level of understanding of local static (stationary) and dynamic (non-stationary) properties of molecules, AIM, reactants, etc. The theoretical framework of the 'thermodynamic' description summarized in this section, 'validated' by its close analogy to the phenomenological thermodynamics, constitutes a good starting point for future investigations of the electronic structure reorganizations (of charges and chemical bonds) in chemical reactions, in a search for an eventual 'dynamic' indexing of reactivity phenomena.

15. ENTROPIC MEASURES OF BOND MULTIPLICITY

As pointed out by Shannon [15], who established the information theory as an autonomous mathematical discipline, the basic problem of communication is that of reproducing at one point (*receiver*, *output*), exactly or approximately, a message sent at another point (*source*, *input*). The free (isolated) constituent atoms, defining the 'promolecule', can be viewed as the molecular 'message' *source*. The information contained in the probability distributions of this reference state is mostly preserved in the molecule, the molecular 'message' *receiver*. Indeed, the bonded (chemical) AIM are known to be only slightly perturbed in their valence shell relative to their free analogs. However, these small deformations in the electron distribution, due to the polarization and CT between bonded atoms, as well as the associated changes in the many-electron probabilities due to the electron delocalization in the molecule, account for the chemical bonds and all their attributes.

Therefore, as in the real communication channel, the molecular system is characterized by disturbances of a random character (*noise*), which perturb the molecular signal of atomic allocations of electrons in a molecule. This uncertainty in ascribing electrons to AIM originates from the electron delocalization through a network of chemical bonds. It is reflected by the conditional probabilities of finding valence electrons originating from a given free atom of the 'promolecule' on specified AIM. In a recent search for the information-theoretic, entropic measures of the chemical bond multiplicity and its covalent and ionic components it has been demonstrated [28] that the effect of this quantum–mechanical, delocalization noise, e.g., measured by the average *conditional entropy* in atomic resolution, reproduces the overall *covalent* bond index in selected model systems. It has also been found, that the so called *mutual information* in atomic resolution, measuring the amount of information flowing through the molecular 'communication' system, can be used as an indicator of the *ionic* bond component. The direct entropic bond-orders of the localized chemical bonds have also been suggested [28] and the role of the three-electron entropies in model open-shell and transition-state systems have been examined [27].

This novel approach indicates, that a chemical bond-order concept can be also considered as exhibiting an entropic origin [147]. Thus, the concepts of the Information Theory provide appropriate tools for extracting the chemical interpretation in terms of both bonded atoms and bonds which connect them in a molecule.

16. INFORMATION-DISTANCE ANALYSIS OF MOLECULAR ELECTRON DENSITIES

An important property of the 'stockholder' molecular fragments is manifested by their equalization of the local values of a given measure of the entropy deficiency density at the corresponding global value, for the system as a whole [30,33]. An example of such locally equalized information quantities are the subsystem-independent local *enhancement factors* of the Hirshfeld subsystem densities (equation (91a)):

$$w_\alpha(\mathbf{r}) \equiv \rho_\alpha^{\mathrm{H}}(\mathbf{r})/\rho_\alpha^0(\mathbf{r}) = w_\beta(\mathbf{r}) = \cdots = w(\mathbf{r}) \equiv \rho(\mathbf{r})/\rho^0(\mathbf{r}) \qquad (123)$$

This implies an equalization of all functions of $\{w_\alpha(\mathbf{r})\}$, e.g., of the Kullback–Leibler (directed divergence) integrands $\{\Delta h_\alpha(\mathbf{r})\}$ (equations (92) and (93)) per single electron of the corresponding free atom:

$$\begin{aligned} h_\alpha(\mathbf{r}) &\equiv \Delta h_\alpha(\mathbf{r})/\rho_\alpha^0(\mathbf{r}) = [\rho_\alpha^{\mathrm{H}}(\mathbf{r})/\rho_\alpha^0(\mathbf{r})]\ \ln\ [\rho_\alpha^{\mathrm{H}}(\mathbf{r})/\rho_\alpha^0(\mathbf{r})] \equiv w_\alpha^{\mathrm{H}}(\mathbf{r}) I_\alpha[w_\alpha^{\mathrm{H}}(\mathbf{r})] \\ &= h_\beta(\mathbf{r}) = h(\mathbf{r}) \equiv \Delta h(\mathbf{r})/\rho^0(\mathbf{r}) = [\rho(\mathbf{r})/\rho^0(\mathbf{r})] \ln [\rho(\mathbf{r})/\rho^0(\mathbf{r})] \\ &\equiv w(\mathbf{r}) I(\mathbf{r}) \end{aligned} \tag{124}$$

where $I(\mathbf{r}) \equiv \ln[\rho(\mathbf{r})/\rho^0(\mathbf{r})] = \ln w(\mathbf{r})$ is the global *surprisal* function, identical with that characterizing any Hirshfeld subsystem:

$$I_\alpha[w_\alpha^{\mathrm{H}}(\mathbf{r})] \equiv \ln\ [\rho_\alpha^{\mathrm{H}}(\mathbf{r})/\rho_\alpha^0(\mathbf{r})] = I_\beta[w_\beta^{\mathrm{H}}(\mathbf{r})] = I(\mathbf{r}) \equiv \ln\ [\rho(\mathbf{r})/\rho^0(\mathbf{r})] \tag{125}$$

An alternative measure of the subsystem local information distance relative to the corresponding reference density is defined by the entropy deficiency 'intensive' conjugate of the fragment electron density ('extensive' state-function). The Kullback–Leibler functional of equations (92) and (93) gives:

$$\begin{aligned} h_\alpha^{\mathrm{H}}(\mathbf{r}) &\equiv \delta\Delta\mathcal{H}_\alpha[\rho_\alpha|\rho_\alpha^0]/\delta\rho_\alpha(\mathbf{r})|_H = h_\beta^{\mathrm{H}}(\mathbf{r}) = \cdots \\ &= h(\mathbf{r}) \equiv \delta\Delta\mathcal{H}[\rho|\rho^0]/\delta\rho(\mathbf{r}) = I(\mathbf{r}) + 1 \end{aligned} \tag{126}$$

Several approximate, semi-quantitative relations linking the above information-distance densities with the density difference function $\Delta\rho(\mathbf{r})$ have been derived and numerically tested for selected linear molecules [29,30]. Since the molecular density is in general only slightly changed relative to the 'promolecular' reference density, as a result of the mainly valence shell, minor reconstruction of the electron distribution,

$$\begin{aligned} |\Delta\rho(\mathbf{r})| \equiv |\rho(\mathbf{r}) - \rho^0(\mathbf{r})| \ll \rho(\mathbf{r}) \cong \rho^0(\mathbf{r}) \qquad \text{or} \\ w(\mathbf{r}) = \rho(\mathbf{r})/\rho^0(\mathbf{r}) = 1 + \Delta\rho(\mathbf{r})\rho^0(\mathbf{r}) \approx 1 \end{aligned} \tag{127}$$

the first-order Taylor expansion of the global surprisal function gives:

$$I(\mathbf{r}) \cong \Delta\rho(\mathbf{r})/\rho^0(\mathbf{r}) \approx \Delta\rho(\mathbf{r})/\rho(\mathbf{r}) \tag{128}$$

so that the approximate expression for the Kullback–Leibler integrand reads:

$$\Delta h(\mathbf{r}) = \rho(\mathbf{r}) \ln [\rho(\mathbf{r})/\rho^0(\mathbf{r})] \cong [\rho(\mathbf{r})/\rho^0(\mathbf{r})]\Delta\rho(\mathbf{r}) \approx \Delta\rho(\mathbf{r}) \tag{129}$$

Hence, the corresponding approximate expressions in terms of $\Delta\rho(\mathbf{r})$ for alternative, inter-subsystem equalized information-distance densities read:

$$\begin{aligned} h(\mathbf{r}) &\equiv w(\mathbf{r}) I(\mathbf{r}) \cong w(\mathbf{r})\Delta\rho(\mathbf{r})/\rho^0(\mathbf{r}) \approx \Delta\rho(\mathbf{r})/\rho^0(\mathbf{r}), \\ h(\mathbf{r}) &= I(\mathbf{r}) + 1 \cong w(\mathbf{r}) = 1 + \Delta\rho(\mathbf{r})/\rho^0(\mathbf{r}) \approx 1 \end{aligned} \tag{130}$$

These approximate expressions attribute to the familiar $\Delta\rho(\mathbf{r})$ function a new information-theoretic interpretation. It follows from the above expressions that the dominant feature of these alternative missing information densities is the global surprisal function, $I(\mathbf{r})$, related to the density difference per electron [equation (128)] and indicating the regions of increased, $I(\mathbf{r}) > 0$, or decreased, $I(\mathbf{r}) < 0$, entropy deficiency with respect to the free-atomic 'promolecular' reference. Information-distance density plots can thus serve as additional tools, complementary to the density and entropy difference diagrams, for diagnosing the origins of the chemical bond. They indeed exhibit missing information displacements reminiscent of those observed in the associated density difference diagrams, reflecting the contraction of the overall atomic electron distribution in a molecule, changes due to the bond covalency and/or ionicity (CT), the atomic *polarization* due to the AO hybridization, electron excitation to the higher atomic orbitals (AIM 'promotion'), etc. [29,30].

To conclude this section, we examine the illustrative example of such an analysis carried out to study the central bond in propellane systems shown in Fig. 4 [29]. The main purpose of this study was to examine the effect of an increase in the bridge

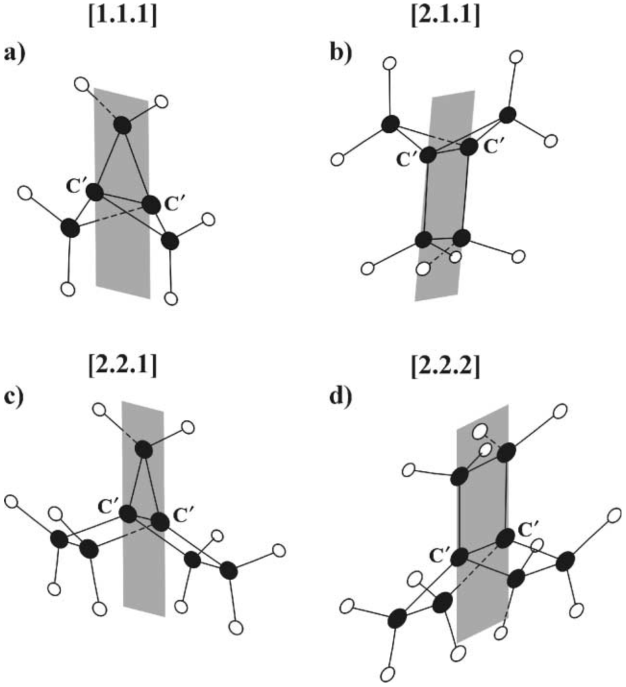

Fig. 4. The propellane structures and the planes of sections containing the bridge and bridgehead (C′) atoms for the contour diagrams of Fig. 5 [29].

sizes in the series of the [1.1.1], [2.1.1], [2.2.1], and [2.2.2] propellanes on the central (C′–C′) bond between the bridgehead atoms.

Figure 5 reports a comparison between the contour maps of the density difference, $\Delta\rho(\mathbf{r})$, the Kullback–Leibler integrand, $\Delta h(\mathbf{r})$, and the entropy displacement function [equation (94)], $\Delta\mathfrak{H}(\mathbf{r})$, for the planes of sections shown in Fig. 4. The corresponding central bond profiles of the density and entropy difference functions are compared in Fig. 6. The optimized geometries of propellanes have been determined from the UHF calculations (GAMESS program) using the 3-21 G basis set. The contour maps have been obtained from the DFT calculations (deMon program) in DZVP basis set.

The density difference plots of Figs 5 and 6 show that there is an average density depletion, relative to the promolecule, between the bridgehead carbon atoms in the [1.1.1] and [2.1.1] propellanes, whereas the [2.2.1] and [2.2.2] systems exhibit a net electron density buildup in this region. A similar conclusion follows from the entropic quantities shown in the same figures. The entropic diagrams are indeed seen to be qualitatively similar to the corresponding density difference plots. The bond-orders from the difference approach, reported in Fig. 6, and the corresponding profiles shown in this figure reveal a changing nature of the central bond in the four propellanes under consideration. The smallest bridges, lacking the bond accumulation of the electron density or the entropy (entropy deficiency) density, is seen to be mostly ‘through-bridges’ in character. A gradual emergence of the ‘through-space’ component, due to the electron density or the entropy (entropy deficiency) density accumulation between the bridgehead carbons is observed when the bridges are enlarged. One roughly estimates a full single bond in the [2.2.1] and [2.2.2] propellanes and approximately 0.8 bond in the [1.1.1] propellane. Using the latter estimate as a measure of the ‘through-bridges’ component in the largest propellane one predicts about 0.2 bond-order measure of the ‘through-space’ component of the central bond in the [2.2.2] propellane.

17. INFORMATION-DISTANCE AFFINITIES FOR THE CT IN THE DONOR–ACCEPTOR REACTIVE SYSTEMS

Consider now a CT A ← B, for the fixed molecular external potential $v(\mathbf{r})$, in the reactive system consisting of the B(*basic*, donor) and A(*acidic*, acceptor) reactants. For such processes within the externally closed A–B system, for which $N_A + N_B = N = \text{const.}$, the current overall electron populations on both these complementary subsystems of the reactive system, $\boldsymbol{N} = (N_A, N_B)$, which result from the integration of the reactant densities $\boldsymbol{\rho} = (\rho_A, \rho_B)$, determine the current amount of CT, relative to the electron populations $\boldsymbol{N}^0 = (N_A^0, N_B^0)$ of the infinitely separated (free) reactants,

$$N_{CT} = N_A - N_A^0 = N_B^0 - N_B \tag{131}$$

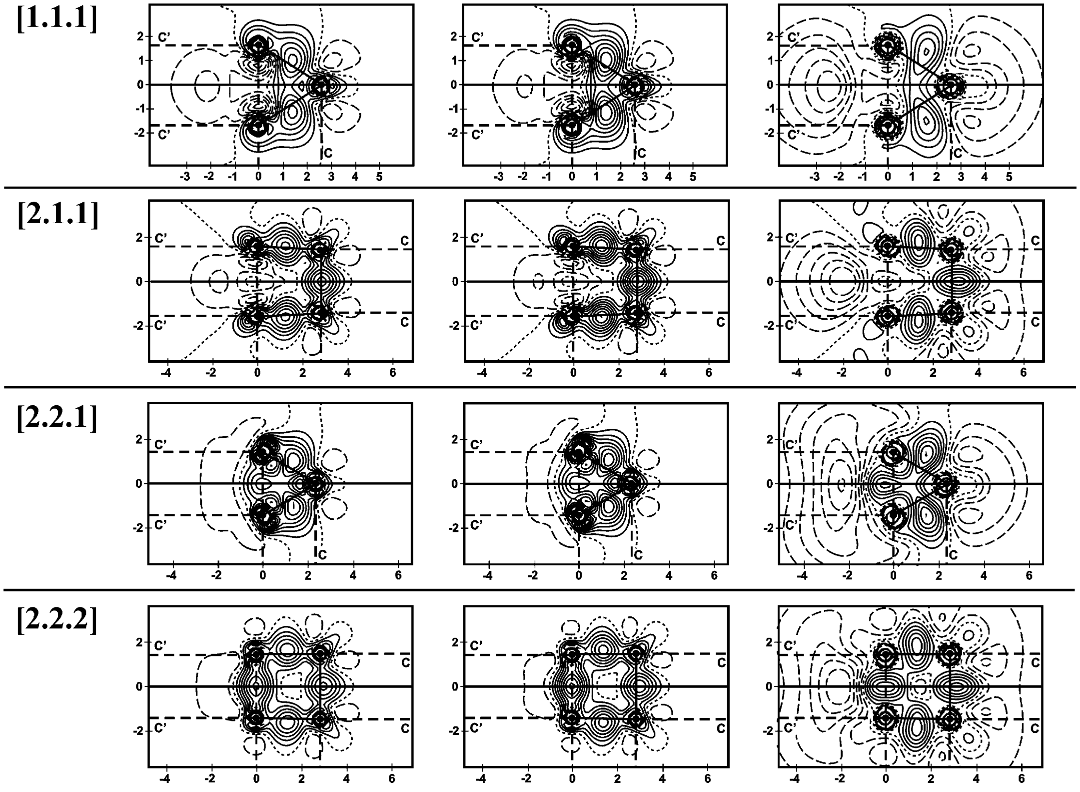

Fig. 5. A comparison between the (equidistant) contour maps of the density difference (first column), the information-distance density (second column), and the entropy displacement density (third column), for the four propellanes of Fig. 4 [29].

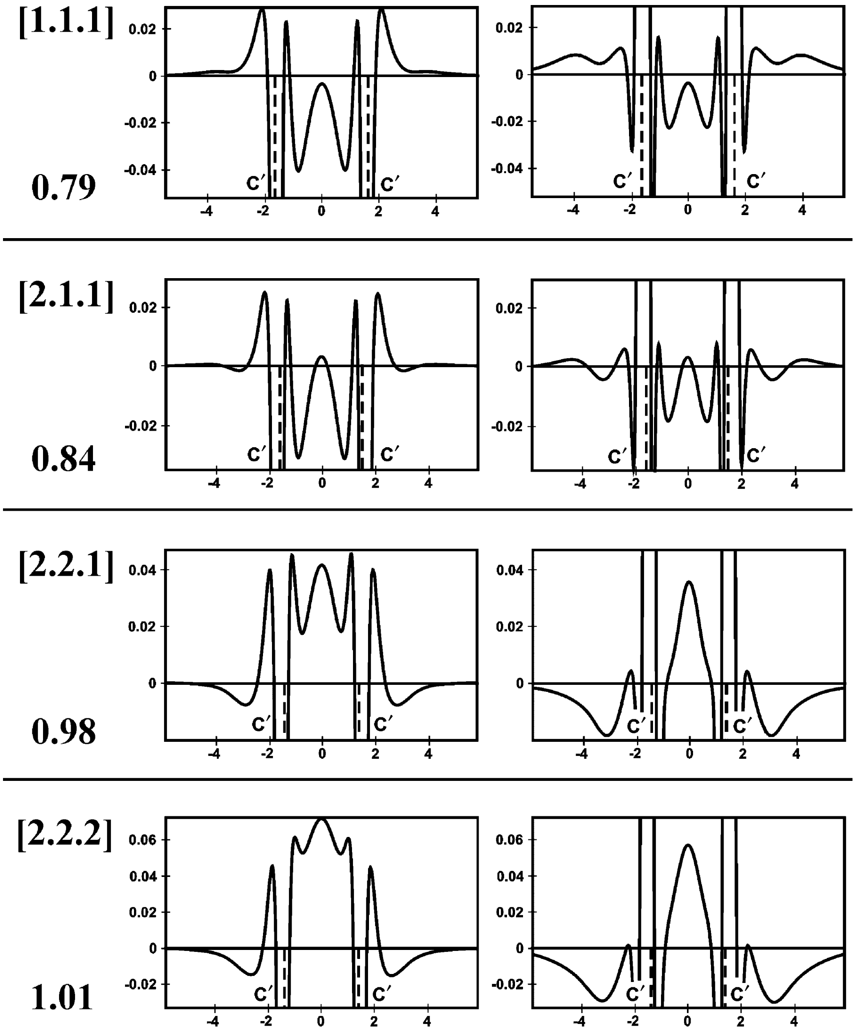

Fig. 6. The bridgehead bond profiles of the density difference function (left panel) and molecular entropy displacement (right panel) for the four propellanes of Fig. 4. For comparison the numerical values of the bond multiplicities from the difference approach (R. F. Nalewajski, J. Mrozek, G. Mazur (1996) *Can. J. Chem.*, **74**, 1121) are also reported [29].

Therefore, N_{CT} represents the independent reaction *coordinate* for such an internal electron displacement in A–B.

The subsystem densities for the specified average numbers of electrons in subsystem, $\boldsymbol{\rho} = \boldsymbol{\rho}(\mathbf{N})$, can be obtained from the modified minimum entropy deficiency principle [30]:

$$\delta\{\Delta\mathcal{H}[\boldsymbol{\rho}|\boldsymbol{\rho}^0] - \sum_\alpha \lambda_\alpha \int \rho_\alpha(\mathbf{r})\,d\mathbf{r}\} = 0 \tag{132}$$

where, for the case of the externally closed A–B system, i.e., for the fixed value of the sum $N = N_A + N_B$, only one Lagrange term due to the subsystem density-normalization constraint, say for A, is required to simultaneously enforce the specified numbers of electrons on both reactants.

Should one additionally require, that the optimum subsystem densities reproduce a given molecular density, $\sum_\beta \rho_\beta(\mathbf{r}) = \rho(\mathbf{r})$, as is the case in the Hirshfeld division, one has to include the additional local constraint of the exhaustive partitioning:

$$\delta\left\{\Delta\mathcal{H}[\boldsymbol{\rho}|\boldsymbol{\rho}^0] - \int \lambda(\mathbf{r})[\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})]d\mathbf{r} - \lambda_A \int \rho_A(\mathbf{r})\,d\mathbf{r}\right\} = 0 \tag{133}$$

since the overall density already fixes the global number of electrons: $\int \rho(\mathbf{r})\,d\mathbf{r} = N$. The corresponding Euler equations for the unknowns $\{N_A, \rho_A, \rho_B\}$ are [30]:

$$\begin{gathered}\mathcal{F}_A - \int \lambda(\mathbf{r})[F_{A,A}(\mathbf{r}) + F_{A,B}(\mathbf{r})]d\mathbf{r} - \lambda_{\mathbf{A}} = 0,\\ h_A(\mathbf{r}) - \lambda(\mathbf{r}) - \lambda_A = 0, \qquad h_B(\mathbf{r}) - \lambda(\mathbf{r}) = 0\end{gathered} \tag{134}$$

where the electron population 'force' $\mathcal{F}_A$ is the entropy deficiency conjugate of N_A, $\mathcal{F}_A = \partial\Delta\mathcal{H}/\partial N_A$, the *Fukui-functions* ([4,5,83,92]) of reactants $\mathbf{F}(\mathbf{r}) \equiv \{F_{\alpha,\beta}(\mathbf{r}) = [\partial\rho_\beta(\mathbf{r})/\partial N_\alpha]_{\beta\neq\alpha}\}$ [equation (78b)], and the subscript $\beta \neq \alpha$ stands for the fixed external potential and the electron population of the other subsystem. The FF matrix elements in the reactant resolution satisfy the usual normalizations:

$$\begin{gathered}\int F_{\beta(\neq\alpha),\alpha}(\mathbf{r})\,d\mathbf{r} = [\partial N_\beta/\partial N_\alpha]_{\beta\neq\alpha} = 0 \quad \text{and}\\ \int F_{\alpha,\alpha}(\mathbf{r})\,d\mathbf{r} = [\partial N_\alpha/\partial N_\alpha]_{\beta\neq\alpha} = 1\end{gathered} \tag{135}$$

Equations (134) have the following solutions:

$$\begin{gathered}\rho_A(\mathbf{r}) \equiv \rho_A[N, \rho; \mathbf{r}] = \rho_A^0(\mathbf{r})C(\mathbf{r})D \quad \text{and}\\ \rho_B(\mathbf{r}) \equiv \rho_B[N, \rho; \mathbf{r}] = \rho_B^0(\mathbf{r})C(\mathbf{r})\end{gathered} \tag{136}$$

where $\ln C(\mathbf{r}) = \lambda(\mathbf{r}) - 1$ and $\ln D = \lambda_A$. The local factor $C(\mathbf{r})$ can be determined from the exhaustive division constraint:

$$C(\mathbf{r}) = \rho(\mathbf{r})/[D\rho_A^0(\mathbf{r}) + \rho_B^0(\mathbf{r})] \tag{137}$$

with constant D satisfying the integral equation $N_{\mathrm{A}} = \int \rho_{\mathrm{A}}(\mathbf{r})\mathrm{d}\mathbf{r}$, to be solved numerically. It should be observed that the Hirshfeld densities are recovered for $D = 1$, i.e., for $\lambda_{\mathrm{A}} = 0$, when the extra global constraint term in equation (133) is not present.

We have introduced in the Euler equations (134) the entropy deficiency conjugate of the subsystem overall number of electrons,

$$\begin{aligned}\mathcal{F}_{\alpha} &\equiv \partial\Delta\mathcal{H}/\partial N_{\alpha} = \sum_{\beta=\mathrm{A,B}} \int [\partial\rho_{\beta}(\mathbf{r})/\partial N_{\alpha}][\delta\Delta\mathcal{H}_{\beta}/\delta\rho_{\beta}(\mathbf{r})]\mathrm{d}\mathbf{r} \\ &= \sum_{\beta} \int F_{\alpha,\beta}(\mathbf{r})h_{\beta}(\mathbf{r})\,\mathrm{d}\mathbf{r}, \quad \alpha = \mathrm{A,B} \qquad (138)\end{aligned}$$

which define the information-distance force ('intensive') parameters associated with the corresponding electron populations of reactants ('extensive' parameters). The derivatives $\mathcal{F}_{\mathrm{A}}$ and $\mathcal{F}_{\mathrm{B}}$ determine the entropic *CT-force*, $\mathcal{F}_{\mathrm{CT}}$, for the internal CT between the two reactants of the externally closed A–B system, for which $N = N_{\mathrm{A}} + N_{\mathrm{B}} = \text{const.}$, or $\mathrm{d}N_{\mathrm{A}} = -\mathrm{d}N_{\mathrm{B}} = \mathrm{d}N_{\mathrm{CT}} > 0$, defined by the entropy deficiency conjugate of the amount of CT:

$$\begin{aligned}\mathcal{F}_{\mathrm{CT}} &\equiv \partial\Delta\mathcal{H}/\partial N_{\mathrm{CT}} = \sum_{\beta} (\partial N_{\beta}/\partial N_{\mathrm{CT}})(\partial\Delta\mathcal{H}/\partial N_{\beta}) = \mathcal{F}_{\mathrm{A}} - \mathcal{F}_{\mathrm{B}} \\ &= \int \{[F_{\mathrm{A,A}}(\mathbf{r}) - F_{\mathrm{B,A}}(\mathbf{r})]h_{\mathrm{A}}(\mathbf{r}) + [F_{\mathrm{A,B}}(\mathbf{r}) - F_{\mathrm{B,B}}(\mathbf{r})]h_{\mathrm{B}}(\mathbf{r})\}\mathrm{d}\mathbf{r} \\ &\equiv \int \{F_{\mathrm{A}}^{\mathrm{CT}}(\mathbf{r})h_{\mathrm{A}}(\mathbf{r}) + F_{\mathrm{B}}^{\mathrm{CT}}(\mathbf{r})h_{\mathrm{B}}(\mathbf{r})\}\mathrm{d}\mathbf{r} \qquad (139)\end{aligned}$$

where we have introduced the reactant *in situ* FF, $\{F_{\alpha}^{\mathrm{CT}}(\mathbf{r}) = \partial\rho_{\alpha}(\mathbf{r})/\partial N_{\mathrm{CT}}\} \equiv \mathbf{F}^{\mathrm{CT}}(\mathbf{r}) = [F_{\mathrm{A,A}}(\mathbf{r}) - F_{\mathrm{B,A}}(\mathbf{r}), F_{\mathrm{A,B}}(\mathbf{r}) - F_{\mathrm{B,B}}(\mathbf{r})]$ [4,5]. The derivatives of equations (138) and (139) combine the information distance densities of reactants $\{h_{\alpha}(\mathbf{r})\}$ and the corresponding subsystem FF. The generalized force $\mathcal{F}_{\mathrm{CT}}$ can be called, by analogy to the irreversible thermodynamics ([146]), the CT *affinity* of the A–B system.

Consider now the molecular density constrained CT, of the 'vertical' electronic structure problem, for which the Hirshfeld electron populations of both subsystems, $\boldsymbol{N}^{\mathrm{H}} = \{N_{\alpha}^{\mathrm{H}} = \int \rho_{\alpha}^{\mathrm{H}}(\mathbf{r})\mathrm{d}\mathbf{r}\}$, for which $h_{\mathrm{A}}^{\mathrm{H}}(\mathbf{r}) = h_{\mathrm{B}}^{\mathrm{H}}(\mathbf{r}) = h(\mathbf{r})$, determine the optimum amount of CT: $N_{\mathrm{CT}}^{\mathrm{H}} = N_{\mathrm{A}}^{\mathrm{H}} - N_{\mathrm{A}}^{0} = N_{\mathrm{B}}^{0} - N_{\mathrm{B}}^{\mathrm{H}}$. Indeed, it follows from the Euler equations (134) that the CT affinity exactly vanishes for the 'stockholder' reactants:

$$\begin{aligned}(\mathcal{F}_{\mathrm{CT}}^{\mathrm{H}})_{\rho} &= [(\partial\Delta\mathcal{H}/\partial N_{\mathrm{CT}})^{\mathrm{H}}]_{\rho}\\ &= \int\{[F_{\mathrm{A,A}}(\mathbf{r})+F_{\mathrm{A,B}}(\mathbf{r})]-[F_{\mathrm{B,B}}(\mathbf{r})+F_{\mathrm{B,A}}(\mathbf{r})]\}_{\rho}h(\mathbf{r})\mathrm{d}\mathbf{r}\\ &= \int\{[\partial\rho(\mathbf{r})/\partial N_{\mathrm{A}}]_{\rho}-[\partial\rho(\mathbf{r})/\partial N_{\mathrm{B}}]_{\rho}\}h(\mathbf{r})\mathrm{d}\mathbf{r} = \int[\partial\rho(\mathbf{r})/\partial N_{\mathrm{CT}}]_{\rho}h(\mathbf{r})\mathrm{d}\mathbf{r}\\ &\equiv \int[F_{\mathrm{CT}}(\mathbf{r})]_{\rho}h(\mathbf{r})\mathrm{d}\mathbf{r} = 0 \qquad (140)\end{aligned}$$

18. FUKUI FUNCTION DESCRIPTORS OF HIRSHFELD REACTANTS

Let us again examine the A–B reactive system and its A^0–B^0 'promolecule' reference, the latter consisting of the free reactant densities brought to their current positions in A–B, for the finite separation between the two subsystems. It should be observed, that this hypothetical state also corresponds to the electrostatic stage of the interaction between reactants, when the electron distributions and internal subsystem geometries are held 'frozen' at finite inter-reactant separations. When the subsequent Hirshfeld partitioning of the known overall ground-state density of A–B is performed, one obtains the uniquely defined, equilibrium subsystems in the reactive system.

Both A^0–B^0 and A–B constitute a collection of the uniquely defined reactant subsystems, before and after their density relaxation at finite distances, respectively. It is of interest in the theory of chemical reactivity to determine how the reactivity indices of reactants, e.g. FF, change as a result of their interaction; one would also like to know how their response properties relate to those of the system as a whole, at both these limits: the molecular, in A–B, and the corresponding quantities, in A^0–B^0 [28].

Let us first examine the promolecule A^0–B^0, defined by the subsystem densities $\boldsymbol{\rho}^0 = (\rho_{\mathrm{A}}^0, \rho_{\mathrm{B}}^0)$ generating the 'promolecular' density $\rho^0 = \rho_{\mathrm{A}}^0 + \rho_{\mathrm{B}}^0$. A number of related FF-type derivatives of the electronic densities, with respect to either $\boldsymbol{N}^0 = (N_{\mathrm{A}}^0, N_{\mathrm{B}}^0)$ or $N^0 = N_{\mathrm{A}}^0 + N_{\mathrm{B}}^0$, can be defined for this reference system:

$$\begin{aligned}&\mathbf{F}^0(\mathbf{r}) \equiv \{F_{\alpha,\beta}^0(\mathbf{r}) \equiv \partial\rho_{\beta}^0(\mathbf{r})/\partial N_{\alpha}^0\} \equiv \partial\boldsymbol{\rho}^0(\mathbf{r})/\partial\boldsymbol{N}^0, \qquad f^0(\mathbf{r}) \equiv \partial\rho^0(\mathbf{r})/\partial N^0,\\ &\mathbf{f}^0(\mathbf{r}) = \partial\boldsymbol{\rho}^0(\mathbf{r})/\partial N^0 = [f_{\mathrm{A}}^0(\mathbf{r}), f_{\mathrm{B}}^0(\mathbf{r})]\end{aligned} \qquad (141)$$

Analogous derivatives, with respect to either $\boldsymbol{N}^{\mathrm{H}} = (N_{\mathrm{A}}^{\mathrm{H}}, N_{\mathrm{B}}^{\mathrm{H}})$ or $N = N_{\mathrm{A}}^{\mathrm{H}} + N_{\mathrm{B}}^{\mathrm{H}} = N^0$, can be defined for the reactive system A–B, consisting of the corresponding Hirshfeld reactant densities, $\boldsymbol{\rho}^{\mathrm{H}} = (\rho_{\mathrm{A}}^{\mathrm{H}}, \rho_{\mathrm{B}}^{\mathrm{H}})$, which sum up to the overall molecular density $\rho = \rho_{\mathrm{A}}^{\mathrm{H}} + \rho_{\mathrm{B}}^{\mathrm{H}}$:

$$\begin{aligned}&\mathbf{F}^{\mathrm{H}}(\mathbf{r}) \equiv \{F_{\alpha,\beta}^{\mathrm{H}}(\mathbf{r}) \equiv \partial\rho_{\beta}^{\mathrm{H}}(\mathbf{r})/\partial N_{\alpha}^{\mathrm{H}}\} \equiv \partial\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})/\partial\boldsymbol{N}^{\mathrm{H}}, \qquad f(\mathbf{r}) \equiv \partial\rho(\mathbf{r})/\partial N,\\ &\mathbf{f}^{\mathrm{H}}(\mathbf{r}) = \partial\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})/\partial N = [f_{\mathrm{A}}^{\mathrm{H}}(\mathbf{r}), f_{\mathrm{B}}^{\mathrm{H}}(\mathbf{r})]\end{aligned} \qquad (142)$$

It directly follows from the definition of the 'stockholder' subsystem densities [equation (91a)], $\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r}) = [\boldsymbol{\rho}^0(\mathbf{r})/\rho^0(\mathbf{r})]\rho(\mathbf{r}) \equiv \mathbf{p}^0(\mathbf{r})\rho(\mathbf{r})$, where the conditional probability densities of subsystems $\mathbf{p}(\mathbf{r}) \equiv [\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})/\rho(\mathbf{r})] = \mathbf{p}^0(\mathbf{r}) \equiv [\boldsymbol{\rho}^0(\mathbf{r})/\rho^0(\mathbf{r})]$, that the local values of the FF quantities of the Hirshfeld reactant subsystems are the $\mathbf{p}(\mathbf{r})$ fractions of the corresponding overall FF [see equation (109)]:

$$\mathbf{f}^{\mathrm{H}}(\mathbf{r}) = \mathbf{p}(\mathbf{r})[\partial\rho(\mathbf{r})/\partial N] = \mathbf{p}(\mathbf{r})f(\mathbf{r}) \tag{143}$$

A similar relation can be derived for the partitioning of the 'promolecular' FF, by reversing the roles of the Hirshfeld and the free reactant densities in the minimum entropy deficiency principle, so that now $\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})$ play the role of the reference densities, while $\boldsymbol{\rho}^0(\mathbf{r})$ are the optimum densities satisfying the constraint $\sum_\alpha \rho_\alpha^0(\mathbf{r}) = \rho^0(\mathbf{r})$:

$$\delta\{\Delta\mathcal{H}[\boldsymbol{\rho}^0|\boldsymbol{\rho}^{\mathrm{H}}] - \int \kappa(\mathbf{r})[\rho_{\mathrm{A}}^0(\mathbf{r}) + \rho_{\mathrm{B}}^0(\mathbf{r})]\mathrm{d}\mathbf{r}\} = 0 \tag{144}$$

As expected by analogy to the ordinary Hirshfeld partitioning problem of equation (93a), the solution of this modified missing information variational principle gives:

$$\boldsymbol{\rho}^0(\mathbf{r}) = [\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})/\rho(\mathbf{r})]\rho^0(\mathbf{r}) = \mathbf{p}(\mathbf{r})\rho^0(\mathbf{r}). \tag{145}$$

This demonstration of the minimum information-distance character of the free subsystem densities, with respect to the molecular/Hirshfeld reference, implies that the separated subsystem densities can be regarded as representing the mutually open equilibrium subsystems of the 'promolecule', thus justifying the definition of the global FF for the 'promolecule', $f^0(\mathbf{r})$ [equation (141)], as the partial derivative of $\rho^0(\mathbf{r})$ with respect to N^0. The differentiation of these optimum free subsystem densities for the 'frozen' Hirshfeld reference gives:

$$\mathbf{f}^0(\mathbf{r}) = \mathbf{p}(\mathbf{r})[\partial\rho^0(\mathbf{r})/\partial N^0] = \mathbf{p}(\mathbf{r})f^0(\mathbf{r}) \tag{146}$$

Combining equations (143) and (146) gives the following proportionality relation between FF of the reactant subsystems in A–B and A^0–B^0:

$$f_{\mathrm{A}}^0(\mathbf{r})/f_{\mathrm{A}}^{\mathrm{H}}(\mathbf{r}) = f_{\mathrm{B}}^0(\mathbf{r})/f_{\mathrm{B}}^{\mathrm{H}}(\mathbf{r}) = f^0(\mathbf{r})/f(\mathbf{r}) \tag{147}$$

It implies, that the Hirshfeld subsystems change their FF in the molecular reactive system, relative to that in the 'promolecular' reference, in the proportion determined by the ratio of the corresponding global FF. It follows from this rule that the locally soft (hard) free reactant of the 'promolecule' remains locally soft (hard) as the Hirshfeld (bonded) subsystem of the molecular reactive system.

The same proportionality relations follow from the entropy deficiency rules, in which the Kullback–Leibler functional is formulated directly in terms of the subsystem FF distributions, instead of the electron densities:

$$\begin{aligned}&\delta\{\Delta\mathcal{H}[\mathbf{f}^{\mathrm{H}}|\mathbf{f}^{0}] - \int \zeta(\mathbf{r})[f_{\mathrm{A}}^{\mathrm{H}}(\mathbf{r}) + f_{\mathrm{B}}^{\mathrm{H}}(\mathbf{r})]\mathrm{d}\mathbf{r}\} = 0, \quad \Rightarrow f_{\alpha}^{\mathrm{H}}(\mathbf{r}) = f_{\alpha}^{0}(\mathbf{r})[f(\mathbf{r})/f^{0}(\mathbf{r})]\\ &\delta\{\Delta\mathcal{H}[\mathbf{f}^{0}|\mathbf{f}^{\mathrm{H}}] - \int \varphi(\mathbf{r})[f_{\mathrm{A}}^{0}(\mathbf{r}) + f_{\mathrm{B}}^{0}(\mathbf{r})]\mathrm{d}\mathbf{r}\} = 0, \quad \Rightarrow f_{\alpha}^{0}(\mathbf{r}) = f_{\alpha}^{\mathrm{H}}(\mathbf{r})[f^{0}(\mathbf{r})/f(\mathbf{r})]\end{aligned} \tag{148}$$

Dividing the solutions of these two variational principles yields equation (147). It should be realized, however, that the FF cannot be exactly considered as 'probability' distribution, since it can assume negative values. We would like to observe, however, that this quantity has been successfully used in several overlap criteria of molecular similarity.

The FF proportionality rule of equation (147) is related to the asymptotic properties of the stockholder AIM [26]. Let us assume for simplicity a diatomic system $M = AB$, consisting of the Hirshfeld (bonded) atoms A^{H} and B^{H}, $\rho = \rho_{A}^{H} + \rho_{B}^{H}$, the free analogs of which exhibit the *relative* electron *acceptor* (acidic) and *donor* (basic) properties, respectively:

$$\mu_{A}^{0} = -I_{A}^{0} < \mu_{B}^{0} = -I_{B}^{0} \tag{149}$$

where μ_{α}^{0} and I_{α}^{0} denote the chemical potential (negative electronegativity) and ionization potential of the free atom α. Rewriting the expressions for the 'stockholder' density pieces gives them in terms of the molecular density and the ratio $x = \rho_{B}^{0}/\rho_{A}^{0}$:

$$\rho_{A}^{H} = \rho(1 + x)^{-1} \qquad \text{and} \qquad \rho_{B}^{H} = \rho(1 + x^{-1})^{-1} \tag{150}$$

For locations at large distances from the molecule, $r \rightarrow \infty$, when the distances from both nuclei become very large, $x \rightarrow \infty$, since the asymptotic behavior of the free atoms is determined by the ionization potentials, i.e., the negative energies of the KS orbitals (chemical potentials):

$$\rho_{\alpha}^{0} \rightarrow \exp[-2(2I_{\alpha}^{0})r] \qquad (r \rightarrow \infty), \qquad \alpha = \mathrm{A, B} \tag{151}$$

Thus, for $r \rightarrow \infty$, $\rho_{A}^{H} \rightarrow 0$, and $\rho_{B}^{H} \rightarrow \rho$, so that the density of the *softer* (donor) atom *B* will have the dominant contribution to the molecular density at distances from the molecule large compared to the inter-atomic distance. This result is in agreement with the conclusions of the subsystem KS analysis [148].

19. CONCLUSION

As we have demonstrated in this survey, there is a wide range of problems in the theory of electronic structure and chemical reactivity, which can be tackled using concepts and techniques of the density functional and information theories. These two descriptions are complementary in character, providing the *energy* and *entropy representations* of molecular systems, respectively. Together they constitute the *complete* theoretical framework for describing both 'horizontal' and 'vertical' displacements in the system electronic structure. The former are associated with changes in the system ground-state density and energy, while the latter are carried out for the fixed ground-state density, and thus, the energy of the system as a whole, with only the embedded subsystems changing their densities and energies as a result of shifting electrons between the constituent subsystems. The 'vertical' problem is vital for extracting the *chemical interpretation* from the known molecular electron density in terms of AIM, functional groups, reactants, and bonds which connect these subsystems in the molecule. The information theory provides the entropic justification of the 'stockholder' AIM and the Hammond postulate [149], the criteria of molecular similarity, the polarization (promotion) and CT stages of the reorganization of atoms, when they form chemical bonds in a molecule, a thermodynamic-like description of molecular systems and their fragments, as well as descriptors of the electron-transfer phenomena in reactive systems, bond multiplicities, etc. The density fluctuations and the flows of electrons between subsystems can be also tackled in the local 'thermodynamic' description, which closely follows the ordinary irreversible thermodynamics. Other applications of the Information Theory in chemical physics, besides the known applications in statistical thermodynamics, include problems of chemical kinetics [150–154], definition of molecular 'lodges' [25,142,155], the surprisal analysis and synthesis of the electron density [156–159], the Compton profiles and momentum density [160–164], density functionals and DFT as thermodynamics, and the electron correlation problem [3,19, 159,165–173] transferability of molecular subsystems ([112]), and more general topics in quantum mechanics [174,175]. The Information Theory plays the unifying role in physics as well, by facilitating the derivations of its basic laws from the common *extreme physical* (Fisher) *information* principle [19].

The DFT rooted charge sensitivities constitute attractive concepts in terms of which the truly two-reactant reactivity criteria can be defined for both the externally (or mutually) closed and open subsystems. The effective external potentials of the embedded (unbiased) Hirshfeld subsystems can be rigorously defined within DFT as the corresponding functional derivative of the non-additive kinetic energy functional. This common sense 'stockholder' partitioning scheme of a known molecular density into the AIM pieces, which uses the free subsystem reference of the corresponding 'promolecular' system, has been given a solid information theoretic basis by demonstrating, that it results from the minimum entropy deficiency (information distance) principle, relative to the 'promolecular' data for the free atomic fragments. It was also shown that the same approach results in a generalized 'stockholder' scheme for dividing molecular many-electron densities and probabilities [22]. In particular, the two-electron probabilities in the subsystem resolution, characterizing the 'communication' channels in a molecule, are vital for determining the *entropic* bond-orders [27,28]). An ensemble interpretation of the Hirshfeld partitioning has also been given [22].

Several important properties of these 'stockholder' atoms, the entropy deficiency equilibrium and stable pieces of the molecular electron density, make them attractive concepts for interpretations in chemistry. They preserve as much as possible the information contained in the electron densities of the free atoms, exhibit a single cusp at the atomic nucleus, decay exponentially at large distances from the molecule exhibiting the expected asymptotic behavior; they also reflect the intuitively predicted changes due to formation of a single covalent bond: the overall contraction of the AIM densities and their polarization towards the bonding partner [21,29–30]. The Hirshfeld subsystems satisfy the chemical potential equalization principle, as do all mutually open fragments of the molecular ground-state density, and they locally equalize the subsystem information-distance densities at the corresponding value for the system as a whole [20,33]. The missing information- and entropy-displacement densities have been semi-quantitatively related to the density difference function [29,30], which uses the same 'promolecule' reference and is widely used by chemist in their interpretation of the origins of the chemical bond. With this novel development the importance of the *surprisal* function of the molecular electron density has been stressed and the density difference function has been attributed a new, missing information interpretation. This information-theoretic treatment of molecular subsystems also allows one to derive useful relations between the response properties (local softnesses or Fukui functions) exhibited by the Hirshfeld molecular fragments. The same minimum entropy deficiency principle of the Information Theory can be used to extend the *one-electron* 'stockholder' rule of the Hirshfeld partition to divisions of the joint many-electron densities and probabilities [22,24]. This is vital for extracting entropic measures of the chemical *connectivities* (bonds) [27,28].

The illustrative applications of the Information Theory to the electronic structure phenomena have demonstrated the theory potential in extracting the chemical interpretation from the calculated electron distributions, in terms of atoms and bonds which connect them in a given molecular environment. The theory allows one to describe various stages, intermediate and final, of the atomic density reconstruction in chemical processes, and to determine the average uncertainties in a transmission of the AIM allocation 'signals' throughout the molecular 'communication' system, which can be used to probe the covalent and ionic bond components [27,28]. It has already been amply demonstrated how important this entropic tool is for gaining a better understanding of the 'chemistry' behind the calculated molecular electron densities and probability distributions. In the future these information-theoretic concepts should facilitate a more direct connection between the *ab initio* results of computational quantum chemistry and the intuitive *language* of chemistry, in which such concepts as AIM, bond multiplicities, promotion energy, amount of CT, electronegativity, and the hardness/softness characteristics of the electron gas in a molecule are paramount.

The generalized forces driving changes in the electronic structure, e.g., the CT affinities, have also been defined. They combine the familiar Fukui function response properties of molecular fragments (derivatives of the system energy) with their information-distance densities (derivatives of the system information entropy), thus providing more general descriptors of molecular fragments in reactive systems.

The information-theoretic elements of a 'thermodynamic' description of the electronic structure of molecules and reactive systems cover both the 'vertical', fixed ground-state density problems, and the 'horizontal' transitions between the two ground-state densities. Both equilibrium states and non-equilibrium processes of the 'vertical', molecular fragment description can be tackled in close analogy to the ordinary thermodynamics. This development emphasizes the importance of the complementary energetic and entropy representations, with the Information Theory providing the hitherto missing entropy part of the electronic structure interpretations in chemistry. The energy minimum principle of DFT [1] yields the ground-state density matching a given external potential due to the nuclei, while the 'entropic', fixed density search of Levy [124] delivers the external potential matching a given *v*-representable density [24,93,137,138].

The criteria for the equilibrium electron distributions in molecular systems, including the constrained case of the mutually closed subsystems, have also been reexamined and the effective external potential representability of the molecular fragment densities have been discussed in some detail within the subsystem resolved DFT. It has been argued, that the embedded subsystem density can be viewed as representing the separate (free) system defined by the appropriately defined effective external potential. This result introduces an important element of causality into the subsystem description. Namely, each manipulation performed on the density of a molecular fragment can thus be interpreted as the ground-state response to the concomitant displacement in the subsystem effective external potential, and *vice versa*. Moreover, a given set of non-equilibrium densities of subsystems can be attributed an effective ground-state (constrained equilibrium) interpretation, which is vital for the thermodynamic-like interpretation of intermediate reconstructions of the electron distribution in molecular processes.

The thermodynamic analogies in the entropic description of 'vertical' processes in molecular systems have been extended to the non-equilibrium, instantaneous electron distributions and irreversible processes, covering both the density fluctuations relative to the (stationary) Hirshfeld values, and electron flows between constituent fragments [23]. In this development the 'stockholder' subsystems are viewed as averages of the instantaneous (dynamic) entities, with the distribution of local fluctuations being related to the relevant entropy deficiency density in the thermodynamic-like fashion. This opens a possibility to extend the range of applications of the information-theoretic treatment of the submolecular processes to the realm of non-equilibrium states of subsystems, e.g., in the course of chemical reaction. In other words, this analysis establishes a phenomenological framework for an eventual 'dynamic' indexing the *rates* of chemical reactions.

The 'vertical', submolecular reality of molecular fragments, e.g., AIM, functional groups, reactants, etc., so important for the *language* of chemistry, cannot be directly validated experimentally, since it is not an '*observable*'. It can only be verified indirectly, by the demonstrated close analogy to phenomenological thermodynamics. Indeed, consistent chemical interpretations call for thermodynamic-like causal relations between perturbations and responses in molecular subsystems. With the information-theoretic outlook on the molecular and submolecular electronic structure the whole experience of the ordinary thermodynamics can be employed in treating a variety of subtle processes in chemistry.

In the theory of chemical reactivity the second-order Taylor expansion in the subsystem resolution, defined by the relevant derivatives (electron potentials and charge sensitivities) of the subsystem resolved density functional for the system electronic energy, play an essential role in designing the adequate *two-reactant* reactivity criteria [4,5]. In this survey an overview of such derivative hardness and softness (or Fukui Function) properties has been given, emphasizing similarities and essential differences between such descriptors of the system as a whole (*global* resolution) and those characterizing the interacting, mutually closed molecular fragments (*subsystem* resolution). The latter case is of particular importance for the theory of chemical reactivity, which traditionally uses the reactant resolution. The advantages of DFT in this regard, particularly when supplemented by the information-distance entropic development, have been emphasized throughout this review.

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Kramers Pairs in Configuration Interaction

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Abstract

The theory of symmetry-preserving Kramers pair creation operators is reviewed and formulas for applying these operators to configuration interaction calculations are derived. A new and more general type of symmetry-preserving pair creation operator is proposed and shown to commute with the total spin operator and with all of the symmetry operations which leave the core Hamiltonian of a many-electron system invariant. The theory is extended to cases where orthonormality of orbitals of different configurations cannot be assumed.

Contents

1. INTRODUCTION

In configuration interaction calculations, it is desirable to have methods for generating states of a given symmetry, in order to make the configuration-based matrix representation of the total Hamiltonian block-diagonal. The group of symmetry operators R which commute with the core Hamiltonian of a many-electron system has irreducible representations which characterize convenient symmetry-adapted basis sets for configuration interaction calculations. For example, in nonrelativistic calculations of atomic spectra, sets of Russell–Saunders states form a convenient basis. In this basis, the matrix representation of the core Hamiltonian is diagonal, and the total Hamiltonian, including interelectron repulsion, is block-diagonal, the blocks being characterized by eigenvalues of the

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total angular momentum operator L^2, its z-component L_z, the total spin operator S^2, and its z-component S_z.

In the present paper, we shall discuss a method for generating many-electron states of a given symmetry using Kramers pair creation operators and other symmetry-preserving pair creation and annihilation operators. We will first develop the formalism for the case where orthonormality between the orbitals of different configurations can be assumed. Afterwards we will extend the method to cases where this orthonormality is lost, so that the method also can be used in generalized Sturmian calculations [11–13] and in valence bond calculations.

2. TIME REVERSAL

Very early in the history of quantum theory, H.A. Kramers introduced a time reversal operator [1–3] for N-electron systems.

$$K = \prod\nolimits_{j=1}^{N} (\sigma_y)_j K_0 \tag{1}$$

Kramers' time-reversal operator, shown in equation (1), is a product of Pauli spin matrices

$$\sigma_y \equiv \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{2}$$

in the y direction, preceded by the complex conjugation operator K_0. In equation (1), the subscript j indicates that the Pauli matrix should act on the spin coordinates of the jth electron. To see why Kramers identified this operator with time reversal, we can consider its effect on spin, momentum, angular momentum, and coordinates. The total spin operator is given by:

$$\mathbf{S} = \frac{1}{2} \sum_{j=1}^{N} (\boldsymbol{\sigma})_j \tag{3}$$

where

$$\sigma \equiv \{\, \sigma_x, \quad \sigma_y, \quad \sigma_z \,\} = \left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\} \tag{4}$$

With a little work, one can verify that

$$K\mathbf{S}K^{-1} = -\mathbf{S} \tag{5}$$

In other words, Kramers' time reversal operator changes the sign of total spin. Also one can verify that Kramers' operator K changes the sign of the total momentum,

$$\mathbf{P} \equiv \sum_{j=1}^{N} \mathbf{p}_j \equiv \sum_{j=1}^{N} \frac{1}{\mathrm{i}} \frac{\partial}{\partial \mathbf{x}_j} \tag{6}$$

$$K\mathbf{P}K^{-1} = -\mathbf{P} \tag{7}$$

and total orbital angular momentum

$$\mathbf{L} \equiv \sum_{j=1}^{N} x_j \times \mathbf{p}_j \tag{8}$$

$$K\mathbf{L}K^{-1} = -\mathbf{L} \tag{9}$$

On the other hand, the coordinates are left invariant by Kramers' operator:

$$\mathbf{X} \equiv \sum_{j=1}^{N} \mathbf{x}_j \tag{10}$$

$$K\mathbf{X}K^{-1} = \mathbf{X} \tag{11}$$

This behavior is what one would expect from the operation of time reversal. Spin, momentum, and angular momentum all are reversed, while the coordinates are unchanged.

Kramers next investigated the effect of squaring his operator. He found that $K^2 = (-1)^N$, since

$$\begin{aligned} K^2 &= (\sigma_y)_1(\sigma_y)_2 \ldots K_0(\sigma_y)_1(\sigma_y)_2 \ldots K_0 \\ &= (\sigma_y)_1(\sigma_y)_2 \ldots (\sigma_y)_1^*(\sigma_y)_2^* \ldots K_0^2 \\ &= (-1)^N \end{aligned} \tag{12}$$

This result led Kramers to the following theorem: If the Hamiltonian H of an N-electron system is invariant under time reversal

$$KHK^{-1} = H \tag{13}$$

and if N is odd, then the eigenfunctions must be at least two-fold degenerate. The proof is as follows: Let $|\varphi_\mu\rangle$ be an eigenfunction of H corresponding to the eigenvalue E,

$$H|\varphi_\mu\rangle = E|\varphi_\mu\rangle \tag{14}$$

Then $K|\varphi_\mu\rangle$ must also be an eigenfunction, and it must correspond to the same eigenvalue, since

$$HK|\varphi_\mu\rangle = KH|\varphi_\mu\rangle = EK|\varphi_\mu\rangle \tag{15}$$

Now assume that $K|\varphi_\mu\rangle$ is really the same state as $|\varphi_\mu\rangle$, i.e., assume that it is not a new linearly independent state, but differs from the original eigenfunction only by a phase factor:

$$K|\varphi_\mu\rangle = \mathrm{e}^{\mathrm{i}\delta}|\varphi_\mu\rangle \tag{16}$$

Then

$$K^2|\varphi_\mu\rangle = K\mathrm{e}^{\mathrm{i}\delta}|\varphi_\mu\rangle = \mathrm{e}^{-\mathrm{i}\delta}K|\varphi_\mu\rangle = \mathrm{e}^{-\mathrm{i}\delta}\mathrm{e}^{\mathrm{i}\delta}|\varphi_\mu\rangle = |\varphi_\mu\rangle \tag{17}$$

which contradicts equation (12), since N is odd. Therefore the assumption of equation (16) cannot be true, and $K|\varphi_\mu\rangle$ must be a new linearly independent state, QED.

Let us now specialize to the case where $N = 1$, and let us introduce the notation

$$K|\varphi_\mu\rangle = \omega_\mu|\varphi_{T\mu}\rangle \tag{18}$$

where ω_μ is a phase factor. Similarly,

$$K|\varphi_{T\mu}\rangle = \omega_{T\mu}|\varphi_\mu\rangle \tag{19}$$

where $\omega_{T\mu}$ is another phase factor, and where T stands for 'time reversed'. Then from equation (12) we have

$$K^2|\varphi_\mu\rangle = K\omega_\mu|\varphi_{T\mu}\rangle = \omega_\mu^* K|\varphi_{T\mu}\rangle = \omega_\mu^*\omega_{T\mu}|\varphi_\mu\rangle = -|\varphi_\mu\rangle \tag{20}$$

so that

$$\omega_\mu^*\omega_{T\mu} = -1 \tag{21}$$

A few examples will illustrate the notation introduced in equations (18) and (19), showing why the phase factors are needed in the relationships linking the original state $|\varphi_\mu\rangle$ with its time-reversed partner, $|\varphi_{T\mu}\rangle$. Suppose, for example, that the original state is a spin-up plane wave

$$|\varphi_{\mathbf{k}}\rangle = \frac{1}{\sqrt{V}}\mathrm{e}^{\mathbf{i}\mathbf{k}\cdot\mathbf{x}_1}\begin{pmatrix}1\\0\end{pmatrix} \tag{22}$$

Applying the Kramers time reversal operator we have

$$K|\varphi_{\mathbf{k}}\rangle = \begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}K_0\frac{1}{\sqrt{V}}\mathrm{e}^{\mathbf{i}\mathbf{k}\cdot\mathbf{x}_1}\begin{pmatrix}1\\0\end{pmatrix} = \frac{\mathrm{i}}{\sqrt{V}}\mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{x}_1}\begin{pmatrix}0\\1\end{pmatrix} = \mathrm{i}|\varphi_{T\mathbf{k}}\rangle \tag{23}$$

where

$$|\varphi_{T\mathbf{k}}\rangle = \frac{1}{\sqrt{V}}\mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{x}_1}\begin{pmatrix}0\\1\end{pmatrix} \tag{24}$$

is a spin-down plane wave traveling in the opposite direction. Similarly,

$$K|\varphi_{T\mathbf{k}}\rangle = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} K_0 \frac{1}{\sqrt{V}} \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}_1} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{-\mathrm{i}}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}_1} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -\mathrm{i}|\varphi_{\mathbf{k}}\rangle \quad (25)$$

Notice that in this example, the phase factors $\omega_k = \mathrm{i}$ and $\omega_{Tk} = -\mathrm{i}$ fulfill the requirement shown in equation (21).

As a second example, we can think of the case where the original state is a spin-up atomic orbital of the form:

$$|\varphi_m\rangle = R_{nl}(r_1)Y_{lm}(\theta_1, \phi_1)\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (26)$$

Applying Kramers' time reversal operator we obtain

$$\begin{aligned} K|\varphi_m\rangle &= \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} K_0 R_{nl}(r_1)Y_{lm}(\theta_1, \phi_1)\begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \mathrm{i}R_{nl}(r_1)Y^*_{lm}(\theta_1, \phi_1)\begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \mathrm{i}(-1)^m R_{nl}(r_1)Y_{l,-m}(\theta_1, \phi_1)\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \mathrm{i}|\varphi_{Tm}\rangle \end{aligned} \quad (27)$$

where

$$|\varphi_{Tm}\rangle = (-1)^m R_{nl}(r_1)Y_{l,-m}(\theta_1, \phi_1)\begin{pmatrix} 0 \\ 1 \end{pmatrix} = (-1)^m|\varphi_{-\bar{m}}\rangle \quad (28)$$

We can see that the time-reversed state corresponding to the original atomic orbital is a spin-down orbital with reversed angular momentum. Notice that if magnetic fields are present, time-reversal symmetry is lost.

3. KRAMERS PAIR CREATION OPERATORS

Let R be an element of the group of symmetry operations which leave the one-electron Hamiltonian operator h invariant. Then

$$RhR^{-1} = h \quad (29)$$

If φ_k is a symmetry-adapted eigenfunction of h belonging to a due-degenerate set of states γ, then

$$R|\varphi_k\rangle = \sum_{j\in\gamma} |\varphi_j\rangle D^{\gamma}_{jk}(R) \quad (30)$$

where

$$D^{\gamma}_{jk}(R) = \langle \varphi_j | R | \varphi_k \rangle \tag{31}$$

is a unitary matrix representing the symmetry operation R in the γth irreducible representation. The dimension of the matrix $D^{\gamma}_{jk}(R)$ is N, the number of due-degenerate states in the subshell γ.

These relationships can also be expressed in second-quantized form [4–8] by introducing Fermion creation and annihilation operators, which obey the anti-commutation relations

$$\begin{aligned} b_i^{\dagger} b_j + b_j b_i^{\dagger} &= \delta_{ij} \\ b_i^{\dagger} b_j^{\dagger} + b_j^{\dagger} b_i^{\dagger} &= 0 \\ b_i b_j + b_j b_i &= 0 \end{aligned} \tag{32}$$

In this notation, the one-electron spin-orbital $|\varphi_k\rangle$ becomes

$$|\varphi_k\rangle \equiv b_k^{\dagger} |0\rangle \tag{33}$$

where $|0\rangle$ is the vacuum state. If an annihilation operator acts on the vacuum state, the result is zero, i.e., $b_k|0\rangle = 0$. The second-quantized formalism is isomorphic with the usual Slater-determinant formalism for many-electron wave functions, but it has some advantages. In particular, the second-quantized formalism allows the derivation of some useful commutation relations, as we shall see below.

In second-quantized notation, the relationship shown in equation (30) becomes

$$R b_k^{\dagger} R^{-1} = \sum_{j \in \gamma} b_j^{\dagger} D^{\gamma}_{jk}(R) \tag{34}$$

The Hermitian adjoint of equation (34) is

$$R^{-1} b_k R = \sum_{j \in \gamma} D^{\gamma *}_{kj}(R) b_j \tag{35}$$

Equations (34) and (35) tell us how many-electron states, constructed by letting electron creation operators act on the vacuum state, transform under the elements of the symmetry group of the core Hamiltonian. The vacuum state is assumed to be invariant under the action of these symmetry operations, i.e., $R|0\rangle = |0\rangle$.

Using Kramers' concept of time-reversal, it is possible to construct symmetry preserving pair creation operators of the form [5,7,8]

$$B_{\gamma}^{\dagger} \equiv \frac{1}{\sqrt{2\mathcal{N}}} \sum_{j \in \gamma} \omega_j b_j^{\dagger} b_{Tj}^{\dagger} \tag{36}$$

In equation (36), γ denotes a set of due-degenerate eigenfunctions of the one-electron Hamiltonian h, while $\mathcal{N}$ denotes the number of states in this set. Taking the Hermitian conjugate of equation (36) gives us the corresponding pair annihilation operator:

$$B_\gamma = \frac{1}{\sqrt{2\mathcal{N}}} \sum_{j\in\gamma} \omega_j^* b_{Tj} b_j \tag{37}$$

To see that these operators preserve the symmetry of the many-electron states on which they act, we make use of equations (34) and (35). From equation (34), it follows that

$$\begin{aligned} RB_\gamma^\dagger R^{-1} &= \frac{1}{\sqrt{2\mathcal{N}}} \sum_{j\in\gamma} \omega_j (Rb_j^\dagger R^{-1})(Rb_{Tj}^\dagger R^{-1}) \\ &= \frac{1}{\sqrt{2\mathcal{N}}} \sum_{j,k,l\in\gamma} \omega_j b_k^\dagger b_{Tl}^\dagger D_{kj}^\gamma(R) D_{Tl,Tj}^\gamma(R) \end{aligned} \tag{38}$$

But from equations (31), (19), and (21) we have [5–7]

$$D_{Tl,Tj}^\gamma(R) = \omega_l \omega_j^* D_{lj}^{\gamma *}(R) \tag{39}$$

Finally, making use of the unitarity of $D_{ij}^\gamma(R)$, we obtain

$$\begin{aligned} RB_\gamma^\dagger R^{-1} &= \frac{1}{\sqrt{2\mathcal{N}}} \sum_{j,k,l\in\gamma} \omega_l b_k^\dagger b_{Tl}^\dagger D_{kj}^\gamma(R) D_{lj}^{\gamma *}(R) \\ &= \frac{1}{\sqrt{2\mathcal{N}}} \sum_{k,l\in\gamma} \omega_l b_k^\dagger b_{Tl}^\dagger \delta_{kl} \\ &= \frac{1}{\sqrt{2\mathcal{N}}} \sum_{k\in\gamma} \omega_k b_k^\dagger b_{Tk}^\dagger = B_\gamma^\dagger \end{aligned} \tag{40}$$

If we take the Hermitian conjugate of equation (40), we obtain (since R is unitary)

$$RB_\gamma R^{-1} = B_\gamma \tag{41}$$

Thus, the Kramers pair creation and annihilation operators defined by equations (36) and (37) preserve the symmetry of the states on which they act.

Using the anticommutation relations (32), we can obtain the following commutation relations for the Kramers pair creation and annihilation operators [8]:

$$\begin{aligned} \left[B_{\gamma'}^\dagger, B_\gamma^\dagger\right] &= 0 \\ \left[B_{\gamma'}, B_\gamma\right] &= 0 \\ \left[B_{\gamma'}, B_\gamma^\dagger\right] &= \delta_{\gamma',\gamma}\left(1 - \frac{2}{\mathcal{N}} \sum_{j\in\gamma} b_j^\dagger b_j\right) \end{aligned} \tag{42}$$

The first two of these commutation relations are identical with the commutation relations for Boson creation and annihilation operators, while the last relation in the set differs slightly from the commutation relation, which would hold for bosons. Thus the operators $B_\gamma^\dagger$ and B_γ can be thought of as creating or annihilating 'quasi-bosons'.

As an example of the symmetry-preserving Kramers pair creation operators, we can think of the case of D_3 symmetry, where they have the form [8]:

$$\begin{aligned}
B^\dagger_{A_1} &= \mathrm{i} b^\dagger_{a_1} b^\dagger_{\overline{a_1}} \\
B^\dagger_{A_2} &= \mathrm{i} b^\dagger_{a_2} b^\dagger_{\overline{a_2}} \\
B^\dagger_{E} &= \frac{\mathrm{i}}{\sqrt{2}}\left(b^\dagger_e b^\dagger_{\overline{e}} + b^\dagger_{e'} b^\dagger_{\overline{e'}}\right)
\end{aligned} \tag{43}$$

Notice that the summation of equation (36) has been simplified. Since each state in the set γ appears twice in the sum, coupled with its time-reversed partner, equation (32) can be used to cut the number of terms in half. Strictly speaking, each of the pair creation operators shown in equation (43) ought to have an additional index specifying the particular set of molecular orbitals to which it corresponds.

As a second example, we can think of the case where the one-electron Hamiltonian has spherical symmetry. Then the Kramers pair creation operator corresponding to the shell n and subshell l is given by

$$B^\dagger_{nl} \equiv \frac{\mathrm{i}}{\sqrt{2l+1}} \sum_{m=-l}^{l} (-1)^m b^\dagger_m b^\dagger_{-\overline{m}} \tag{44}$$

Here, just as in equation (43) we have cut the number of terms in the sum in half, since each orbital appears twice in the sum shown in equation (36). In equation (44) we have included the shell index n explicitly in the label of the symmetry-preserving pair creation operator. In the individual one-electron creation operators of equation (44), this index is implied, as is the subshell index l.

4. NORMALIZATION OF DAUGHTER STATES

The commutation relations (42) can be used to normalize the N-electron states obtained by acting on $(N-2)$-electron states with Kramers pair creation operators [8]. Suppose that $|P\rangle$ is a properly normalized $(N-2)$-electron state which is annihilated by B_γ; i.e., suppose that

$$\langle P|P\rangle = 1 \tag{45}$$

and

$$B_\gamma |P\rangle = 0 \tag{46}$$

We would like to choose the normalizing constant α in such a way that the N-electron state

$$|A\rangle = B^\dagger_\gamma |P\rangle \alpha \tag{47}$$

will be properly normalized. Taking the scalar product of $|A\rangle$ with its Hermitian conjugate, and making use of the commutation relations (42), we obtain

$$\begin{aligned}\langle A|A\rangle &= \alpha^2\langle P|B_\gamma B_\gamma^\dagger|P\rangle \\ &= \alpha^2\langle P|B_\gamma^\dagger B_\gamma + [B_\gamma, B_\gamma^\dagger]|P\rangle \\ &= \alpha^2\langle P|\left(1 - \frac{2}{\mathcal{N}}\sum_{j\in\gamma} b_j^\dagger b_j\right)|P\rangle = \alpha^2\left(1 - \frac{2\lambda}{\mathcal{N}}\right) = 1\end{aligned} \tag{48}$$

so that

$$\alpha = \frac{1}{\sqrt{1 - 2\lambda/\mathcal{N}}} \tag{49}$$

where λ is the ‘seniority’ of the parent state $|P\rangle$:

$$\sum_{j\in\gamma} b_j^\dagger b_j|P\rangle = \lambda|P\rangle \tag{50}$$

In other words, λ is the number of electrons in the subshell γ in the parent state $|P\rangle$. This need not be zero, even though B_γ annihilates $|P\rangle$. More generally, one can show that [8]

$$\langle P|(B_\gamma)^n(B_\gamma^\dagger)^n|P\rangle = \prod_{t=1}^{n}\left[t\left(1 - \frac{2\lambda}{\mathcal{N}}\right) - \frac{2t(t-1)}{\mathcal{N}}\right] \tag{51}$$

This last relationship can be used to normalize the states obtained by creating successively larger numbers of Kramers pairs in a subshell until no more states with the symmetry and seniority of the parent state can be created by further filling of the subshell.

5. CONFIGURATION INTERACTION USING KRAMERS PAIR CREATION OPERATORS

We are now in a position to generate a set of many-electron states of a given symmetry for use in configuration interaction calculations [8]. Suppose that our N-electron system has a total Hamiltonian of the form

$$H = H^c + H' \tag{52}$$

where H^c is the core Hamiltonian, and where H' represents the effects of interelectron repulsion. In second-quantized notation we can represent the core Hamiltonian by the operator

$$H^c = \sum_s \epsilon_s b_s^\dagger b_s \tag{53}$$

The simple form of this operator is due to the fact that the creation and annihilation operators $b_s^\dagger\ b_s$ refer to one-electron spin-orbitals which are eigenfunctions of the core Hamiltonian h^c with one-electron energies ϵ_s.

$$h^c(1)\varphi_s(1) = \epsilon_s\varphi_s(1) \tag{54}$$

Often configuration interaction calculations are performed after an initial Hartree–Fock calculation. In such cases the one-electron creation and annihilation operators would refer to eigenfunctions of the Fock operator, and the Fock operator would have a simple form similar to that shown in equation (53).

In second-quantized notation, the operator representing interelectron repulsion has the form:

$$H' = \frac{1}{2}\sum_{s,t,u,v} g_{st|uv} b_s^\dagger b_t^\dagger b_u b_v \tag{55}$$

where

$$g_{st|uv} \equiv \int \mathrm{d}\tau_1 \int \mathrm{d}\tau_2 \varphi_s^*(1)\varphi_t^*(2)\frac{1}{r_{12}}\varphi_u(2)\varphi_v(1) \tag{56}$$

The symbol $\int \mathrm{d}\tau_j$ in equation (56) stands for both integration over the space coordinates of the jth electron and also a scalar product involving the spin coordinates.

In CI calculations, we need to construct a matrix representation of the Hamiltonian based on the configurations. For this purpose, we would like to be able to evaluate matrix elements of the form:

$$\langle A|B_{\gamma'}HB_\gamma^\dagger|A\rangle = \frac{1}{2\sqrt{\mathcal{N}'\mathcal{N}}}\sum_{j\in\gamma'}\sum_{k\in\gamma}\omega_j^*\omega_k\langle A|b_{Tj}b_jHb_k^\dagger b_{Tk}^\dagger|A\rangle \tag{57}$$

For off-diagonal matrix elements we have (from the orthogonality of the one-electron spin-orbitals)

$$\begin{aligned}\langle A|B_{\gamma'}HB_\gamma^\dagger|A\rangle = {}& \frac{1}{2\sqrt{\mathcal{N}'\mathcal{N}}}\sum_{j\in\gamma'}\sum_{k\in\gamma}\omega_j^*\omega_k \times \int \mathrm{d}\tau_1\int \mathrm{d}\tau_2\varphi_{Tj}^*(1)\varphi_j^*(2)\frac{1}{r_{12}} \\ & \times(1-\mathcal{P}_{12})\varphi_k(2)\varphi_{Tk}(1) \qquad \text{if } \gamma'\neq\gamma\end{aligned} \tag{58}$$

where $\mathcal{P}_{12}$ interchanges the coordinates of electrons 1 and 2. In the case of spherical symmetry, equation (58) becomes

$$\begin{aligned}\langle A|B_{n'l'}HB_{nl}^\dagger|A\rangle = {}& \frac{1}{\sqrt{(2l'+1)(2l+1)}}\sum_{m'=-l'}^{l'}\sum_{m=-l}^{l}(-1)^{m'+m} \\ & \times\int \mathrm{d}^3x_1\int \mathrm{d}^3x_2\varphi_{n',l',-m'}^*(\mathbf{x}_1)\varphi_{n',l',m'}^*(\mathbf{x}_2)\frac{1}{r_{12}}\varphi_{n,l,m}(\mathbf{x}_2)\varphi_{n,l,-m}(\mathbf{x}_1) \\ & \text{if } (n',l')\neq(n,l)\end{aligned} \tag{59}$$

We can use the sum rule for spherical harmonics to get rid of the double sum over m and m' in equation (59), since

$$\begin{aligned}
&\sum_{m=-l}^{l} (-1)^m \varphi_{n,l,m}(\mathbf{x}_2)\varphi_{n,l,-m}(\mathbf{x}_1) \\
&\quad = R_{nl}(r_1)R_{nl}(r_2) \sum_{m=-l}^{l} (-1)^m Y_{l,-m}(\theta_1,\phi_1)Y_{l,m}(\theta_2,\phi_2) \\
&\quad = R_{nl}(r_1)R_{nl}(r_2) \sum_{m=-l}^{l} Y^*_{l,m}(\theta_1,\varphi_1)Y_{l,m}(\theta_2,\phi_2) \\
&\quad = \frac{2l+1}{4\pi} R_{nl}(r_1)R_{nl}(r_2)P_l(\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2)
\end{aligned} \tag{60}$$

and similarly

$$\sum_{m'=-l'}^{l'} (-1)^{m'} \varphi^*_{n',l',-m'}(\mathbf{x}_1)\varphi^*_{n',l',m'}(\mathbf{x}_2) = \frac{2l'+1}{4\pi} R_{n'l'}(r_1)R_{n'l'}(r_2)P_{l'}(\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2) \tag{61}$$

The interaction $1/r_{12}$ can also be expressed in terms of Legendre polynomials:

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2) \tag{62}$$

Thus equation (59) can be written in the form:

$$\begin{aligned}
\langle A|B_{n'l'}HB^\dagger_{nl}|A\rangle = \sqrt{(2l'+1)(2l+1)} \sum_{k=|l-l'|}^{l+l'} I_{k,l,l'} \int_0^\infty \mathrm{d}r_1 r_1^2 R_{n'l'}(r_1)R_{nl}(r_1) \\
\times \int_0^\infty \mathrm{d}r_1 r_2^2 R_{n'l'}(r_2)R_{nl}(r_2) \frac{r_<^k}{r_>^{k+1}} \quad \text{if } (n',l') \neq (n,l)
\end{aligned} \tag{63}$$

where

$$I_{k,l,l'} \equiv \frac{1}{(4\pi)^2} \int \mathrm{d}\Omega_2 \int \mathrm{d}\Omega_1 P_k(\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2)P_l(\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2)P_{l'}(\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2) \tag{64}$$

The angular integral $I_{k,l,l'}$ can be simplified by letting $\mathbf{x}_2$ be the z-axis during the integration over $\mathrm{d}\Omega_1$. Then $\hat{\mathbf{x}}_1\cdot\hat{\mathbf{x}}_2 = \cos\theta_1$. Since the result of the integration over $\mathrm{d}\Omega_1$ is independent of $\hat{\mathbf{x}}_2$, we can write

$$I_{k,l,l'} = \frac{1}{4\pi} \int \mathrm{d}\Omega_1 P_k(\cos\theta_1)P_l(\cos\theta_1)P_{l'}(\cos\theta_1) \tag{65}$$

We next make use of the identity

$$P_l(\cos\theta_1) = \sqrt{\frac{4\pi}{2l+1}}\, Y_{l,0}(\theta_1,\phi_1) \tag{66}$$

to express the angular integral in the form

$$I_{k,l,l'} = \sqrt{\frac{4\pi}{(2k+1)(2l+1)(2l'+1)}} \int d\Omega_1 Y_{k,0} Y_{l,0} Y_{l',0} \tag{67}$$

But this integral can be expressed as a Condon–Shortly coefficient [7], which in turn can be expressed in terms of $3-j$ coefficients [9,10]. In this way we obtain a simple result in which the angular integral of equation (63) is shown to be the square of a $3-j$ coefficient:

$$I_{k,l,l'} = \left| \begin{pmatrix} k & l & l' \\ 0 & 0 & 0 \end{pmatrix} \right|^2 \tag{68}$$

In order for this coefficient to be nonzero, the indices k, l, and l' must fulfill a triangular relationship, and must add up to an even number. Thus, in equation (63), the sum runs in steps of 2 from $|l-l'|$ to $l+l'$ rather than running in steps of 1 from 0 to ∞.

6. DIAGONAL MATRIX ELEMENTS

We next turn to the case where $\gamma' = \gamma$ in equation (57). For diagonal matrix elements of this form, the core Hamiltonian makes a contribution, but luckily this contribution can be expressed very simply. From equations (53) and (32), we can derive the commutation relation:

$$\left[H^c, b_j^\dagger b_{Tj}^\dagger\right] = 2\epsilon_\gamma b_j^\dagger b_{Tj}^\dagger \tag{69}$$

where ϵ_γ is the one-electron energy characterizing the subshell to which both φ_j and φ_{Tj} belong. Since this energy is the same for all the one-electron spin-orbitals in the subshell, we can factor it out from the sum in equation (36), which can be combined with equation (69) to yield:

$$\left[H^c, B_\gamma^\dagger\right] = 2\epsilon_\gamma B_\gamma^\dagger \tag{70}$$

From the commutation relation (70), it follows that if

$$H^c|A\rangle = E_A|A\rangle \tag{71}$$

then

$$\langle A|B_\gamma H^c B_\gamma^\dagger|A\rangle = (E_A + 2\epsilon_\gamma)\langle A|B_\gamma B_\gamma^\dagger|A\rangle \tag{72}$$

In other words, when a Kramers pair creation operator acts on an $(N-2)$-electron state $|A\rangle$, which is an eigenfunction of the core Hamiltonian, it produces an N-electron state which is also an eigenfunction of H^c, with an eigenvalue increased by twice the energy of the subshell to which the pair creation operator corresponds. This simple result holds not only for cases of spherical symmetry, but for all types of symmetry.

The contribution of interelectron repulsion to diagonal matrix elements of the type shown in equation (56) is more complex. However, it turns out that in the case of spherical symmetry one can get rid of the m-summations by making use of the sum rule for spherical harmonics. The result is as follows:

$$\begin{aligned}\langle A|B_{nl}H'B^{\dagger}_{nl}|A\rangle = {} & \langle A|H'|A\rangle + (2l+1)\sum_{k=0}^{2l}\left|\begin{pmatrix} k & l & l \\ 0 & 0 & 0 \end{pmatrix}\right|^{2}\int_{0}^{\infty} \mathrm{d}r_1 r_1^2 |R_{nl}(r_1)|^2 \\ & \times \int_0^{\infty} \mathrm{d}r_2 r_2^2 |R_{nl}(r_2)|^2 \frac{r_<^k}{r_>^{k+1}} + \sum_j \langle A|b_j^{\dagger} b_j|A\rangle \left[2\int_0^{\infty} \mathrm{d}r_1 r_1^2 |R_{nl}(r_1)|^2 \right. \\ & \times \int \mathrm{d}^3x_2 |\varphi_j(\mathbf{x}_2)|^2 \frac{1}{r_{12}} - \frac{1}{4\pi}\int \mathrm{d}^3x_1 R_{nl}(r_1) R_{nl}(r_2) \\ & \left. \times \int \mathrm{d}^3x_2 \varphi_j^*(\mathbf{x}_2)\varphi_j(\mathbf{x}_1) P_l(\hat{\mathbf{x}}_1 \cdot \hat{\mathbf{x}}_2) \frac{1}{r_{12}} \right] \end{aligned} \tag{73}$$

We will discuss the derivation of this result in a later section.

7. MORE GENERAL SYMMETRY-PRESERVING PAIR CREATION OPERATORS

Although we can obtain many N-electron states with the same symmetry and spin as an $(N-2)$-electron parent state by acting with Kramers creation operators, one cannot reach them all in this way. For example, one cannot reach singly excited states. Therefore it is interesting to ask whether it might be possible to find other symmetry-preserving pair creation and annihilation operators, analogous to the Kramers pair creation operators $B^{\dagger}_{\gamma}$ and B_{γ} but of greater generality. For example, if we consider the case of spherical symmetry, we can ask whether the operator

$$W^{\dagger}_{n',n,l} \equiv \frac{1}{\sqrt{2(2l+1)}}\sum_{m=-l}^{l}(-1)^{m}\left(b^{\dagger}_{n',l,m}b^{\dagger}_{n,l,-\overline{m}} + b^{\dagger}_{n,l,m}b^{\dagger}_{n',l,-\overline{m}}\right) \tag{74}$$

where n and n' are not necessarily equal, will commute with all the components of the total spin operator $\mathbf{S}$ and the total angular momentum operator $\mathbf{L}$. The answer is yes. All of the components of $\mathbf{L}$ commute with $W^{\dagger}_{n',n,l}$ for the following reason: The matrices $D^{\gamma}_{jk}(R)$ which appear in equations (38–40) involve only the angular parts of the one-electron orbitals. The radial parts, which are the only parts dependent on n and n', are invariant under rotations and can be factored out from the summations in equations (38–40). Thus we obtain an equation analogous to equation (40) for the more general operator $W^{\dagger}_{n',n,l}$, and therefore,

$$\left[\mathbf{L}, W^{\dagger}_{n',n,l}\right] = 0 \tag{75}$$

We next turn to the question of whether the total spin operator commutes with $W^{\dagger}_{n',n,l}$. In Ref. [8] it is shown that the components of the total spin operator can be expressed in second-quantized form by means of the relationships:

$$\begin{aligned} S_{+} &= S_x + \mathrm{i}S_y = \sum_k b^{\dagger}_k b_{\bar{k}} \\ S_{-} &= S_x - \mathrm{i}S_y = \sum_k b^{\dagger}_{\bar{k}} b_k \\ S_z &= \tfrac{1}{2}\sum_k \left(b^{\dagger}_k b_k - b^{\dagger}_{\bar{k}} b_{\bar{k}}\right) \end{aligned} \tag{76}$$

where the overbar denotes a spin-down spin-orbital. It is also shown in Ref. [8] that

$$\left[\mathbf{S}, (b^{\dagger}_i b^{\dagger}_{\bar{j}} + b^{\dagger}_j b^{\dagger}_{\bar{i}})\right] = 0 \tag{77}$$

However, $W^{\dagger}_{n',n,l}$ can be rewritten so that each of the terms in the summation will have the form $(b^{\dagger}_i b^{\dagger}_{\bar{j}} + b^{\dagger}_j b^{\dagger}_{\bar{i}})$. To do this, we notice that since the sum in equation (74) runs over all m values, it will be unchanged if we interchange m and $-m$ in the first term in the round brackets. Thus we can write

$$W^{\dagger}_{n',n,l} \equiv \frac{1}{\sqrt{2(2l+1)}} \sum_{m=-l}^{l} (-1)^m \left(b^{\dagger}_{n',l,-m} b^{\dagger}_{n,l,\bar{m}} + b^{\dagger}_{n,l,m} b^{\dagger}_{n',l,-\bar{m}}\right) \tag{78}$$

In this form, it is easy to see from equation (77) that the terms in round brackets have the right form to commute with **S**, and therefore,

$$\left[\mathbf{S}, W^{\dagger}_{n',n,l}\right] = 0 \tag{79}$$

From the argument given above, it can also be seen that the Kramers pair creation operators $B^{\dagger}_{n,l}$ commute with **S**, since $W^{\dagger}_{n,n,l} = \sqrt{2}B^{\dagger}_{n,l}$.

Most of the formalism derived in previous sections for $B^{\dagger}_{\gamma}$ and B_{γ} can be carried through with only slight changes for the more general operators $W^{\dagger}_{n',n,l}$ and $W_{n',n,l}$. For example, the commutation relation with the core Hamiltonian is found to be

$$\left[H^c, W^{\dagger}_{n',n,l}\right] = (\epsilon_{n'l} + \epsilon_{nl}) W^{\dagger}_{n',n,l} \tag{80}$$

while the off-diagonal matrix elements analogous to equation (63) become

$$
\begin{aligned}
\langle A|W_{n''',n'',l'}HW^{\dagger}_{n',n,l}|A\rangle = \sqrt{(2l'+1)(2l+1)}\sum_{k=|l-l'|}^{l+l'}\left|\begin{pmatrix} k & l & l' \\ 0 & 0 & 0 \end{pmatrix}\right|^2 \\
\times\left[\int_0^{\infty}\mathrm{d}r_1 r_1^2 R_{n''l'}(r_1)R_{n'l}(r_1)\right. \\
\times\int_0^{\infty}\mathrm{d}r_2 r_2^2 R_{n'''l'}(r_2)R_{nl}(r_2)\frac{r_<^k}{r_>^{k+1}} \\
+\int_0^{\infty}\mathrm{d}r_1 r_1^2 R_{n''l'}(r_1)R_{nl}(r_1) \\
\left.\times\int_0^{\infty}\mathrm{d}r_2 r_2^2 R_{n'''l'}(r_2)R_{n'l}(r_2)\frac{r_<^k}{r_>^{k+1}}\right]
\end{aligned}
\tag{81}
$$

Commutation relations analogous to (42) can also be derived for the more general symmetry-preserving pair creation operators:

$$
\begin{aligned}
\left[W^{\dagger}_{n''',n'',l'}, W^{\dagger}_{n',n,l}\right] &= 0 \\
\left[W_{n''',n'',l'}, W_{n',n',l}\right] &= 0 \\
\left[W_{n',n,l}, W^{\dagger}_{n',n,l}\right] &= 1 - \frac{1}{2(2l+1)}\left(\sum_{j\in n'l} b_j^{\dagger}b_j + \sum_{j\in nl} b_j^{\dagger}b_j\right)
\end{aligned}
\tag{82}
$$

from which we obtain

$$
\langle A|W_{n',n,l}W^{\dagger}_{n',n,l}|A\rangle = 1 - \frac{\lambda_{n'l}+\lambda_{nl}}{2(2l+1)}
\tag{83}
$$

provided that $W_{n',n,l}|A\rangle = 0$. In equation (83), λ_{nl} represents the number of electrons in the *nl* subshell in $|A\rangle$.

The example discussed above was the case of spherical symmetry. We can ask whether general symmetry-preserving pair creation operators analogous to $W^{\dagger}_{n',n,l}$ can be constructed for other types of symmetry. For example, does the operator

$$
W^{\dagger}_{n',n,E} = \frac{\mathrm{i}}{2}\left(b^{\dagger}_{n',e}b^{\dagger}_{n,\overline{e}} + b^{\dagger}_{n,e}b^{\dagger}_{n',\overline{e}} + b^{\dagger}_{n',e'}b^{\dagger}_{n,\overline{e'}} + b^{\dagger}_{n,e'}b^{\dagger}_{n',\overline{e'}}\right)
\tag{84}
$$

commute with **S** and with all the elements of D_3? From equation (77), it is easily seen that $W^{\dagger}_{n',n,E}$ commutes with all the components of **S**, since the first two terms in the round brackets have the right form to commute with the spin operator, as do the last two. What about the group elements of D_3? Let us think of a molecule which has

D_3 symmetry. Let

$$\begin{aligned} |\chi_{n,j}\rangle &\equiv \chi_{n,1,0}(\mathbf{x}-\mathbf{X}_j)\begin{pmatrix}1\\0\end{pmatrix} \\ |\chi_{n,\bar{j}}\rangle &\equiv \chi_{n,1,0}(\mathbf{x}-\mathbf{X}_j)\begin{pmatrix}0\\1\end{pmatrix} \end{aligned} \tag{85}$$

represent, respectively, spin-up and spin-down atomic orbitals located on the three identical atoms in the molecule, whose positions, $\mathbf{X}_1$, $\mathbf{X}_2$, and $\mathbf{X}_3$, are carried over into each other by the elements of D_3. All of these atomic orbitals have $l = 1$ and $m = 0$, the z-axis being chosen perpendicular to the plane of the molecule, while n is the principal quantum number. Then

$$\begin{aligned} |\varphi_{n,e}\rangle &= \sqrt{\tfrac{2}{3}}\Big(|\chi_{n,1}\rangle - \tfrac{1}{2}|\chi_{n,2}\rangle - \tfrac{1}{2}|\chi_{n,3}\rangle\Big) \\ |\varphi_{n,e'}\rangle &= \tfrac{1}{\sqrt{2}}\Big(|\chi_{n,2}\rangle - |\chi_{n,3}\rangle\Big) \end{aligned} \tag{86}$$

(to which the creation operators in equation (82) refer) form the basis of the two-dimensional irreducible E representation of the group D_3. The matrices representing the group elements in terms of these basis functions are independent of n. Similar considerations hold for the matrices based on the corresponding spin-down functions. Since the transformation matrices $D^{\gamma}_{kl}(R)$ are independent of these indices, equations (38–40) go through as before, and the pair creation operator shown in equation (82) preserves the symmetry under D_3 of any state on which it acts.

In general, the irreducible representations of a molecular point group can be derived from the regular representation of the group (i.e., from the representation based on the group elements themselves). Obviously indices like n' and n have no chance of entering the matrices $D^{\gamma}_{jk}(R)$ when the irreducible representations are derived in this way. If the one-electron orbitals to which the creation and annihilation operators refer are chosen to be basis functions for these purely group-theoretical representations of the elements R, then general symmetry-preserving pair creation operators of the W-type discussed above can always be constructed from them.

The importance of the W operators derives from the fact that single excitations from the ground state can be expressed in terms of them. By contrast, the B operators are only able to represent double excitations.

8. GENERALIZED STURMIANS; NONORTHOGONALITY

In the preceding discussion, the creation and annihilation operators always referred to a set of orthonormal spin-orbitals. We can ask how much of the formalism holds in cases where complete orthonormality can no longer be assumed, for example, in valence-bond calculations or in the generalized Sturmian method.

The generalized Sturmian method for solving the N-electron Schrödinger equation [11–20] is a direct configuration interaction method, using basis functions which are antisymmetrized isoenergetic solutions of the approximate N-electron equation

$$\left[-\tfrac{1}{2}\Delta + \beta_\nu V_0(\mathbf{x}) - E\right]\Phi_\nu(\mathbf{x}) = 0 \tag{87}$$

where

$$\Delta \equiv \sum_{j=1}^{N} \nabla_j^2 \tag{88}$$

In equation (87), V_0 is as near as possible to the actual potential V, and the weighting-constants β_ν are chosen in such a way as to make all of the solutions correspond to the same energy, regardless of the quantum numbers.

In atomic calculations, equation (87) can be solved exactly if V_0 is set equal to the nuclear attraction potential

$$V_0(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j} \tag{89}$$

Then Slater determinants of the form

$$|\Phi_\nu\rangle = |\chi_{n,l,m,m_s}\chi_{n',l',m',m'_s}\chi_{n'',l'',m'',m''_s}\cdots| \tag{90}$$

will be exact solutions to equation (87) if the functions χ_{n,l,m,m_s}, χ_{n',l',m',m'_s}, etc. are hydrogen-like spin-orbitals corresponding to a nucleus with effective charge

$$Q_\nu = \beta_\nu Z = \left(\frac{-2E}{\frac{1}{n^2} + \frac{1}{n'^2} + \cdots}\right)^{1/2} \tag{91}$$

Each configuration $|\Phi_\nu\rangle$ is characterized by its own effective charge Q_ν, chosen in such a way as to make all of the solutions to the approximate equation (87) correspond to the actual energy E of the true solution of the Schrödinger equation. Thus radial orthonormality between the one-electron orbitals of different configurations cannot be assumed, although orthogonality with respect to the quantum numbers l, m, and m_s is retained. Since complete orthogonality of the one-electron orbitals cannot be assumed, it is necessary to use the generalized Slater–Condon rules [20–23] when constructing off-diagonal matrix elements of the configuration-based matrix representation of the Hamiltonian. Let Φ_ν and $\Phi_{\nu'}$ be two Slater determinants, defined by:

$$\sqrt{N!}\,\Phi_\nu \equiv F \equiv \begin{vmatrix} f_1(1) & f_2(1) & \cdots & f_N(1) \\ f_1(2) & f_2(2) & \cdots & f_N(2) \\ \vdots & \vdots & & \vdots \\ f_1(N) & f_2(N) & \cdots & f_N(N) \end{vmatrix} \tag{92}$$

and

$$\sqrt{N!}\,\Phi_{\nu'} \equiv G \equiv \begin{vmatrix} g_1(1) & g_2(1) & \cdots & g_N(1) \\ g_1(2) & g_2(2) & \cdots & g_N(2) \\ \vdots & \vdots & & \vdots \\ g_1(N) & g_2(N) & \cdots & g_N(N) \end{vmatrix} \tag{93}$$

and let S be the matrix of overlap integrals between the one-electron orbitals of the two:

$$S \equiv \begin{pmatrix} \langle f_1|g_1\rangle & \langle f_1|g_2\rangle & \cdots & \langle f_1|g_N\rangle \\ \langle f_2|g_1\rangle & \langle f_2|g_2\rangle & \cdots & \langle f_2|g_N\rangle \\ \vdots & \vdots & & \vdots \\ \langle f_N|g_1\rangle & \langle f_N|g_2\rangle & \cdots & \langle f_N|g_N\rangle \end{pmatrix} \tag{94}$$

Then (as is shown in Ref. [20]) the first generalized Slater–Condon rule can be expressed in the form:

$$\langle \Phi_\nu | \Phi_{\nu'} \rangle = |S| \tag{95}$$

The matrix elements of the core Hamiltonian

$$H^c = -\frac{1}{2}\Delta + V_0 = \sum_{j=1}^{N} h(j) \tag{96}$$

and the interelectron repulsion term H' can be found using the second and third generalized Slater–Condon rules in the form developed in Ref. [20].

$$\langle \Phi_\nu | H^c | \Phi_{\nu'} \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} (-1)^{i+j} \langle f_i | h^c | g_j \rangle |S_{ij}| \tag{97}$$

while

$$\langle \Phi_\nu | H' | \Phi_{\nu'} \rangle = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{k=1}^{N} \sum_{l=k+1}^{N} (-1)^{i+j+k+l} C_{ij;kl} |S_{ij;kl}| \tag{98}$$

where

$$C_{ij;kl} \equiv \int d\tau_1 \int d\tau_2 f_i^*(1) f_j^*(2) \frac{1}{r_{12}} \left[g_k(1) g_l(2) - g_l(1) g_k(2) \right] \tag{99}$$

In equation (95), $|S|$ is the determinant of the overlap matrix. In (97), $|S_{ij}|$ is the determinant of the matrix formed from S by deleting the ith row and jth column. In (98), $|S_{ij;kl}|$ is the determinant of the matrix formed from S by deleting the ith and jth rows and the kth and lth columns.

Although the radial orthogonality of the one-electron spin-orbitals in different configurations is lost when the generalized Sturmian method is applied to atoms, the angular orthogonality and spin orthogonality remain, and in many important cases the overlap matrix can be brought into the form:

$$S = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & x & x & x & \cdots \\ 0 & 0 & x & x & x & \cdots \\ 0 & 0 & x & x & x & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{pmatrix} \tag{100}$$

where the first two rows and the first two columns consist entirely of zeros, but where the remaining elements may be nonzero. Whenever this is possible, the four-fold sum in equation (98) disappears, and we have only a single contribution to the interelectron repulsion matrix element.

$$\langle \Phi_\nu | H' | \Phi_{\nu'} \rangle = C_{12;12} |S_{12;12}| \tag{101}$$

In many cases, equation (101) can be used to simplify matrix elements of the type shown in equation (59), even in the generalized Sturmian method, where radial orthonormality is lost for configurations corresponding to different values of the effective charge Q_ν. Suppose, for example, that the state $B_{nl}^\dagger |A\rangle$ is a sum of Slater determinants, all of which are characterized by the same value of Q_ν. Suppose also that a different value of effective charge, $Q_{\nu'}$, characterizes all of the Slater determinants which add together to form the conjugate state $\langle \tilde{A} | \tilde{B}_{n'l'}$. We use a tilde above the letters A and B to remind ourselves that the hydrogen-like one-electron spin-orbitals from which the conjugate state is constructed correspond to this different effective nuclear charge. We further suppose that $l \neq l'$, and that neither

l nor l' appears in $|A\rangle$. Then equation (101) can be used to obtain the simple result.

$$\langle\tilde{A}|\tilde{B}_{n'l'}H'B^{\dagger}_{nl}|A\rangle = \sqrt{(2l'+1)(2l+1)}|S_{12;12}| \sum_{k=|l-l'|}^{l+l'} \left|\begin{pmatrix} k & l & l' \\ 0 & 0 & 0 \end{pmatrix}\right|^2$$
$$\times \int_0^\infty \mathrm{d}r_1 r_1^2 \tilde{R}_{n'l'}(r_1)R_{nl}(r_1) \int_0^\infty \mathrm{d}r_1 r_2^2 \tilde{R}_{n'l'}(r_2)R_{nl}(r_2)\frac{r_<^k}{r_>^{k+1}}$$
$$\text{if } l' \neq l \tag{102}$$

Furthermore, using equations (97) and (100) we obtain:

$$\langle\tilde{A}|\tilde{B}_{n'l'}H^c B^{\dagger}_{nl}|A\rangle = 0 \qquad \text{if } \; l' \neq l \tag{103}$$

We can next ask whether any simplifications of the four-fold sum in equation (98) are possible when the overlap matrix S has the form:

$$S = \begin{pmatrix} x & 0 & 0 & 0 & 0 & \cdots \\ 0 & x & 0 & 0 & 0 & \cdots \\ 0 & 0 & x & x & x & \cdots \\ 0 & 0 & x & x & x & \cdots \\ 0 & 0 & x & x & x & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{pmatrix} \tag{104}$$

In that case equation (98) reduces to

$$\begin{aligned}\langle\Phi_\nu|H'|\Phi_{\nu'}\rangle = {} & C_{12;12}|S_{12;12}| \\ & + \sum_{i=3}^{N}\sum_{k=3}^{N}(-1)^{i+k}\big(C_{1i;1k}|S_{1i;1k}| + C_{i2;k2}|S_{i2;k2}|\big) \\ & + \sum_{i=3}^{N}\sum_{j=i+1}^{N}\sum_{k=3}^{N}\sum_{l=k+1}^{N}(-1)^{i+j+k+l}C_{ij;kl}|S_{ij;kl}|\end{aligned} \tag{105}$$

We now let

$$\begin{aligned} f_1 &= \tilde{\chi}_{n',l,m'} & f_2 &= \tilde{\chi}_{n',l,-\overline{m'}} \\ g_1 &= \chi_{n,l,m} & g_2 &= \chi_{n,l,-\overline{m}} \end{aligned} \tag{106}$$

Then

$$\begin{aligned} \langle f_1|g_1\rangle &= \langle f_2|g_2\rangle = \delta_{m'm}\int_0^\infty \mathrm{d}r_1 r_1^2 \tilde{R}_{n'l}(r_1)R_{nl}(r_1) \\ \langle f_1|g_2\rangle &= \langle f_2|g_1\rangle = 0 \end{aligned} \tag{107}$$

Combining equations (105), (106), and (107), and making use of the sum rule for spherical harmonics, we obtain:

$$\begin{aligned}\langle \tilde{A}|\tilde{B}_{n'l}H'B^{\dagger}_{nl}|A\rangle &= \left|\int_0^{\infty} \mathrm{d}r_1 r_1^2 \tilde{R}_{n'l}(r_1)R_{nl}(r_1)\right|^2 \langle \tilde{A}|H'|A\rangle + (2l+1)|S_{12;12}| \\ &\times \sum_{k=0}^{2l} \left|\begin{pmatrix} k & l & l \\ 0 & 0 & 0 \end{pmatrix}\right|^2 \int_0^{\infty} \mathrm{d}r_1 r_1^2 \tilde{R}_{n'l}(r_1)R_{nl}(r_1) \\ &\times \int_0^{\infty} \mathrm{d}r_1 r_2^2 \tilde{R}_{n'l}(r_2)R_{nl}(r_2) \frac{r_<^k}{r_>^{k+1}} + \Delta \end{aligned} \qquad (108)$$

where

$$\Delta = \sum_{i=3}^{N} \sum_{k=3}^{N} (-1)^{i+k} \frac{|S_{1i;1k}|}{2l+1} \sum_{m=-l}^{l} \left(C^m_{1i;1k} + C^m_{i2;k2}\right) \qquad (109)$$

with the definitions

$$C^m_{1i;1k} \equiv \int \mathrm{d}\tau_1 \int \mathrm{d}\tau_2 \tilde{\chi}^*_{n'lm}(1) f_i^*(2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_{nlm}(1) g_k(2) \qquad (110)$$

and

$$C^m_{i2;k2} \equiv \int \mathrm{d}\tau_1 \int \mathrm{d}\tau_2 \tilde{\chi}^*_{n'l-\bar{m}}(1) f_i^*(2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_{nl-\bar{m}}(1) g_k(2) \qquad (111)$$

Making use of the sum rule for spherical harmonics

$$\sum_{m=-l}^{l} Y^*_{l,m}(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2) = \frac{2l+1}{4\pi} P_l(\hat{\mathbf{x}}_1 \cdot \hat{\mathbf{x}}_2) \qquad (112)$$

which in the case $\theta_1 = \theta_2$, $\phi_1 = \phi_2$ reduces to

$$\sum_{m=-l}^{l} Y^*_{l,m}(\theta_1, \phi_1) Y_{l,m}(\theta_1, \phi_1) = \frac{2l+1}{4\pi} P_l(1) = \frac{2l+1}{4\pi} \qquad (113)$$

we obtain

$$\begin{aligned}\mathit{\Delta} = \sum_{i=3}^{N} \sum_{k=3}^{N} \delta_{m_{si},m_{sk}} (-1)^{i+k} \frac{|S_{1i;1k}|}{4\pi} \int \mathrm{d}^3x_1 \int \mathrm{d}^3x_2 \frac{1}{r_{12}} \\ \times \left[2\tilde{R}_{n'l}(r_1)R_{nl}(r_1) f_i^*(\mathbf{x}_2) g_k(\mathbf{x}_2) \right. \\ \left. -\tilde{R}_{n'l}(r_1)R_{nl}(r_2) f_i^*(\mathbf{x}_2) g_k(\mathbf{x}_1) P_l(\hat{\mathbf{x}}_1 \cdot \hat{\mathbf{x}}_2)\right] \end{aligned} \qquad (114)$$

In the case where $n = n'$, equation (108) reduces to (73).

The examples discussed here show that even in the case where the generalized Sturmian method is applied to atoms, a case in which radial orthonormality between different configurations is sometimes lost, simplified formulas for the matrix elements can often be derived. However, even when this is not possible, the symmetry-preserving pair creation operators offer advantages in configuration interaction calculations because they allow appropriate basis sets to be chosen automatically, and because use of these operators greatly reduces the order of the secular equations. Implementation of the method is in progress, and numerical results will be discussed in a future publication.

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Natural Orbitals from Generalized Sturmian Calculations

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Abstract

The generalized Sturmian method is a direct configuration interaction method for solving the Schrödinger equation of a many-electron system. The configurations in the basis set are solutions to an approximate Schrödinger equation with a weighted potential $\beta_\nu V_0(\mathbf{x})$, the weighting factors β_ν being chosen in such a way as to make the set of solutions isoenergetic. The method is illustrated by calculation of atomic excited states and used to generate natural orbitals.

Contents

1. INTRODUCTION

The generalized Sturmian method [1–22] for solving the Schrödinger equation of an N-particle system is a direct configuration interaction method, in which the configurations are chosen to be isoenergetic solutions to the approximate many-particle Schrödinger equation

$$\left[-\frac{1}{2}\Delta + \beta_\nu V_0(\mathbf{x}) - E\right]\Phi_\nu(\mathbf{x}) = 0 \tag{1}$$

Here

$$\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\} \tag{2}$$

$$\mathbf{x}_j \equiv \{x_j, y_j, z_j\} \quad j = 1, 2, \ldots, N \tag{3}$$

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and

$$\Delta \equiv \sum_{j=1}^{N} \nabla_j^2 \tag{4}$$

In equation (1), the approximate potential V_0 is chosen so that (1) is soluble, and it should resemble the actual potential as closely as possible. The weighting constants β_ν are especially chosen in such a way that all the solutions to equation (1) correspond to the same energy, E, regardless of their quantum numbers ν. Thus we have what might be called a ‘conjugate eigenvalue problem’, in which the weighting constants β_ν play the role of eigenvalues. Sets of isoenergetic solutions to equation (1) are analogous to the one-particle Sturmian basis functions introduced by Shull and Löwdin, [2–4] but they are more general.

2. ATOMIC CALCULATIONS USING GENERALIZED STURMIANS

In the case of N-electron atoms, equation (1) can be solved exactly [1] by setting V_0 equal to the nuclear attraction potential of the atom

$$V_0(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j} \tag{5}$$

and letting

$$|\Phi_\nu\rangle = |\chi_{n,l,m,m_s}\chi_{n',l',m',m'_s}\chi_{n'',l'',m'',m''_s}\cdots| \tag{6}$$

be a Slater determinant built up of hydrogen-like spin–orbitals with the effective charge

$$Q_\nu = \beta_\nu Z = \left(\frac{-2E}{\frac{1}{n^2} + \frac{1}{n'^2} + \cdots} \right)^{1/2} \tag{7}$$

To see that equation (6) is an exact solution to equation (1), we note that each of the hydrogen-like spin–orbitals obeys the one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla_j^2 + \frac{Q_\nu^2}{2n^2} - \frac{Q_\nu}{r_j} \right] \chi_{n,l,m,m_s}(\mathbf{x_j}) = 0 \tag{8}$$

and therefore

$$\begin{aligned} \left[-\frac{1}{2}\Delta \right] \Phi_\nu(\mathbf{x}) &= \left[-\frac{Q_\nu^2}{2}\left(\frac{1}{n^2} + \frac{1}{n'^2} + \cdots \right) + \frac{Q_\nu}{r_1} + \frac{Q_\nu}{r_2} + \cdots \right] \Phi_\nu(\mathbf{x}) \\ &= \left[E - \beta_\nu V_0(\mathbf{x}) \right] \Phi_\nu(\mathbf{x}) \end{aligned} \tag{9}$$

It can be shown that a set of isoenergetic configurations of the form shown in equation (6) obeys the potential-weighted orthonormality relation

$$\int \mathrm{d}x\, \Phi^*_{\nu'}(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) = \delta_{\nu',\nu} \frac{2E}{\beta_\nu} \tag{10}$$

when the constituent hydrogen-like spin–orbitals are normalized in the usual way. It is convenient to introduce the quantities p_0 and R_ν defined by

$$p_0 \equiv \sqrt{-2E} \tag{11}$$

and

$$\mathcal{R}_\nu \equiv \sqrt{\frac{1}{n^2} + \frac{1}{n'^2} + \cdots} \tag{12}$$

Then in terms of these quantities we can rewrite equation (7) in the form:

$$Q_\nu = \beta_\nu Z = \frac{p_0}{\mathcal{R}_\nu} \tag{13}$$

Also, from equation (11) it follows that:

$$E = -\frac{p_0^2}{2} \tag{14}$$

We are now in a position to try to build up solutions to the actual Schrödinger equation

$$\left[-\tfrac{1}{2}\Delta + V(\mathbf{x}) - E\right]\Psi(\mathbf{x}) = 0 \tag{15}$$

where

$$V(\mathbf{x}) = V_0(\mathbf{x}) + V'(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j} + \sum_{i>i}^{N} \sum_{i=1}^{N} \frac{1}{r_{ij}} \tag{16}$$

now includes a term representing interelectron repulsion. If we let

$$T^0_{\nu',\nu} \equiv -\frac{1}{p_0} \int \mathrm{d}x\, \Phi^*_{\nu'}(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) \tag{17}$$

then from the potential-weighted orthonormality relation (10) and from equation (13) it follows that:

$$T^0_{\nu',\nu} = \delta_{\nu'\nu} Z \mathcal{R}_\nu \tag{18}$$

Notice that this diagonal matrix is independent of p_0 and hence also independent of E. Similarly, it can be shown that with the definition

$$T'_{\nu',\nu} \equiv -\frac{1}{p_0}\int dx\; \Phi^*_{\nu'}(\mathbf{x})V'(\mathbf{x})\Phi_\nu(\mathbf{x}) \tag{19}$$

the matrix $T'_{\nu',\nu}$ is also independent of p_0 and E. Substituting the expansion

$$\psi(\mathbf{x}) = \sum_\nu \Phi_\nu(\mathbf{x})B_\nu \tag{20}$$

into the Schrödinger equation (15), we obtain

$$\sum_\nu \left[-\tfrac{1}{2}\Delta + V(\mathbf{x}) - E\right]\Phi_\nu(\mathbf{x})B_\nu = 0 \tag{21}$$

If we now remember that the configurations Φ_ν satisfy equation (1), we can rewrite equation (21) in the form:

$$\sum_\nu \left[V(\mathbf{x}) - \beta_\nu V_0(\mathbf{x})\right]\Phi_\nu(\mathbf{x})B_\nu = 0 \tag{22}$$

Multiplying equation (22) on the left by a conjugate basis function, $\Phi^*_{\nu'}$, and integrating over all coordinates, we have:

$$\sum_\nu \int dx\; \Phi^*_{\nu'}(\mathbf{x})\left[V(\mathbf{x}) - \beta_\nu V_0(\mathbf{x})\right]\Phi_\nu(\mathbf{x})B_\nu = 0 \tag{23}$$

Finally, dividing by p_0, and making use of equations (16)–(19), we can write the generalized Sturmian secular equation for our N-electron atom in the form:

$$\sum_\nu \left[\delta_{\nu',\nu}Z\mathcal{R}_\nu + T'_{\nu',\nu} - p_0\delta_{\nu',\nu}\right]B_\nu = 0 \tag{24}$$

The Sturmian secular equation shown in equation (24) differs in several ways from the conventional secular equations which are obtained when one diagonalizes the Hamiltonian of a system. The kinetic energy term has vanished, and the matrix representing the nuclear attraction potential is diagonal. Furthermore the eigenvalues are not energy eigenvalues. One obtains instead a spectrum of values of the scaling parameter p_0, which is related to the binding energy through equations (11) and (14). The largest value of p_0 corresponds to the ground state of the system, and for this value the functions in the generalized Sturmian basis set correspond to large values of the effective charge $Q_\nu = p_0/\mathcal{R}_\nu$ (equation (13)). Smaller values of p_0 correspond to excited states, and for these states the functions in the generalized Sturmian basis set correspond to smaller values of effective charge, and hence they are more diffuse. Thus in the generalized Sturmian method, one obtains at one stroke not only a spectrum of energies, but also an appropriate basis set, scaled [23] in such a way as to be diffuse for highly excited states, and contracted for states of lower

Table 1. ^{1}S excited state energies (in Hartrees) for the two-electron isoelectronic series

	He	Li$^+$	Be^{2+}	B^{3+}	C^{4+}	N^{5+}
1s2s ^{1}S	−2.1429	−5.0329	−9.1730	−14.564	−21.206	−29.098
Expt.	−2.1458	−5.0410	−9.1860	−14.582	−21.230	−29.131
1s3s ^{1}S	−2.0603	−4.7297	−8.5099	−13.402	−19.406	−26.521
Expt.	−2.0611	−4.7339	−8.5183	−13.415	−19.425	−26.548
1s4s ^{1}S	−2.0332	−4.6276	−8.2837	−13.003	−18.785	−25.629
Expt.	−2.0334	−4.6299	−8.2891			−25.654
1s5s ^{1}S	−2.0210	−4.5811	−8.1806	−12.820	−18.500	−25.220
Expt.	−2.0210	−4.5825				−25.241
1s6s ^{1}S	−2.0144	−4.5562	−8.1250	−12.721	−18.346	−24.998
Expt.	−2.0144	−4.5571				
1s7s ^{1}S	−2.0105	−4.5412	−8.0917	−12.662	−18.253	−24.865
Expt.	−2.0104	−4.5418				
1s8s ^{1}S	−2.0080	−4.5315	−8.0701	−12.624	−18.194	−24.779
Expt.	−2.0079					
1s9s ^{1}S	−2.0063	−4.5248	−8.0554	−12.598	−18.153	−24.720
Expt.	−2.0062					
1s10s ^{1}S	−2.0051	−4.5201	−8.0449	−12.579	−18.124	−24.678
Expt.	−2.0050					
1s11s ^{1}S	−2.0042	−4.5166	−8.0371	−12.566	−18.102	−24.647
Expt.	−2.0041					
1s12s ^{1}S	−2.0034	−4.5140	−8.0312	−12.555	−18.086	−24.624
Expt.	−2.0034					

In making this table, the basis set used consisted of 63 generalized Sturmians. Singlet and triplet states were calculated simultaneously, 0.5 s of 499 MHz Intel Pentium III time being required for the calculation of 154 states. Experimental values are taken from the NIST tables (http://physics.nist.gov/asd). Discrepancies between calculated and experimental energies for the ions may be due to experimental inaccuracies, since, for an isoelectronic series, the accuracy of the generalized Sturmian method increases with increasing atomic number.

energy. Some singlet excited states of the two-electron isoelectronic series of atoms and ions, calculated by diagonalizing equation (24), are shown in Table 1.

3. CALCULATION OF THE FIRST-ORDER DENSITY MATRIX; NONORTHOGONALITY

The first-order density operator [24–39] for an N-electron system in the state Ψ is defined by the relation:

$$\rho_1(x, x') \equiv N \int \mathrm{d}\tau_2 \int \mathrm{d}\tau_3 \cdots \int \mathrm{d}\tau_N \, \Psi(x, x_2, x_3, \ldots, x_N) \, \Psi^*(x', x_2, x_3, \ldots, x_N) \quad (25)$$

where x denotes both the spin and space coordinates of an electron, and where $\int \mathrm{d}\tau$ represents integration over both space and spin. When the wave function is represented by a superposition of configurations, $\Psi = \sum_\nu \Phi_\nu B_\nu$, the first-order density operator can be represented as a sum of cross-terms between the configurations, ν and ν'.

$$\rho_1(x, x') = \sum_{\nu,\nu'} B_\nu \rho^{\nu,\nu'}(x, x') B^*_{\nu'} \tag{26}$$

where

$$\rho^{\nu,\nu'}(x, x') \equiv N \int \mathrm{d}\tau_2 \int \mathrm{d}\tau_3 \cdots \int \mathrm{d}\tau_N \Phi_\nu(x, x_2, x_3, \ldots, x_N) \Phi^*_{\nu'}(x', x_2, x_3, \ldots, x_N) \tag{27}$$

In the generalized Sturmian method, the calculation of $\rho^{\nu,\nu'}(x, x')$ is complicated by the fact that orthonormality between the spin–orbitals of two different configurations cannot be assumed, since each configuration is characterized by its own effective charge Q_ν. Orthogonality between orbitals differing in spin or angular momentum quantum numbers remains, but orthogonality between different radial functions no longer holds. Thus we must use a method reminiscent of the generalized Slater–Condon rules discussed in Refs. [12,13]. Each configuration is a Slater determinant, which can be expanded in terms of its minors:

$$\begin{aligned} \Phi_\nu(x, x_2, \ldots, x_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1^{(\nu)}(x) & \chi_2^{(\nu)}(x) & \cdots & \chi_N^{(\nu)}(x) \\ \chi_1^{(\nu)}(x_2) & \chi_2^{(\nu)}(x_2) & \cdots & \chi_N^{(\nu)}(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_1^{(\nu)}(x_N) & \chi_2^{(\nu)}(x_N) & \cdots & \chi_N^{(\nu)}(x_M) \end{vmatrix} \\ &= \sum_i (-1)^{i+1} \chi_i^{(\nu)}(x) \Phi_{\nu,i}(x_2, \ldots, x_N) \end{aligned} \tag{28}$$

In equation (28), $\Phi_{\nu,i}(x_2, \ldots, x_N)$ is the minor obtained from $\Phi_\nu(x, x_2, \ldots, x_N)$ by deleting the first row and the ith column. Similarly,

$$\Phi^*_{\nu'}(x', x_2, \ldots, x_N) = \sum_j (-1)^{j+1} \chi_j^{(\nu')*}(x') \Phi^*_{\nu',j}(x_2, \ldots, x_N) \tag{29}$$

where $\Phi^*_{\nu',j}$ is the minor formed from $\Phi^*_{\nu'}$ by deleting the first row and the jth column. From the first of the generalized Slater–Condon rules in the form discussed in Refs. [12,13], it follows that:

$$N \int \mathrm{d}\tau_2 \int \mathrm{d}\tau_3 \cdots \int \mathrm{d}\tau_N \Phi_{\nu,i}(x_2, \ldots, x_N) \Phi^*_{\nu',j}(x_2, \ldots, x_N) = |S_{i,j}^{(\nu,\nu')}| \tag{30}$$

where $|S_{i,j}^{(\nu,\nu')}|$ is the minor formed from the overlap determinant

$$|S^{(\nu,\nu')}| = \begin{vmatrix} \langle\chi_1^{(\nu')}|\chi_1^{(\nu)}\rangle & \langle\chi_1^{(\nu')}|\chi_2^{(\nu)}\rangle & \cdots & \langle\chi_1^{(\nu)'}|\chi_N^{(\nu)}\rangle \\ \langle\chi_2^{(\nu')}|\chi_1^{(\nu)}\rangle & \langle\chi_2^{(\nu')}|\chi_2^{(\nu)}\rangle & \cdots & \langle\chi_2^{(\nu')}|\chi_N^{(\nu)}\rangle \\ \vdots & \vdots & & \vdots \\ \langle\chi_N^{(\nu')}|\chi_1^{(\nu)}\rangle & \langle\chi_N^{(\nu')}|\chi_2^{(\nu)}\rangle & \cdots & \langle\chi_N^{(\nu')}|\chi_N^{(\nu)}\rangle \end{vmatrix} \tag{31}$$

by deleting the *i*th column and the *j*th row. Inserting equations (28) and (29) into equation (27) and making use of equation (30), we obtain an expression for the partial density operator:

$$\rho^{\nu,\nu'}(x,x') = \sum_{i,j=1}^{N} \chi_i^{(\nu)}(x)(-1)^{i+j}|S_{i,j}^{(\nu,\nu')}|\chi_j^{(\nu')*}(x') \tag{32}$$

A matrix representation of this operator can be obtained, based on any convenient orthonormal set of one-electron spin–orbitals $\varphi_a(x)$ by means of the relationship

$$\begin{aligned} \rho_{ab}^{\nu,\nu'} &\equiv \int \mathrm{d}\tau \int \mathrm{d}\tau' \; \varphi_a^*(x)\rho^{\nu,\nu'}(x,x')\varphi_b(x') \\ &= \sum_{i,j=1}^{N} \langle\varphi_a|\chi_i^{(\nu)}\rangle(-1)^{i+j}|S_{i,j}^{(\nu,\nu')}|\langle\chi_j^{(\nu')}|\varphi_b\rangle \end{aligned} \tag{33}$$

Finally, performing a double sum over configurations, we obtain the first-order density matrix:

$$\rho_{a,b} = \sum_{\nu,\nu'} B_\nu \rho_{a,b}^{(\nu,\nu')} B_{\nu'}^* \tag{34}$$

4. NATURAL ORBITALS

Natural orbitals [28–39] are defined to be a basis set in terms of which the first-order density matrix is diagonal. Thus if $C_{b,i}$ is a unitary transformation matrix which brings $\rho_{a,b}$ into a diagonal form, i.e. if $C_{b,i}$ is a solution to the secular equation

$$\sum_b \left[\rho_{a,b} - n_i\delta_{a,b}\right] C_{b,i} = 0 \tag{35}$$

then the natural orbitals are defined by

$$\alpha_i(x) = \sum_b \varphi_b(x) C_{b,i} \tag{36}$$

Expressed in terms of the natural orbitals, the first-order density operator becomes

$$\rho_1(x,x') = \sum_i \alpha_i(x) n_i \alpha_i^*(x') \tag{37}$$

The eigenvalues n_i of the first-order density matrix can be shown to obey the relations

$$0 \leq n_i \leq 1, \quad \sum_i n_i = N \tag{38}$$

which is consistent with their physical interpretation as occupation numbers. Natural orbitals for the two lowest triplet states of helium, calculated using the generalized Sturmian method, are shown in Figs 1 and 2. These figures show the radial distribution functions, $|\alpha_i|^2 r^2$ as functions of the radius for the natural orbitals with largest occupation numbers. In fact, the calculated occupation

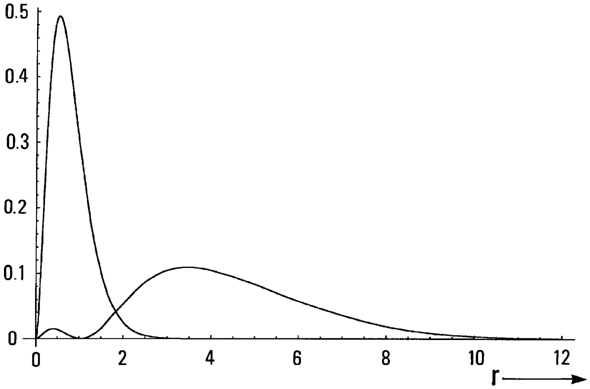

Fig. 1. Radial distribution functions $|\alpha_i|^2 r^2$ for the two natural orbitals with largest occupation numbers in the lowest triplet state of helium, the 1s2s ^{3}S state. Values of the radius are measured in atomic units.

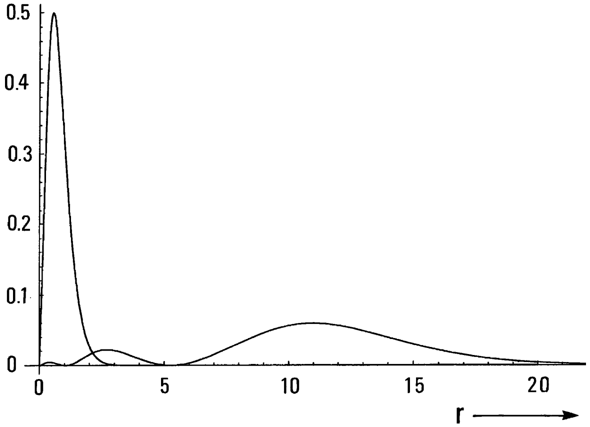

Fig. 2. This figure shows the radial distribution functions of the two most highly occupied natural orbitals in the the 1s3s ^{3}S state of helium.

numbers fall off very rapidly in value, those corresponding to Fig. 1 being given by $n_i = 0.99999,\ 0.99910,\ 0.00014, \ldots$. This rapid decrease in the values of the occupation numbers corresponds to another one of their properties, since it can be shown that the most compact multiconfigurational representation of the wave function Ψ results when it was expressed in terms of natural orbitals.

5. DISCUSSION

The generalized Sturmian method offers a rapid and convenient method for generating natural orbitals of both atoms and molecules. The method is especially well suited for the study of large numbers of excited states of few-electron systems and for studies of the effects of strong external fields. Natural orbitals are interesting in themselves, but having generated good approximate natural orbitals by means of a generalized Sturmian calculation, one might think of using them as a basis for a more refined multiconfigurational calculation. In this way the generalized Sturmian method might be extended to large values of N.

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Comment from Experimental Results on "Was H_2^- Observed in Solid H_2? A Theoretical Answer" (H. U. Suter, B. Engels and S. Lunell, Adv. Quantum Chem. 40 (2001) 133)

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We observed ESR spectra of new reactive species produced by γ-rays irradiation of solid *para*-hydrogen at 4 K [1]. The species was assigned as H_2^- anions by experimental results [2–4]. Quantum tunneling diffusion of the H_2^- anions was reported [5]. The stabilization of H_2^- anions was discussed theoretically by the vacancy-assisted model in the hydrogen crystal [6,7]. The recent paper of Suter *et al.* [8] does not explain the important experimental results that H_2^- anions change into electron bubbles.

Figure 1 shows the yields of H_2^- anions and electron bubbles against concentration of D_2 in γ-rays irradiated solid *para*-hydrogen at 4 K [4]. The results indicate that H_2^- anions diffuse by tunneling through solid hydrogen [5] and change into electron bubbles at the D_2 sites, which exist in solid *para*-hydrogen. The theoretical possibility of this reaction was discussed by Ichikawa *et al.* [7].

$$H_2^- + D_2 \rightarrow H_2 + D_2 + e^-_{\text{bubble}} \tag{1}$$

The results cannot be explained by the model of H_2^+ cluster proposed by Suter *et al.* [8] and Symons *et al.* [9].

Recently Symons *et al.* have argued that the previously reported *g*-value (2.0033) of ESR spectrum is larger than the value (2.0023) expected for H_2^- anions [9]. The correct *g*-value has been reported later as 2.0023 [6], which coincides with the *g*-value for H_2^- anions.

The yields of H_2^- anions in γ-rays irradiated solid H_2 are roughly 1/30 000 of those of H atoms, which are produced uniformly in hydrogen crystal. The very small yields of H_2^- anions suggest that the anions are produced only in some special sites such as vacancies or impurity defects. Ichikawa *et al.* discussed theoretically the stabilization of H_2^- anions at vacancies [6,7]. Sullivan *et al.* measured the vacancy formation energy in solid hydrogen as 91 K [10]. The concentration of vacancies

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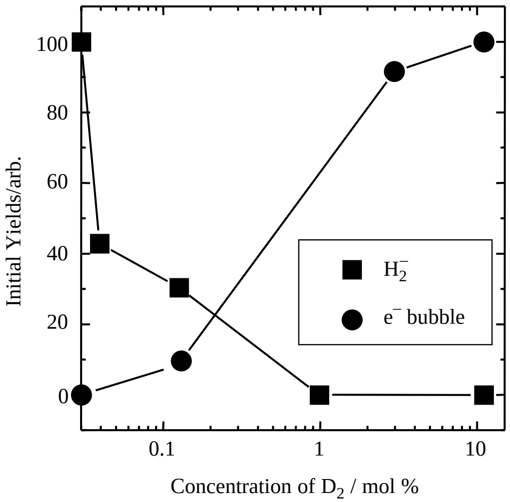

Fig. 1. Initial yields of H_2^- anions and electron bubbles in γ-rays irradiated solid p-H_2–D_2 mixtures at 4 K. The initial yields of H_2^- anions in pure p-H_2 and electron bubbles in p-H_2–D_2 (11 mol%) are normalized to 100.

at 4.2 K can be estimated from the vacancy formation energy, estimated to be 4×10^{-10} mole fraction, which is larger than the concentration (2×10^{-11} mole fraction) of H_2^- anions. Thus, mobile electrons produced initially by γ-rays irradiation migrate through solid hydrogen to be trapped as H_2^- anions at vacancies or impurity defects.

Therefore, the formation of H_2^- anions in hydrogen crystal should be discussed by taking into consideration the special properties of the crystal, such as the rigidity of lattice, vacancies, and defects. The cluster model by Suter *et al.* does not include the characteristic properties of hydrogen crystal.

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