

Density Functional Theory and Molecular Interactions: Dispersion Interactions

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Abstract We are definitely witnessing an ever-increasing need to study dispersion molecular interactions that govern a weakly bound molecular world within the density functional theory. This chapter outlines the basic approaches currently undertaken to resolve this density functional paradigm.

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1 Density Functional Theory: Background

In the last two decades, since Walther Kohn was awarded the Nobel Prize 1991 in Chemistry for the density functional theory (DFT), the latter has become the most popular and useful computational approach to study many-electron systems in the ground states because of its physically transparent underlying concept and lower computational cost [1–8]. The Kohn–Sham version of DFT [1–3, 7] is the most widely used many-body method for electronic structure calculations of atoms, molecules, solids, and solid surfaces.

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Generally speaking, a molecule \mathbf{M} is a stable quantum Coulomb system that consists of the following two subsystems:

- The electronic—of N electrons of the mass m_e and the charge $-e$ which positions in the spin-configurational space are determined by the corresponding radii vectors $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ where each \mathbf{r}_i , $i = 1, 2, \dots, N$ belongs to the real three-dimensional space \mathbb{R}^3 and the spins $\sigma_1, \sigma_2, \dots, \sigma_N$ where each σ_i , $i = 1, 2, \dots, N$ takes the value from $\mathbb{Z}_2 = \{\pm 1/2\}$, the discrete two-dimensional spin space
- The nuclear—of M nuclei carrying the nuclear charges $\{Z_\alpha\}_{\alpha=1}^M$ and located at $\{\mathbf{R}_\alpha \in \mathbb{R}^3\}_{\alpha=1}^M$.

According to Löwdin's definition [9, 10]: “A system of electrons and atomic nuclei is said to form a molecule if the Coulombic Hamiltonian H' —with the center of mass motion removed—has a discrete ground-state energy E_0 ” (see also [11–13] and references therein) where the total Hamiltonian $H := \hat{H} = \hat{H}_e + \hat{T}_{nn} + \hat{U}_{nn}$ is, respectively, the sum of the electronic Hamiltonian operator, the nuclear kinetic energy operator, and the nuclear–nuclear Coulomb interaction energy operator. Consider, within the Born–Oppenheimer approximation, the electronic Hamiltonian operator (in the atomic units) of \mathbf{M} :

$$\hat{H}_e = \hat{T}_e + \hat{U}_{ee} + \hat{V}_{en} = -\frac{1}{2} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 + \sum_{1 \leq i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N \hat{v}(\mathbf{r}_i), \quad (1)$$

where \hat{T}_e is the nuclear kinetic energy operator, \hat{U}_{ee} the nuclear–nuclear Coulomb interaction energy operator, and the “external,” electron–nuclear potential is defined as

$$\hat{v}(\mathbf{r}_i) := \sum_{\alpha=1}^M \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}. \quad (2)$$

\hat{H}_e acts on the class \mathcal{L}_N of “admissible” N -electron wavefunctions $\Psi(\mathbf{r}_1, s_1; \dots; \mathbf{r}_N, s_N)$ obeying the following conditions:

(Fi) the wavefunction normalization:

$$\langle \Psi | \Psi \rangle = \sum_{s_1, \dots, s_N} \int d^3\mathbf{r}_1 \dots \int d^3\mathbf{r}_N |\Psi(\mathbf{r}_1, s_1; \dots; \mathbf{r}_N, s_N)|^2 < \infty \quad (3)$$

implying that $\mathcal{L}_N \subset \mathcal{L}_\sigma^2(\mathbb{R}^{3N} \otimes \mathbb{Z}_2^N)$, the Hilbert space of antisymmetric, square-integrable N -electron wavefunctions. Henceforth it is assumed that an arbitrary $\Psi \in \mathcal{L}_N$ is normalized to unity: $\langle \Psi | \Psi \rangle = 1$;

(Fii) the boundness from below of the expectation value $\langle \Psi | \hat{H}_e | \Psi \rangle > -\infty$: In fact, (Fii) results from the aforementioned definition of molecule which lowest energy is finite. If \hat{U}_{ee} and \hat{V}_{en} are of Coulomb type, (Fii) is equivalent to

$$T_e[\Psi] = \langle \Psi | T_e | \Psi \rangle < \infty \quad (4)$$

implying that $\Psi \in \mathcal{L}_N$ is a differentiable function of all spatial coordinates, together with each component of $\nabla_{\mathbf{r}}, \Psi \in \mathcal{L}_N$.

One can prove [4, 14] that the conditions (Fi) and (Fii) fully determine \mathcal{L}_N of “admissible” N -electron wavefunctions where the energy functional

$$E[\Psi] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle \quad (5)$$

is thus well defined. Its lowest energy, the infimum, equal to the ground-state electronic energy E_0 as the lowest eigenenergy of the N -body Schrödinger equation

$$\hat{H}_e \Psi_0 = E_0 \Psi_0, \quad (6)$$

is attained at the ground-state electronic wavefunction Ψ_0 , that is

$$E_0 \equiv \inf_{\Phi \in \mathcal{L}_N} \{E[\Phi]\} = E[\Phi]|_{\Phi=\Psi_0 \in \mathcal{L}_N}. \quad (7)$$

The stationary quantum mechanical variational principle then reads as

$$\delta E[\Phi]|_{\Phi=\Psi_0} = 0. \quad (8)$$

The basic postulate of the many-electron density functional theory [1–8] suggests, first, the existence of the so-called functional

$$\mathcal{E}[\rho(x)] = \begin{cases} \mathcal{E}[\rho(\mathbf{r})] & \text{spin – restricted functional} \\ \mathcal{E}[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})] & \text{spin – polarized functional} \end{cases} \quad (9)$$

that has the meaning of the energy and depends, in some functional manner, on one-electron density $\rho(\mathbf{r})$,

$$\rho_{\Psi}(\mathbf{r}) := N \sum_{s_1, \dots, s_N} \int d^3 \mathbf{r}_2 \dots \int d^3 \mathbf{r}_N |\Psi(\mathbf{r}, s_1; \mathbf{r}_2, s_2; \dots; \mathbf{r}_N, s_N)|^2, \Psi \in \mathcal{L}_N \quad (10)$$

or on its both spin components, $\rho_{\Psi_{\uparrow}}(\mathbf{r})$ and $\rho_{\Psi_{\downarrow}}(\mathbf{r})$,

$$\begin{aligned} \rho_{\Psi_s}(\mathbf{r}) &:= \rho_{\Psi}(\mathbf{r}, s) \\ &= N \sum_{s_1, \dots, s_N} \int d^3 \mathbf{r}_2 \dots \int d^3 \mathbf{r}_N |\Psi(\mathbf{r}, s; \mathbf{r}_2, s_2; \dots; \mathbf{r}_N, s_N)|^2, s = \uparrow, \downarrow. \end{aligned} \quad (11)$$

The latter yield together $\rho_{\Psi}(\mathbf{r}) = \rho_{\Psi_{\uparrow}}(\mathbf{r}) + \rho_{\Psi_{\downarrow}}(\mathbf{r})$. Each $\rho_{\Psi_s}(\mathbf{r})$ is normalized to N_s so that $N_{\uparrow} + N_{\downarrow} = N$. The second suggestion is that the infimum of $\mathcal{E}[\rho(\mathbf{r})]$ does exist and

$$E_0 \equiv \inf_{\Phi \in \mathcal{L}_N} \{E[\Phi]\} = E[\Phi]_{\Phi=\Psi_0} = \inf_{\rho \in \mathcal{P}_N} \{\mathcal{E}[\rho(\mathbf{r})]\} = \mathcal{E}[\rho_\Phi(\mathbf{r})]_{\Phi=\Psi_0} \quad (12)$$

where \mathcal{P}_N is a set of one-electron densities associated with \mathcal{L}_N (see below). Formally, this postulate looks rather strong, however it is widely accepted that it is guaranteed by the Hohenberg–Kohn theorem [1] (for the new proof of the Hohenberg–Kohn theorem see [15, 16]).

Equation (9) assumes the existence of the “Functional mapping”

$$F : E[\Psi] \mapsto \mathcal{E}[\rho_\Psi(\mathbf{r})] \quad (13)$$

that implicitly presumes the existence of the “Variable mapping”

$$\Psi \leftrightarrow \rho_\Psi(\mathbf{r}). \quad (14)$$

Obviously, the mapping (14) is valid if, first, there are defined the sets of “variables” on its left- and right-hand sides. Second, the symbol \leftrightarrow does not mean at all that this is precisely a one-to-one correspondence. The sub-mapping of (14), $V:\Psi \rightarrow \rho_\Psi(\mathbf{r})$, is given by the reduction mapping, either (10) or (11), that is, $\rho_\Psi(\mathbf{r}) = V(\Psi)$ and $\mathcal{P}_N \equiv V\mathcal{L}_N$. Besides, the reduction mapping has another facet—this is a so-called N -representability: any one-electron density obtained via V possesses its own image in \mathcal{L}_N . Generally speaking, the inverse mapping V^{-1} is one-to-many, that is, a given one-electron density has many preimages in \mathcal{L}_N . It is trivial to show this. Let us consider any stable two-electron system which ground-state wavefunction and one-electron density are $\Psi_0(\mathbf{r}_1, \mathbf{r}_2)[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]$ and $\rho_0(\mathbf{r})$, respectively. The two-electron Slater determinant $\sqrt{\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)}[\alpha(s_1)\alpha(s_2) - \beta(s_1)\alpha(s_2)]/2$ possesses the same one-electron-density $\rho_0(\mathbf{r})$ as well. Q. E. D. The Hohenberg–Kohn theorem [1] (see also [15, 16]) states however that there exists a one-to-one correspondence between the ground-state wavefunctions and ground-state densities.

2 Kohn–Sham Density Functional Theory: The Hohenberg–Kohn Theorem

The Hohenberg–Kohn theorem [1] underlies the foundation of the density functional theory [2–7], the Kohn–Sham density functional theory. On p. B864 of their work [1], Hohenberg and Kohn state that they “... develop an exact formal variational principle for the ground-state energy, in which the density” $\rho(\mathbf{r})$ (in a widely accepted notation) “is the variable function. Into this principle enters a universal functional” $F[\rho(\mathbf{r})]$, “which applies to all electronic systems in their ground state no matter what the external potential is.” Following Hohenberg and Kohn [1], let us consider “a collection of an arbitrary number of electrons, enclosed in a large box and moving under the influence of an external potential $v(\mathbf{r})$ and

mutual Coulomb repulsion.” The total Hamiltonian H of a given N -electron system is written as Eq. (1), viz.

$$H = T_e + V_{ee} + V, \quad (15)$$

where T_e is the kinetic energy operator of N electrons, V_{ee} is the interelectronic Coulomb operator, and

$$V = \sum_{i=1}^N v(\mathbf{r}_i) \quad (16)$$

is the total external potential. Hohenberg and Kohn [1] further assume (p. B865) that H possesses the least bound-state (ground-state) wavefunction $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \in \mathcal{H}_N$ (spins are omitted for simplicity) and the latter is nondegenerate. \mathcal{H}_N is the Hilbert space of square integrable N -electron wavefunctions and $\mathbf{r}_i \in \mathbb{R}^3$, $i = 1, 2, \dots, N$. Let us define the corresponding ground-state one-electron density [3]

$$\rho_0(\mathbf{r}) \equiv \int \prod_{i=2}^N d^3\mathbf{r}_i |\Psi_0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2, \quad (17)$$

“which is clearly a functional of $v(\mathbf{r})$ ” ([1], p. B865), that is, there exist such mappings

$$v(\mathbf{r}) \Rightarrow \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Rightarrow \rho_0(\mathbf{r}). \quad (18)$$

Hohenberg–Kohn Theorem [1]. “ $v(\mathbf{r})$ is a unique functional” of $\rho(\mathbf{r})$, “apart from a trivial additive constant.”

Proof ([1], p. B865). “The proof proceeds by *reductio ad absurdum*.” We assume the existence of two “external” potentials $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ such that

$$v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + \text{constant}. \quad (19)$$

Via Eqs. (16) and (15), $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ define the Hamiltonians H_1 and H_2 associated with two different N -electron systems. Let us further assume the existence of the ground-state normalized wavefunctions $\Psi_0^{(1)} \in \mathcal{H}_N$ and $\Psi_0^{(2)} \in \mathcal{H}_N$ of H_1 and H_2 , respectively. By virtue of Eq. (17), $\Psi_0^{(1)}$ and $\Psi_0^{(2)}$ yield the corresponding ground-state one-electron densities $\rho_0^{(1)}$ and $\rho_0^{(2)}$. Hohenberg and Kohn [1] finally assume that

- (i) $\Psi_0^{(1)} \neq \Psi_0^{(2)}$
- (ii) $\rho_0^{(1)}(\mathbf{r}) = \rho_0^{(2)}(\mathbf{r}) = \rho_0(\mathbf{r})$.

Applying the Rayleigh–Ritz variational principle, one obtains

$$\begin{aligned}
 E_0^{(1)} &= \langle \Psi_0^{(1)} | H_1 | \Psi_0^{(1)} \rangle \stackrel{(i)}{<} \langle \Psi_0^{(2)} | H_1 | \Psi_0^{(2)} \rangle \\
 &\stackrel{Eq.(5)}{=} \langle \Psi_0^{(2)} | H_2 | \Psi_0^{(2)} \rangle + \langle \Psi_0^{(2)} | V_1 - V_2 | \Psi_0^{(2)} \rangle \\
 &= E_0^2 + \int d^3r [v_1(\mathbf{r}) - v_2(\mathbf{r})] \rho_0(\mathbf{r})
 \end{aligned} \tag{20}$$

and

$$\begin{aligned}
 E_0^{(2)} &= \langle \Psi_0^{(2)} | H_2 | \Psi_0^{(2)} \rangle \stackrel{(i)}{<} \langle \Psi_0^{(1)} | H_2 | \Psi_0^{(1)} \rangle \\
 &\stackrel{Eq.(5)}{=} \langle \Psi_0^{(1)} | H_1 | \Psi_0^{(1)} \rangle + \langle \Psi_0^{(1)} | V_2 - V_1 | \Psi_0^{(1)} \rangle \\
 &= E_0^1 + \int d^3r [v_1(\mathbf{r}) - v_2(\mathbf{r})] \rho_0(\mathbf{r})
 \end{aligned} \tag{21}$$

where the used formulas are indicated above the signs.

Hohenberg and Kohn then conclude ([1], p. B865) that adding (20) to (7) “leads to the inconsistency”

$$E_0^{(1)} + E_0^{(2)} < E_0^{(1)} + E_0^{(2)}, \tag{22}$$

and therefore, (22) implies that the assumption (ii) fails. “Thus $v(\mathbf{r})$ is (to within a constant) a unique functional of” $\rho(\mathbf{r})$, “since, in turn, $v(\mathbf{r})$ fixes H we see that the full many-particle ground state is unique functional of” $\rho(\mathbf{r})$. Q. E. D.

Examine Eq. (22). It is obviously self-contradictory (see also [15–17]). Equation (22) is deduced under the assumption that (19) is true together with the to-be-refuted assumptions (i) and (ii) both composing the negation of the Hohenberg–Kohn theorem. Equation (22) then appears to be absurd in a sense of being obviously false and therefore the statement of the Hohenberg–Kohn theorem is true. This might, logically speaking, imply that one of the to-be-refuted assumptions, (i) or (ii), or simultaneously both, (i) and (ii), lead to the contradiction with (19) *or* they are a priori invalid in a sense that one of them *or* both are incompatible with (5) and therefore, the statement of the Hohenberg–Kohn theorem is not true unless it is proved in the other way (see below). Explicitly, all these cases are the following:

$$(I) \Psi_0^{(1)} = \Psi_0^{(2)} = \Psi_0.$$

This directly gives $\rho_0^{(1)} = \rho_0^{(2)} = \rho_0$, that is, (ii) does hold. This also yields that

$$V_1 \equiv V_2 \equiv E_0 - \frac{(T_e + V_{ee})\Psi_0}{\Psi_0} \tag{23}$$

if V_1 and V_2 are multiplicative operators, as suggested by Eq. (16). Equation (23) clearly contradicts (19). However, there is no “inconsistency” because the last terms in the last lines of Eqs. (20) and (21) simply vanish.

- (II) $\Psi_0^{(1)} \neq \Psi_0^{(2)}$ and $\rho_0^{(1)} \neq \rho_0^{(2)}$

This is precisely in the line of the original reasoning by Hohenberg and Kohn [1] proving that different external potentials determine different ground-state one-electron densities.

- (III) $\Psi_0^{(1)} = \Psi_0^{(2)}$ and $\rho_0^{(1)} \neq \rho_0^{(2)}$

These two relations contradict to each other due to (17).

- (IV) A self-contradiction (*ad absurdum*) of Eq. (22) might also mean that the to-be-refuted assumptions (i) or/and (ii) of the Hohenberg–Kohn theorem are self-contradictory with Eq. (19) and this is precisely the case of many-electron Coulomb systems with Coulomb-type class of external potentials. In other words, the original *reductio ad absurdum* proof of the Hohenberg–Kohn theorem based on the assumption (19) is incompatible with the *ad absurdum* assumption (ii) since the Kato theorem is valid for such systems [18].

The Kato theorem [18] (see also [19–29]) determines the character of the singularity of the exact N -electron wavefunction at the electron–nucleus coalescence where the external potential $v(\mathbf{r})$ of the Coulomb form (see Eq. (2.2) and the conditions (i) and (ii) on p. 154 and Theorem I on p. 156 of [19]; in atomic units)

$$v(\mathbf{r}) = - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \quad (24)$$

is singular. In Eq. (24), the α th nucleus with the nuclear charge Z_{α} is placed at $\mathbf{R}_{\alpha} \in \mathbb{R}^3$. Any N -electron eigenwavefunction Ψ of H with $v(\mathbf{r})$ of the form (24) and its one-electron density ρ_{Ψ} then satisfy the electron–nucleus cusp condition, that is, their corresponding nonvanishing radial logarithmic derivatives obey at \mathbf{R}_{α} the following relationships:

$$\begin{aligned} \frac{d}{dr_i} \log \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N) \big|_{\mathbf{r}_i = \mathbf{R}_{\alpha}} &= -Z_{\alpha}, \quad i = 1, 2, \dots, N \\ \frac{d}{dr} \log \rho_{\Psi}(\mathbf{r}) \big|_{\mathbf{r} = \mathbf{R}_{\alpha}} &= -2Z_{\alpha}. \end{aligned} \quad (25)$$

Therefore, the true one-electron density of the given N -electron system exhibits cusps (local maxima) at the positions of the nuclei. Analyzing the topology of the given ground-state one-electron density $\rho_0(\mathbf{r})$ over the whole coordinate space \mathbb{R}^3 , one determines the positions of its cusps and evaluates the lhs of Eq. (25) (the last one) at these points. Altogether, the positions of the electron–nucleus cusps [as being always negative, see Eq. (25)] and the halves of the radial logarithmic derivatives of $\rho_0(\mathbf{r})$, taken with the opposite sign at these points, fully determine the external potential $v(\mathbf{r})$, Eq. (24), of the given system. This constitutes a naïve interpretation of the Hohenberg–Kohn theorem originally proposed by Coleman [30], Bamzai and

Deb [31], Smith [32], and E. Bright Wilson (quoted by Löwdin [33]; for the recent applications of the Kato theorem to the Hohenberg–Kohn theorem see also [34–36]). Therefore, if a given pair of N -electron systems with the Hamiltonians H_1 and H_2 of the type (1) are characterized by the same ground-state one-electron densities (\equiv to-be-refuted assumption (ii)), their external potentials $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ of the form (24) are identical. The latter contradicts (19) and hence, the assumption (ii) cannot be used in the proof via *reductio ad absurdum* of the Hohenberg–Kohn theorem together with the assumption (19). In other words, they are Kato-type incompatible with each other.

Vice versa, the nuclei of the given N -electron system are isolated 3D point attractors behaving topologically as critical points of rank three and signature minus three [37]. However, there exist some “particular many-electron systems” which show local maxima of their ground-state one-electron density at non-nuclear positions ([38–48] and references therein). These local non-nuclear maxima might be the true ones or might appear as a consequence of an incomplete, inadequate quantum mechanical treatment. Therefore, despite the present conclusion that the original proof of the Hohenberg–Kohn theorem by *reductio ad absurdum* is flawed in a sense that its to-be-refuted assumption (ii) is incompatible, by virtue of the Kato theorem, with the assumption (19) (for a similar proof of the ensemble generalization of the Hohenberg–Kohn theorem see Sect. II of [16]), the Kato theorem itself corroborates the existence of the one-to-one correspondence between the Coulomb-type class of external potentials (10) and the ground-state one-electron densities for nearly all many-electron except probably the aforementioned “particular” ones.

According to the work [1] by Hohenberg and Kohn, the Hohenberg–Kohn theorem implies the existence of the universal energy density functional for any isolated many-electron Coulomb system. This statement has been usually interpreted as the second Hohenberg–Kohn theorem [3]. In the density functional theory, there exist two rigorous constructions of the universal energy density functionals based on their own rigorous proofs of the Hohenberg–Kohn theorem. This is the Levy–Lieb energy density functional [49–54] and the universal energy density functional based on the group of the local-scaling deformations in \mathbb{R}^3 consisting of topological deformations mapping or topologically deforming any pair of one-electron densities to each other [4] (see also Sect. 5). The related Jacobian of such deformation gives rise to the first-order nonlinear differential equation, a so-called “Jacobian equation” [55–63] whose solution, namely, the corresponding deformation, does exist within the present approach and it is unique [4]. Solving the “Jacobian equation” enables to determine the deformation for any pair of well-behaved one-electron densities and to consistently extend the action of the local-scaling deformation group onto \mathcal{H}_N [49]. This larger local-scaling transformation group partitions \mathcal{H}_N into disjoint classes, orbits. All orbits exhaust \mathcal{H}_N and within each orbit, there establishes the one-to-one correspondence between its wavefunctions and the one-electron densities. That is, these orbits are endowed with the characteristic that there are no two wavefunctions belonging to the same orbit that have the same density. Each orbit, say $\mathcal{O}^{[\alpha]}$, is determined by its

generator wavefunction $\Psi_g^{[\alpha]}$. Therefore, for a given orbit $\mathcal{O}^{[\alpha]}$, one defines the energy density functional $E_\alpha[\rho(\mathbf{r})]$ as merely the restriction of the energy functional $E[\Psi]$ on those wavefunctions that belong to the α th orbit, $\Psi \in \mathcal{O}^{[\alpha]}$. It is trivial to prove that, first, there are as many different energy density functionals as the orbits in \mathcal{H}_N , and second, that each density functional $E_\alpha[\rho(\mathbf{r})]$ implicitly depends on the generator wavefunction $\Psi_g^{[\alpha]}$. Evidently, the true ground-state N -electron wavefunction of the given Hamiltonian operator H belongs to a certain orbit, called the Hohenberg–Kohn one, $\mathcal{O}^{[\text{HK}]}$ [4]. Within $\mathcal{O}^{[\text{HK}]}$, the Levy–Lieb energy density functional [49] exactly coincides with $E_{\text{HK}}[\rho(\mathbf{r})]$ that is defined within the local-scaling deformation approach [64–75]. The explicit form of any energy density functional $E_\alpha[\rho(\mathbf{r})]$ for any α has been obtained and the corresponding variational Euler–Lagrange equation has been also derived in [64–75] (see also Chaps. 7 and 8 of [4]). The rigorous mathematical framework of the local-scaling deformation approach to the density functional theory based on the “Jacobian equation” has recently been elaborated in [55, 57–63]. The local-scaling deformation approach to the density functional theory has been also generalized to include spin densities, for the momentum space representation, for excited states, for the fractional occupation numbers, and finally to study nonadiabatic effects. The corresponding analogue of the Kohn–Sham approach has been also formulated in terms of the orbit generators (see Chap. 8 in [4]). A variety of theoretical and computational applications of the local-scaling deformation density functional theory to atoms and molecules has recently been elaborated as well (see [76–87] and references therein).

However, in the computational perspective, the Kohn–Sham DFT remains the most widely used many-body approach to conduct the electronic structure calculations of atoms, molecules, solids, and solid surfaces. In the context of this DFT, only the exchange–correlation energy must be approximated as a functional of the electron density [8]. The simplest approximation is the local spin density (LSD) approximation [88] which uses the local electron spin densities $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, as in (9), as the only ingredients. In the development of DFT, a significant step was the introduction of the density gradients $\nabla_{\rho_\uparrow}(\mathbf{r})$ and $\nabla_{\rho_\downarrow}(\mathbf{r})$ as additional local ingredients in the generalized gradient approximation or shortly GGA [89–91].

3 Dispersion Molecular Forces: Introduction

Some people think that there is an air between molecules.

A. S. Kompaneets [92]

According to our current knowledge, there exist four basic types of forces: gravitational, electromagnetic, strong, and weak. The electromagnetic force is the force that binds the electrons and the nuclei inside the atom, and the atoms inside a molecule, and that governs the interaction between atoms and molecules. These are referred to as the so-called intermolecular interactions [92–94, 186, 187]. Indeed,

Table 1 Van der Waals radii R_{vdW} (in Å) of atoms

Atom	R_{vdW}	Atom	R_{vdW}	Atom	R_{vdW}	Atom	R_{vdW}	Atom	R_{vdW}	Atom	R_{vdW}
H	1.20	He	1.30	N	1.50	O	1.40	F	1.35	Ne	1.40
P	1.90	S	1.85	Cl	1.80	Ar	1.70	As	2.00	Se	2.00
Br	1.95	Kr	1.80	Sb	2.20	Te	2.20	I	2.15	Xe	2.05

intermolecular interactions play the important role in the world: it is true that we “touch” them everywhere, at a macroscopic scale, in our everyday life. It is rather hard to imagine what would be the world without them—obviously, the situation would be significantly more dramatic than to have the ideal gases that surround us! Simply imagine that would be no such molecules as the DNA and RNA. Many chemical and biochemical processes involve van der Waals interactions [93].

The intuitively clear idea of that atoms and molecules do interact with each other is a very old indeed and dates back to the ancient times. Recall in particular Democritus, Leukippos, and Lucretius whose philosophical thoughts on the interaction through a direct contact were developed and rationalized by R. Boscovich in “Theory of Natural Science Reduced to the Single Law of Forces Existing in Nature” (1758) and independently by A. C. Clairault in “Théorie de la Figure de la Terre” (1743).

In Nature, atoms are located at different interatomic distances depending on a kind of the forces between them: either by cohesion forces or chemical bonds. The latter prevail at the distances which are smaller or equal to the sum of van der Waals radii of atoms. At such distances atoms form a molecule. By definition, the van der Waals (vdW) radii of a given atom is the half of the shortest distance that is observed in crystals between the nuclei of the same atoms. The vdW radii of atoms are listed in Table 1. At the distances beyond the sum of van der Waals radii of atoms, there exists a specific van der Waals interaction often referred to as the dispersion interaction between atoms, after Johannes Diderik van der Waals who first postulated its existence in his well-known equation of state derived in his PhD thesis in 1837 and which won him the 1910 Nobel Prize in Physics.¹ For the first time van der Waals explained the deviations of gases from the ideal behavior. Let us consider a vessel filled by a gas of atoms. Within this vessel, the pressure exerted by a gas of atoms on its wall is lower compared to that predicted by the ideal gas law since the atoms may collide with the wall and are thus retained by the attraction they undergo from the other atoms in the bulk of the gas that results in the pressure P obeying the equation [94],

$$P = \left(\frac{nRT}{V - nb} \right) - a \left(\frac{n^2}{V^2} \right). \quad (26)$$

Here a is a so-called vdW factor and $b = (16\pi N/3)R_{\text{vdW}}^3$.

¹ <http://www.nobelprize.org/nobelprizes/physics/laureates/1910/waals-bio.html>.

Table 2 Dipole moments d^o of some molecules in D

\mathcal{M}	d^o	\mathcal{M}	d^o	\mathcal{M}	d^o
<i>n</i> -Butane	0.00	Pyridine	2.23	<i>n</i> -Pentane	0.00
<i>n</i> -Hexane	0.00	Cyclohexanone	2.90	Acetone	2.900
Benzene	0.00	Propionitrile	3.20	Dimethylacetamide	3.70
Cyclohexane	0.00	Nitroethane	3.2	Lithium fluoride	6.40
Toluene	0.36	Dimethylsulfoxide	3.92	Lithium chloride	7.09
Triethylamine	0.78	Diethylether	1.21	Tetrahydrofurane	1.76
Hydrogen chloride	1.10	Methylacetate	1.80	Water	1.84
Propylenecarbonate	4.98	Sodium chloride	9.06	Potassium chloride	10.70

It merits to notice that the dispersion interaction energy between the ground-state molecules is always negative. Therefore, such molecules always attract each other—in this regard it is appropriate to notice the celebrated work by E. H. Lieb and W. E. Thirring [95] that proves that the attractive van der Waals force between an atom and a molecule exists only at some mutual orientations and was generalized to any orientation in 2006 by M. Lewin [96]. The leading term of the dispersion energy is the dipole–dipole term which is proportional to $1/R^6$ and determined by a change in the zero-point vibrational energy of electric field created by zero-point vibrations of fluctuating dipole moments of interacting species. Since the zero-point fluctuations are the quantum phenomenon, the dispersion interactions have the quantum origin, as though in the beginning of the 1970s, T. H. Boyer [97] derived the London formula for the dispersion interactions within the classical electrodynamics, additionally assuming the existence of the classical electromagnetic zero-point radiation (Table 2). In fact, the van der Waals forces are cohesive attractions between molecules which operate at long intermolecular separations. From a quantitative viewpoint, van der Waals forces between molecules correspond to interactions between electric dipoles. Generally speaking, there exist three types of electric dipoles in molecules. These are permanent, induced, and temporary dipoles. If a molecule \mathcal{M} under study consists of the positive nuclear charges $q_1 = Z_1, \dots, q_M = Z_M$ and negative electron charges e_1, \dots, e_N , its total permanent dipole moment is defined as

$$\mathbf{d}^o = \sum_{\alpha=1}^M q_{\alpha} \mathbf{R}_{\alpha} + \sum_{i=1}^N e_i \mathbf{r}_i \quad (27)$$

d^o is distinct from zero in some state if the center of charge of the nuclei, $\mathbf{R}_n \equiv \sum_{\alpha=1}^M q_{\alpha} \mathbf{R}_{\alpha} / \sum_{\alpha=1}^M q_{\alpha}$, does not coincide with that of the electron subsystem, $\mathbf{r}_n \equiv \sum_{i=1}^N e_i \mathbf{r}_i / \sum_{i=1}^N e_i$. If $d^o \neq 0$, a molecule \mathcal{M} is called polar. Permanent dipole moments of neutral molecules usually vary from 0 to 15 Debye (D) that is reflected in Table 3.²

² Al. McClellan, Tables of Experimental Dipole Moments. Rahrha Enterprises, El Cerrito, 1974.

Table 3 Intramonomer distances (in Å) and binding energies (in kcal/mol), below, of representative van der Waals complexes, Ne₂, Ar₂, (CH₄)₂(*D*_{3d}), (C₂H₄)₂(*D*_{2d}), T-(C₆H₆)₂, SP-(C₆H₆)₂, P-(C₆H₆)₂, taken from Tables 1 and 2 of [98]

DFT	Ne ₂	Ar ₂	(CH ₄) ₂	(C ₂ H ₄) ₂	T-(C ₆ H ₆) ₂	SP-(C ₆ H ₆) ₂	P-(C ₆ H ₆) ₂
VSXC	2.47	3.59	3.21	3.35	4.65	3.47	3.41
	0.49	1.15	4.33	9.96	8.28	16.95	11.23
PW91	3.00	4.0	4.0	4.0	5.15	5.76	4.22
	0.97	0.36	0.52	1.56	1.65	1.55	0.24
HCTH407	2.58	3.84	3.89	4.05	5.45	5.84	4.22
	0.76	0.48	0.71	1.53	1.41	1.63	0.67
PBE	2.52	3.88	3.86	3.76	5.19	5.76	4.31
	0.69	0.19	0.29	1.30	1.33	1.27	−0.22
PBE1PBE	2.54	3.93	3.90	3.75	5.14	5.76	4.40
	0.53	0.13	0.20	1.16	1.32	1.15	−0.42
BHANDHLYP	2.48	3.93	3.99	3.76	5.20	5.77	U
	0.81	0.03	0.02	0.91	1.00	0.90	
MPW1K	2.62	4.31	4.35	3.82	5.19	5.81	U
	0.34	0.06	0.08	0.69	1.00	0.80	
MPW1PW91	2.61	4.30	4.37	3.88	5.27	5.83	U
	0.40	0.07	0.10	0.62	0.89	0.75	
B3LYP	2.51	U	U	3.85	5.37	5.81	U
	0.63			0.55	0.63	0.60	
B3P86	2.64	U	U	3.76	5.21	5.78	U
	0.04			0.47	0.64	0.48	
CCSD(T)	3.2 ^a	3.8 ^a	3.8 ^a	3.8 ^a	4.89 ^b	3.8 ^b	3.7 ^b
	0.07	0.26	0.495	1.15	2.74	2.78	1.81

U implies that at this computational level, the studied complex is unbound. The notations ^a[99] where the computational level CCSD(T) and the aug-cc-pV5Z basis set are used, and ^b[100], and U for unbounded. The experimental value of the bound distance in Ne₂ dimer is equal to 3.09 Å. The benzene dimer exists in three isomeric structures *T*—*T*-shaped, *P*—parallel, and *SP*—slipped parallel

Any pair of polar molecules, \mathcal{M}_1 and \mathcal{M}_2 , separated by a distance R_{12} , in the states n and m , respectively, interact with each other by their dipoles, $\mathbf{d}_n^{(1)}$ and $\mathbf{d}_m^{(2)}$, via the dipole–dipole interaction read as

$$E_{\text{dd}}^{(1)} = \frac{\mathbf{d}_n^{(1)} \mathbf{d}_m^{(2)}}{R_{12}^3} - \frac{3(\mathbf{d}_n^{(1)} \mathbf{R}_{12})(\mathbf{d}_m^{(2)} \mathbf{R}_{12})}{R_{12}^5}. \quad (28)$$

Structurally, $E_{\text{dd}}^{(1)}$ consists of two terms. A polar molecule \mathcal{M}_1 interacts with the electric field $\mathbf{E}^{(2)}(\mathbf{R}_{12})$ created by another molecule \mathcal{M}_2 at the position of the first molecule. As known from electrostatics [101–103], molecule \mathcal{M}_1 gains the energy $-\mathbf{d}_n^{(1)} \mathbf{E}^{(2)}(\mathbf{R}_{12})$. Expressing the electric field

$$\mathbf{E}^{(2)}(\mathbf{R}_{12}) = \nabla[(\mathbf{d}_m^{(2)} \mathbf{R}_{12})/R_{12}^3] \quad (29)$$

results then in Eq. (28).

Let us consider another, so-called, second-order effect of an external electric field \mathbf{E} on a given molecule \mathcal{M}_2 . This field influences the molecular charges, electrons, and nuclei, causing their displacements, and as a result, there appears the induced dipole moment \mathbf{d}^{ind} ,

$$\mathbf{d}^{\text{ind}} = \alpha \mathbf{E}, \quad (30)$$

where the proportionality coefficient is merely a polarizability α of a given molecule. Assuming that this electric field is generated by the presence of the second molecule \mathcal{M}_1 , one obtains

$$\mathbf{d}_{2,m}^{\text{ind}} = \alpha \nabla[(\mathbf{d}_m^{(1)} \mathbf{R}_{12})/R_{12}^3]. \quad (31)$$

Therefore, the interaction of the permanent dipole $\mathbf{d}_n^{(1)}$ of \mathcal{M}_1 with the dipole $\mathbf{d}_{2,n}^{\text{ind}}$ that is induced on \mathcal{M}_2 by \mathcal{M}_1 takes the following expression:

$$E_{\text{dd}}^{(2)} = \frac{\mathbf{d}_n^{(1)} \mathbf{d}_{2,n}^{\text{ind}}}{R_{12}^3} - \frac{3(\mathbf{d}_n^{(1)} \mathbf{R}_{12})(\mathbf{d}_{2,n}^{\text{ind}} \mathbf{R}_{12})}{R_{12}^5} \quad (32)$$

that is known as the Keesom dipole–dipole interaction [104].

By a straightforward analogy, the dipole–dipole interaction of two mutually induced dipoles on \mathcal{M}_1 and \mathcal{M}_2 is described by the expression

$$E_{\text{dd}}^{(2)} = \frac{\mathbf{d}_{1,n}^{\text{ind}} \mathbf{d}_{2,m}^{\text{ind}}}{R_{12}^3} - \frac{3(\mathbf{d}_{1,n}^{\text{ind}} \mathbf{R}_{12})(\mathbf{d}_{2,m}^{\text{ind}} \mathbf{R}_{12})}{R_{12}^5}. \quad (33)$$

If the distance R_{12} between dipoles is small enough compared to the wavelength λ , corresponding to transitions between the ground and excited states, within the second- and higher-order Rayleigh–Schrödinger perturbation theory as [92, 105, 106] there appear, as first shown by Fritz London [105, 106], the dispersion interaction [105, 106]

$$E_{\text{disp}}^{(2)} = - \sum_{m,n \neq 0} \frac{\left| \langle \Psi_n^{(1)} \Psi_m^{(2)} | V_{12} | \Psi_0^{(1)} \Psi_0^{(2)} \rangle \right|^2}{(E_n^{(1)} - E_0^{(1)}) + (E_m^{(2)} - E_0^{(2)})} \quad (34)$$

where $\Psi_n^{(i)}$ is the n -state eigenfunction of \mathcal{M}_i , $i = 1, 2$ and V_{12} is the electrostatic interaction between molecules \mathcal{M}_1 and \mathcal{M}_2 .

The dispersion energy is traditionally represented by means of the multipole expansion [94]

$$E_{\text{disp}}^{(2)} = - \sum_{n=6}^{\infty} \frac{C_n}{R^n}, \quad (35)$$

where C_n are dispersion constants among which C_6 corresponds to dipole–dipole interaction, C_8 to dipole–quadrupole and C_{10} to dipole–octupole and dipole–quadrupole interactions.

Dispersion interactions play a role of the attractive interaction between rare gas atoms and are also one of the important intermolecular interactions that govern the molecular organic world [93, 107]. Dispersion interactions are mostly responsible for the heats of sublimation of hydrocarbon molecules, make significant contributions to the solvent properties of polar and apolar neutral compounds [108, 109] and are also important for crystal packing of organic molecules [110] as well as for the stacking of nucleic acids in DNA [93, 111]. The world of dispersion interaction is rich (see [112] and references therein), despite the fact that it is a weaker form of intermolecular attractions. Dispersion forces as one of the two types of van der Waals force are also known as “London forces,” named after Fritz London [105, 106].

Density functional theory [113–116] as one of the approaches to evaluate electron correlation is considerably less demanding on computational resources than the MP2 or CCSD(T) methods. DFT might therefore be considered as a powerful computational tool, if it can adequately describe and accurately evaluate intermolecular interactions. The suitability of DFT for the evaluation of dispersion interaction has been an important issue in the recent literature [117–125] that is mirrored in Table 3. While DFT calculations with local exchange–correlation functionals lead to overestimate binding energies of weakly bound systems, it was reported that non-local exchange–correlation functionals very often underestimate the attraction [118–120]. The DFT calculations with Becke’s exchange and Lee, Yang, and Parr’s correlation functionals, BLYP [113, 114], and Becke’s three-parameter functional combined with Lee, Yang, and Parr’s correlation functional, B3LYP [114, 116], also fail to evaluate the attractive dispersion interaction between hydrocarbon molecules [120–122]. Recently Zhang et al. and Wesolowski et al. reported that the Becke exchange functional due to its erroneous asymptotic behavior at low density is responsible for the failure in the evaluation of the attraction between weakly bound systems [123–125]. It was shown, however, that other non-local exchange–correlation functionals such as Perdew and Wang’s exchange and correlation functionals, PW91 [115], are possible alternatives to describe the binding between rare gas dimers or other systems. The performance of some exchange–correlation functionals and the PW91 one in particular for the representative van der Waals systems is demonstrated in Table 3. Notice that the PW91 functional is a general functional, i.e., it is not biased towards the description of intermolecular interaction. In this investigation we will examine the basis set dependence of the interaction energies, and benchmark those against the results obtained from MP2 [188] and CCSD(T) theory. For comparison, the results with the BLYP and B3LYP are also presented. Interestingly, DFT adequately describes, on the one hand, atoms and molecules as stable many-electron systems and on the other hand, the molecules formed under interaction of its composing molecules. However, its description of those molecular interactions is not always perfect. The simplest DFT approximation widely used in computational practice is the local

density approximation (LDA) [2], based on the properties of the uniform electron gas. In principle, DFT yields the exact ground-state energy, including long-range van der Waals energies, very important in organic chemistry and elsewhere. However, the commonly used LDA and GGA, designed for nonuniform electron gases, fail to capture the essence of vdW energies. The latter reflect correlated motions of electrons due to the Coulomb interactions between distant, even non-overlapping atoms, molecules, and solids. In [4] Kohn and coauthors propose a first-principles approach, which contains the following ingredients (i) The density distribution, $\rho(\mathbf{r})$, is approximated by the LDA or GGA. (ii) The Coulomb interaction is divided into short- and long-range parts, of which only the latter contributes to vdW energies. (iii) The contribution of the long-range interactions to the energy is expressed by the so-called adiabatic connection formula. (iv) This expression is transformed into the time domain, avoiding the need to solve a self-consistent equation for the density–density response function.

4 Dispersion-Corrected DFT Approaches

DFT methods with currently available functionals failed completely for London-type clusters for which no minimum was found at the potential energy surfaces.

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Density functional theory is often the preferred electronic structure method to study moderate and large systems. This preference reflects the efficiency of DFT compared to correlated wavefunction theories such as coupled cluster theory even though accuracy, and more importantly, predictability (as in systematic convergence to the right answer) are sacrificed. DFT which incorporates currently accepted exchange-correlation functionals can be used with reasonable reliability on chemically bound systems around the equilibrium geometry but inevitably fail when applied to systems which are bound by weak van der Waals forces [126–130] and to a lesser degree for chemically bound systems away from equilibrium, like transition states [131]. These failings of density functional theory are well known [132]. Here, we address weak interactions. Attempts to compute weak intermolecular forces using DFT fall into two categories. Some would simply modify functionals until reasonable results are obtained (see [133] and references within). Others would focus on an add-on correction that explicitly introduces the van der Waals C_6 coefficient. This can be made to work, but it is unsatisfactory that the weak interactions do not occur naturally as they would in wavefunction methods. This is the experimental or computational fact which has not been still proved. Though, the problem of description of London dispersion in density functional theory (DFT) using (semi) local exchange-correlation functionals is a well-known problem [134, 135] since the first diagnostic in 1994 [134].

A step in the right direction was made by Engel et al. [136] who obtained reasonable results for the helium and neon dimers. In [137], Bartlett and

co-workers proposed *ab initio* density functional theory has been applied for the weakly interacting, He_2 , $[\text{He}-\text{Be}]^{2+}$, Ne_2 and Be_2 that results in fair agreement with the highly accurate coupled-cluster method. Generally, one assumes that the cause lies in the local character of the widely used correlation functionals, which, in contrast to the correlation contribution in post-Hartree–Fock methods such as Møller–Plesset or coupled cluster, only utilize information on the density of the system at one point and are therefore unsuitable for the description of a non-local phenomenon such as dispersion. Attempts to introduce non-local correlation to DFT, such as the random phase approximation (RPA) [138, 139] or the non-local van der Waals functionals [140–143], are being investigated, but unfortunately the improvement comes with a significant increase in the computational cost. Since the relatively low computational cost of DFT is one of the major factors responsible for its status as the most widely used quantum chemical method today, a range of more pragmatic approaches has been developed to correct the performance of DFT for dispersion interactions. Part of these methods rely on reparametrization of existing local correlation functionals [144–146], motivated by the fact that dispersion is partially included in many functionals and that a suitable reparametrization will allow one to achieve the aspired results more consistently. The drawback of such an approach is that the strong empirical character decreases the reliability. For instance, the performance of the reparametrized functionals often decreases for properties other than the electronic energy. Other attempts are based on adding a correction term, representing the dispersion energy, to the energy calculated using standard DFT methods. Also in this category, one can find highly empirical but computationally attractive methods [147] based on parameters fitted to reproduce high-level results, as well as the methods with deeper theoretical foundation but computationally more expensive, where *ab initio* information of the systems is used to evaluate the dispersion energy, such as the static or frequency dependent polarizabilities [148–154] or the dipole moment of the exchange-correlation hole (XDM) [156–159]. Another noteworthy approach is the adaptation of the symmetry adapted perturbation theory [160] to the framework of DFT, i.e., SAPT(DFT) [161–164]. SAPT(DFT) has a significant computational advantage against the highly scaling SAPT as the contribution of intramonomer correlation, already embedded within the Kohn–Sham orbitals, does not need to be evaluated. Although possible to use for the correction of DFT dispersion energies [165], SAPT(DFT) is mostly meant for an evaluation of the total interaction energy. The explicit expression for the repulsive contribution of electron-exchange to the dispersion energy within SAPT(DFT), though rarely calculated fully due to the computational expense, offers a more theoretically attractive alternative to the empirical damping functions used in other methods. SAPT(DFT) does have the disadvantage of requiring explicit separation of the system in two parts, which makes it impossible for application on intramolecular dispersion interactions, such as those occurring, for example, in biomolecules. Table 4 reports some developed dispersion-corrected DFT functionals and their performance for the representatives of the van der Waals dimers.

Table 4 Dispersion-corrected DFT functionals

Method	He ₂	He-Ne	Ne ₂	He-Ar	Ar ₂	(CH ₄) ₂	(C ₂ H ₄) ₂	T-(C ₆ H ₆) ₂
CCSD(T)	-0.02	-0.04	-0.07	-0.06	-0.27	-0.53	-1.51	-2.74
D-B3LYP/A ^a	0.04	0.04	0.05	0.07	0.17	0.38	0.49	0.98
D-BH-B3LYP/A ^a	-0.00	-0.02	-0.05	-0.02	-0.19	-0.49	-1.68	-2.64
D-B3LYP/B ^a	0.05	0.04	0.03	0.08	0.07	0.76	0.40	0.96
D-BH-B3LYP/B ^a	0.03	0.02	-0.03	0.03	-0.08	-1.12	-0.87	-1.89
DFT-B97-D/C ^b			-0.17		-0.26			-2.99

Basis sets A \equiv aug-cc-pVTZ, B \equiv 6-311++G(2d,f,p), and C \equiv TZV2P

^a[166].

^b[167].

One of the most promising new DFT methods is the non-local van der Waals correlation functional vdW-DF-04 in [168, 169], which was derived from first principles, describes dispersion interactions in a seamless fashion, and yields the correct asymptotic form of intermolecular van der Waals forces. Recently we reported a self-consistent implementation of vdWDF-04 with Gaussian basis functions [168, 169]. The code includes analytic gradients of the energy with respect to nuclear displacements, enabling efficient geometry optimizations. The alternative and consistent approach to the dispersion-corrected DFT can be formulated, as we believe, within the so-called local-scaling transformations' (LST') DFT whose key features are given in the next section.

5 Local-Scaling Transformations' DFT

In order to properly assess the local-scaling transformation formulation of the density functional theory, we first consider the concept of local-scaling transformation and second, apply it to the topological features of atomic and molecular one-electron densities.

5.1 Mathematical Preliminaries: Local-Scaling Transformations

Define on the Euclidean \mathbb{R}^3 the following mapping: $\mathbb{R}^3 \xrightarrow{f} \mathbb{R}^3$ such that $r \in \mathbb{R}^3$ is mapped into

$$\mathbf{f}(\mathbf{r}) = f(\mathbf{r})\mathbf{e}_r = f(r; \mathbf{e}_r)\mathbf{e}_r, \quad (36)$$

where $\mathbf{e}_r \equiv \mathbf{r}/r \equiv \mathbf{e}(\Omega)$ is a unit vector, specified in \mathbb{R}^3 and defined by the spherical angles $\Omega = (\theta, \phi)$ and $r = |\mathbf{r}|$. For a given $\mathbf{e}_r(\Omega)$, the transformation (36) that deforms \mathbb{R}^3 onto itself, nonuniformly in general, is referred to as a local-scaling transformation or LST for short [4] and is the special class of point transformation

[170, 171]. LSTs satisfy all axioms of group and hence form the group \mathcal{F} of local-scaling transformations. A scalar function $f(\mathbf{r})$ in Eq. (36) can be arbitrary, though often it belongs to \mathcal{C}^1 or higher. In the former, \mathbf{f} is a \mathcal{C}^1 -diffeomorphism on \mathbb{R}^3 .

Equation (36) nontrivially generalizes the well-known scaling: $\mathbf{f}_\lambda(\mathbf{r}) := \lambda \mathbf{r}$ which Fock [172] used in 1930 to prove the virial theorem. $\lambda \neq 0$ is a constant that means that all vectors $\mathbf{r} \in \mathbb{R}^3$ are scaled uniformly. Bearing in mind that an arbitrary vector \mathbf{r} is uniquely determined by its Cartesian coordinates $\mathbf{r} = (x, y, z)$, the equivalent representation of (36) is the following:

$$\mathbf{r} \equiv \begin{pmatrix} x \\ y \\ z \end{pmatrix} \xrightarrow{f} \mathbf{f}(\mathbf{r}) \equiv \begin{pmatrix} \frac{x}{r}f(x, y, z) \\ \frac{y}{r}f(x, y, z) \\ \frac{z}{r}f(x, y, z) \end{pmatrix} \equiv \begin{pmatrix} f_x(\mathbf{r}) \\ f_y(\mathbf{r}) \\ f_z(\mathbf{r}) \end{pmatrix} \equiv \begin{pmatrix} x\sigma(\mathbf{r}) \\ y\sigma(\mathbf{r}) \\ z\sigma(\mathbf{r}) \end{pmatrix}, \quad (37)$$

where $\mathbf{f}(\mathbf{r}) = \sigma(\mathbf{r})\mathbf{r}$.

The Jacobian of (1) is defined as

$$J\{\mathbf{f}(\mathbf{r}); \mathbf{r}\} \equiv J\{\mathbf{f}; \mathbf{r}\} = \begin{vmatrix} \frac{1}{r}f - \frac{x^2}{r^3}f + \frac{x}{r}\frac{\partial f}{\partial x} & -\frac{xy}{r^3}f + \frac{x}{r}\frac{\partial f}{\partial y} & -\frac{xz}{r^3}f + \frac{x}{r}\frac{\partial f}{\partial z} \\ -\frac{xy}{r^3}f + \frac{y}{r}\frac{\partial f}{\partial x} & \frac{1}{r}f - \frac{y^2}{r^3}f + \frac{y}{r}\frac{\partial f}{\partial y} & -\frac{yz}{r^3}f + \frac{y}{r}\frac{\partial f}{\partial z} \\ -\frac{xz}{r^3}f + \frac{z}{r}\frac{\partial f}{\partial x} & -\frac{yz}{r^3}f + \frac{z}{r}\frac{\partial f}{\partial y} & \frac{1}{r}f - \frac{z^2}{r^3}f + \frac{z}{r}\frac{\partial f}{\partial z} \end{vmatrix} \\ = \frac{f^2}{r^3} \left(x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} \right) = \frac{1}{3r^3} \mathbf{r} \cdot \nabla f^3. \quad (38)$$

In terms of $\sigma(\mathbf{r})$, the Jacobian (38) has the form $J\{\mathbf{f}(\mathbf{r}); \mathbf{r}\} = \sigma(\mathbf{r})[1 + \mathbf{r} \cdot \nabla \ln \sigma(\mathbf{r})]$ [171]. For the uniform scaling $\mathbf{f}_\lambda :=$, the corresponding Jacobian is equal to

$$J\{\mathbf{f}_\lambda; \mathbf{r}\} = \begin{vmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{vmatrix} = \lambda^3. \quad (39)$$

It is trivial to generalize a three-dimensional local-scaling transformation (1) on other dimensions, say \mathbb{R}^D , simply by considering a vector \mathbf{r} as a D -dimensional one. If $D = 1$, $f(r)$ is a function of a single variable r . The corresponding Jacobian $J\{f(r); r\} = df(r)/dr$. Let us consider some examples of local-scaling transformations \mathbf{f}_{LST} :

- (1) $f^{[1]} = \left[\left(\frac{1}{r} \right)^m + \left(\frac{\delta}{\sqrt{r}} \right)^m \right]^{-1/m}$, where δ is the constant [173].
- (2) $f^{[2]} = \begin{cases} r(1 + ar^2)^{1/3} & \text{if } r \leq R \\ \sqrt{\frac{d_{-2}}{r^2} + \frac{d_{-1}}{r}} + d_o + d_1 r + d_L \ln r & \text{otherwise.} \end{cases}$

This form results from the asymptotes at small and large r [174].

- (3) $f^{[3]} = \begin{cases} r & \text{if } r \leq R \\ a\sqrt{\frac{8r}{a} - \frac{8a}{r} + \frac{a^2}{r^2} - 12 \ln\left(\frac{r}{a}\right)} & \text{otherwise} \end{cases}$ [8].

- (4) Let $\Omega :=]-L/2, L/2[^3 \subseteq \mathbb{R}^3$ be a cube with volume $|\Omega| = L^3$. $\mathbf{f}^{[4]}$ is defined as a periodic deformation on the cube Ω if it is a C^1 -diffeomorphism on \mathbb{R}^3 that leaves Ω invariant: $\mathbf{f}^{[4]}(\Omega) = \Omega$ and if $\mathbf{f}^{[4]}(\mathbf{r} + L\mathbf{m}) = \mathbf{f}^{[4]}(\mathbf{r}) + L\mathbf{m}$ for any $\mathbf{m} \in \mathbb{Z}^3$ [175].
- (5) $f_{p,q,r}^{[5]}$ is defined by the inverse function $r\left(f_{p,q,r}^{[5]}\right) = \left[f_{p,q,r}^{[5]}\right]^p \left(1 + \alpha \left[f_{p,q,r}^{[5]}\right]^q\right)^r$ where α, p, q , and r are variational parameters. If $p = q = r = 1$, $r\left(f_{p,q,r}^{[5]}\right)$ refers to Hall's transformation [176]. The other $r\left(f_{p,q,r}^{[5]}\right)$ with $q = r = 1, p = r = 1$ and $p = q = 1$ were defined in [177, 178]. Hall's local-scaling transformation is then $f_{1,1,1}^{[5]} = [(1 + 4\alpha r)^{1/2} - 1]/(2\alpha)$.

Let $\phi(\mathbf{r})$ be an arbitrary function given on domain $\Sigma \subset \mathbb{R}^3$. A local-scaling transformation (16) transforms $\phi(\mathbf{r})$, generally speaking, into another function

$$\psi(\mathbf{r}) := \phi(\mathbf{f}(\mathbf{r})) \quad (40)$$

within the Jacobian (3), depending on the normalization of $\phi(\mathbf{r})$ on Σ if any. If $\phi(\mathbf{r}) = \exp(-r)$ is a simple exponential orbital, under Hall's local-scaling transformation it converts to

$$\psi(\mathbf{r}) = \frac{(1 + 4\alpha r)^{1/2} - 1}{2\alpha r(1 + 4\alpha r)^{1/4}} \exp\left(-[(1 + 4\alpha r)^{1/2} - 1]/(2\alpha)\right) \quad (41)$$

that was used to approximate the 1s orbital.

5.2 One-Electron Densities: Definition

A function $\rho(\mathbf{r}) : \mathbb{R}^3 \rightarrow \mathbb{R}_+^1$ is defined as a one-electron density associated with some system of N electrons iff:

- (Di) $\rho(\mathbf{r})$ is non-negative everywhere in \mathbb{R}^3 ;
- (Dii) $\rho(\mathbf{r})$ is normalized to the total number N of electrons,

$$\int_{\mathbb{R}^3} d^3\mathbf{r} \rho(\mathbf{r}) = N. \quad (42)$$

Here \mathbb{R}_+^1 stands for the non-negative semi-axis of \mathbb{R}^1 . Equation (42) merely implies that the square root of $\rho(\mathbf{r})$ is a square-integrable function, i.e., $[\rho(\mathbf{r})]^{1/2} \in L^2(\mathbb{R}^3)$;

- (Diii) $\rho(\mathbf{r})$ is a continuously differentiable function of \mathbf{r} almost everywhere in \mathbb{R}^3 .
It is a well-behavedness of densities.

Let \mathcal{D}_N be the class of the one-electron densities associated with a Coulomb system of N electrons and obeying the conditions **(Di)**–**(Diii)**. Obviously, $V\mathcal{L}_N \subset \mathcal{D}_N$. The fact that the condition **(Diii)** is valid for $V\mathcal{L}_N$ is the consequence of the following

Proposal 1. For any $\rho_\Psi(\mathbf{r}) = V\Psi$ where $\Psi \in \mathcal{L}_N$, $\nabla_{\mathbf{r}}\rho_\Psi(\mathbf{r}) \in \mathcal{L}^2(\mathbb{R}^3)$.

Proof. [88]: According to the Schwarz inequality, it follows from Eq. (11) that

$$[\nabla_{\mathbf{r}}\rho_\Psi(\mathbf{r})]^2 \leq 4N\rho_\Psi(\mathbf{r}) \sum_{s_1, \dots, s_N} \int d^3\mathbf{r}_2 \cdots \int d^3\mathbf{r}_N |\Psi(\mathbf{r}, s_1; \mathbf{r}_2, s_2; \dots; \mathbf{r}_N, s_N)|^2. \quad (43)$$

□.

Corollary 1.1. $\nabla_{\mathbf{r}}[\rho_\Psi(\mathbf{r})]^{1/2} \in \mathcal{L}^2(\mathbb{R}^3)$.

Proof. [10]:

$$\int d^3\mathbf{r} (\nabla_{\mathbf{r}}[\rho_\Psi(\mathbf{r})]^{1/2})^2 = \frac{1}{4} \int d^3\mathbf{r} \frac{[\nabla_{\mathbf{r}}\rho_\Psi(\mathbf{r})]^2}{\rho_\Psi(\mathbf{r})} \leq T_e[\Psi]. \quad (44)$$

□.

The term $[\nabla_{\mathbf{r}}\rho_\Psi(\mathbf{r})]^2/\rho_\Psi(\mathbf{r})$ is known as the von Weizsäcker kinetic energy $t_W[\rho_\Psi(\mathbf{r})]$ [4]. Hence, in the other words, **Corollary 1.1** tells that $t_W^{1/2}[\rho_\Psi(\mathbf{r})]$ is square-integrable. Usually, the von Weizsäcker term is only a part of the total many-electron kinetic energy [4]. The exception is the Hartree–Fock 2-electron model systems for which $t_W[\rho_\Psi(\mathbf{r})]$ is the exact kinetic energy.³ We further have

Corollary 1.2. Thomas–Fermi [172, 179] one-electron density $\rho_{\text{TF}}(\mathbf{r})$ is not N -representable.

Proof. According to [180, 181], $t_W^{1/2}[\rho_{\text{TF}}(\mathbf{r})]$ is not square-integrable. □.

Furthermore, the Thomas–Fermi energy density functional cannot be inserted in the density functional philosophy presented by the mappings (13) and (14) for all $\rho(\mathbf{r}) \in \mathcal{D}_N$ since the ground-state energies of many Thomas–Fermi atoms and ions⁴ lie below the exact ones.⁵

³ Except H^- which is unstable within the Hartree–Fock picture since its Hartree–Fock ground-state energy is equal to -0.488 hartree and placed above $E_0[H] = -0.5$ hartree. Note that the exact ground-state energy of H^- is -0.5278 hartree.

⁴ Thomas–Fermi molecules are unstable (see [189] and e.g., [4] and references therein).

⁵ Some of the widely used density functionals predict the ground-state energies below the experimental ones. For example, the B3LYP density functional in conjunction with the 6-31+G(d, p) basis set yields the energy -0.500273 hartree $< E_0[H]$ [182]. The B3LYP and B3PW91 show a similar trend for the atoms Li, C, O, F, Na, and Mg, and diatomics O_2 , F_2 , and LiF [183]. This implies that the corresponding ground-state wavefunctions, if do exist, are not square-integrable.

Consider an N -electron atom or ion with the nucleus centered at the origin of the Cartesian coordinate system. Let $\rho(\mathbf{r}) \in \mathcal{D}_N$ be one-electron density associated with a given atom and $\rho(\mathbf{r}) = \{\rho(r, \mathbf{e}_r) | r \in \mathbb{R}_+, \Omega \equiv (\theta, \phi), 0 \leq \theta \leq \pi, 0 \leq \phi \leq \pi\}$ is merely a bundle of one-dimensional curves. $\tilde{\rho}_2(r)$

Let two densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ from \mathcal{D}_N be given. Both of them are represented by the corresponding bundles of curves. Let us choose the unit vector \mathbf{e}_r and in these bundles, the projections of $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ onto \mathbf{e}_r ; the curves $\tilde{\rho}_1(r)$ and $\tilde{\rho}_2(r)$ which are, according to (Diii), continuously differentiable functions of $r = |\mathbf{r}|$. Hence, they are homotopically equivalent, or equivalently, there does exist such topological deformation that maps or deforms $\tilde{\rho}_1(r)$ into $\tilde{\rho}_2(r)$. Formally,

$$\tilde{\rho}_2(r) = J\{\mathbf{f}(\mathbf{r}); \mathbf{r}\} \tilde{\rho}_1(f(r, \mathbf{e}_r)). \quad (45)$$

The Jacobian in (38) ensures the normalization (Dii) for both densities ρ_1 and ρ_2 . Generalizing Eq. (24) over all directions in \mathbb{R}^3 results in that [7]

$$\rho_2(\mathbf{r}) = \frac{1}{3r^3} \mathbf{r} \cdot \nabla f^3 \rho_1(\mathbf{f}(\mathbf{r})). \quad (46)$$

To hold the electron–nuclear Kato cusp, the nuclear position is invariant of f . If f is a uniform scaling f_λ , the latter equation takes the form

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho_1(\lambda \mathbf{r}). \quad (47)$$

Given \mathbf{e}_r , combining Eqs. (36) and (38) yields

$$\frac{df(r, \mathbf{e}_r)}{dr} = \frac{r^2 \rho_2(r, \mathbf{e}_r)}{f^2 \rho_1(f(r, \mathbf{e}_r), \mathbf{e}_r)} \quad (48)$$

or in spherical coordinates, along a chosen unit vector \mathbf{e}_r determined by $\Omega = (\theta_0, \phi_0)$,

$$\frac{df(r, \theta_0, \phi_0)}{dr} = \frac{r^2 \rho_2(r, \theta_0, \phi_0)}{f^2 \rho_1(f(r, \theta_0, \phi_0), \theta_0, \phi_0)}. \quad (49)$$

Equation (49), or (48), is the first-order nonlinear differential equation for deformation $f(\mathbf{r})$ for given densities ρ_1 and ρ_2 . Due to (Diii), its solution exists and it is unique (see e.g., [4] and references therein). Therefore, for any pair of well-behaved densities, one enables to determine the deformation that transforms one of them into another. This means that F acts on \mathcal{D}_N transitively, that is, in algebraic terminology, \mathcal{D}_N is a single orbit with respect to \mathcal{F} . For a given and fixed density $\rho_1(\mathbf{r})$, defined hereafter as the generator density $\rho_g(\mathbf{r})$, Eq. (46) then implies:

Proposal 2. There exists the one-to-one correspondence between \mathcal{F} and \mathcal{D}_N that is explicitly expressed as $f \in \mathcal{F} \Leftrightarrow \rho_f^{[g]}(\mathbf{r}) := J\{\mathbf{f}, \mathbf{r}\} \rho_g(\mathbf{f}(\mathbf{r}))$.

In the integral form, Eq. (28) is as follows:

$$f(r, \theta_0, \phi_0) = \left[3 \int_{r_0}^r dr \frac{r^2 \rho_2(r, \theta_0, \phi_0)}{\rho_1(f(r, \theta_0, \phi_0), \theta_0, \phi_0)} \right]^{1/3}. \quad (50)$$

Note that the rhs of (50) contains a cubic root that reflects that the group \mathcal{F} of local-scaling transformations acts on \mathbb{R}^3 . It is shown in [184] that the dimensionality D of \mathbb{R}^D enters the corresponding Jacobian in the power D and, respectively, the corresponding integral form as $1/D$, this is on the one hand. On the other, there exists another remarkable facet of Eq. (28). This equation is well known in mathematics as the “Jacobian problem” ([55, 57–63, 190], see also [56]).

5.3 Many-Electron Wavefunctions and Concept of Orbit

To build the “variable mapping” (14), let us generalize the concept of the local-scaling transformations on \mathcal{L}_N . This is rather simple and straightforward. For this purpose, let us choose an arbitrary “reference” or generator wavefunction $\Phi_g(\{\mathbf{r}_i, \sigma_i\}_{i=1}^{i=N})$ where σ_i is the spin of the i -th electron and $\rho_g(\mathbf{r}) \in \mathcal{D}_N$ is the associated one-electron density. Then define a new wavefunction

$$\Phi_f(\{\mathbf{r}_i, \sigma_i\}) = \Phi_\rho(\{\mathbf{r}_i, \sigma_i\}) \equiv \left[\prod_{i=1}^N J(\mathbf{f}(\mathbf{r}_i); \mathbf{r}_i) \right]^{1/2} \Phi_g(\{\mathbf{f}(\mathbf{r}_i), \sigma_i\}) \quad (51)$$

with the density $\rho(\mathbf{r}) \equiv \rho_g(\mathbf{f}(\mathbf{r}))$ casting in **Proposal 2**. Φ_f is a locally scaled image of the “reference” wavefunction. Formally, $\Phi_f \equiv F\Phi_g$ where $F \in \mathcal{F}^{\times N} := [\times]^N \mathcal{F}$ and $F = (f, f, \dots, f) := f^{\times N}$ and (51) is nothing then else as the definition of the action of the group $\mathcal{F}^{\times N}$ on \mathcal{L}_N . Arbitrariness in choosing Φ_g ensures the validity of the definition (30) on the entire \mathcal{L}_N . Due to the isomorphism of the groups \mathcal{F} and $\mathcal{F}^{\times N}$, it is obvious that a local-scaling transformation that maps a given pair of N -electron wavefunctions into each other matches unambiguously the local scaling that transforms the corresponding one-electron densities into each other. However, although any pair of densities are locally scaled, this property no longer holds for an arbitrary pair of N -electron wavefunctions. Hence, \mathcal{L}_N is nontrivially partitioned, with respect to the group $\mathcal{F}^{\times N}$ of local-scaling transformations, into the orbits

$$\mathcal{L}_N = \bigcup_i \mathcal{O}^{[i]}. \quad (52)$$

In this sense, the group \mathcal{F} entangles \mathcal{D}_N and \mathcal{L}_N . By construction, an arbitrary orbit $\mathcal{O}^{[i]}$ is closed with respect to $\mathcal{F}^{\times N}$, that is, for any pair Φ_1 and Φ_2 in $\mathcal{O}^{[i]}$, there exists such local-scaling transformation $F_{1 \Rightarrow 2}$ that $\Phi_2 = F_{1 \Rightarrow 2} \Phi_1$. In the other words, if Φ_1 is the generator wavefunction of $\mathcal{O}^{[i]}$, for all $F \in \mathcal{F}^{\times N}$, $F_{1 \Rightarrow 2} \Phi_1 \in \mathcal{O}^{[i]}$. We thus prove:

Proposal 3. There exists a one-to-one map of variables on any orbit in \mathcal{L}_N .

Corollary 3.1. Orbit $\mathcal{O}^{[i]}$ is invariant relative to generator wavefunction.

Corollary 3.2. On each orbit $\mathcal{O}^{[i]} \subset \mathcal{L}_N$, there exists one and only one N -electron wavefunction which one-electron density is $\rho(\mathbf{r}) \in \mathcal{D}_N$.

Corollary 3.3. For any given orbit $\mathcal{O}^{[k]} \subset \mathcal{L}_N$ generated by $\Phi_g^{[k]}$ and the latter one-electron density $\rho_g^{[k]}, \mathcal{F}_{\rho_g^{[k]}}^{[k]}$ exhausts the whole \mathcal{D}_N .

Remark 1: Corollary 3.3 implies that any density $\rho(\mathbf{r}) \in \mathcal{D}_N$ is N -representable. In other words, the group \mathcal{F} of local-scaling transformations and its actions on \mathcal{D}_N and \mathcal{L}_N defined above ensures the N -representability of \mathcal{D}_N .

The uniqueness of the local-scaling transformation as the solution of Eq. (48) guarantees that the transformed wavefunction $\Phi_\rho^{[i]}$ is also unique. Thus, for any $\rho(\mathbf{r}) \in \mathcal{D}_N$ there exists a unique wavefunction $\Phi_\rho^{[i]}$ generated by means of local-scaling transformation from the arbitrary generator wavefunction $\Phi_g^{[k]}$. The orbit in \mathcal{L}_N is actually the set of all the wavefunctions thus generated which yield one-electron densities $\rho(\mathbf{r})$ in \mathcal{D}_N :

$$\mathcal{O}^{[i]} \equiv \left\{ \Phi_\rho^{[i]} | \Phi_\rho^{[i]} \rightarrow \rho(\vec{r}); \Phi_\rho^{[i]} \in \mathcal{L}_N; \rho(\vec{r}) \in \mathcal{D}_N \right\}. \quad (53)$$

Therefore, the orbit patterns in \mathcal{L}_N predetermine the inverse “variable mapping” V that was the premise in (13) and (14) and that naturally generalizes the Hohenberg–Kohn theorem on the entire set \mathcal{D}_N .

Note that \mathcal{L}_N includes N -electron Slater determinants which are structurally invariant with respect to $\mathcal{F}^{\times N}$. Define \mathcal{S}_N as the proper subset of \mathcal{L}_N consisting of Slater determinants. Since $\mathcal{F}^{\times N} \mathcal{S}_N \subseteq \mathcal{S}_N$, then $\mathcal{S}_N = \cup_i \mathcal{O}_S^{[i]}$ over all Slater orbits. Thus, we have:

Corollary 3.4. An arbitrary one-electron density $\rho(\mathbf{r}) \in \mathcal{D}_N$ is N -representable in \mathcal{S}_N .

5.4 Energy Density Functional and Variational Principle

5.4.1 Energy Density Functional: Definition

Proposal 3 definitely allows to propose the following rigorous definition of the energy density functional

$$\mathcal{E}_i[\rho(\mathbf{r})] \equiv \mathcal{E}_i[\rho(\mathbf{r}); \Phi_g^{[i]}] := \mathbf{E}[\Phi] |_{\Phi \in \mathcal{O}^{[i]} \subset \mathcal{L}_N} \quad (54)$$

and hence express the “functional mapping” (13) in the explicit way. It is evident that this mapping is one-to-many and there exist as many density functionals as there are orbits in \mathcal{L}_N . To derive $\mathcal{E}_i[\rho(\mathbf{r})]$ that is defined on the orbit $\mathcal{O}^{[i]} \subset \mathcal{L}_N$

explicitly, let us first write down the explicit expression for the energy functional $E[\Phi_g^{[i]}]$ of the orbit-generating wavefunction $\Phi_g^{[i]}$, in terms of its 1- and 2-matrices, $D_g^{1[i]}(x_1, x'_1)$ and $D_g^{2[i]}(x_1, x_2; x_1, x_2)$, respectively, and its one-electron density $\rho_g(x)$:

$$E[\Phi_g^{[i]}] = \frac{1}{2} \int d^4x_1 \nabla_{x_1} \nabla_{x'_1} D_g^{1[i]}(x_1; x'_1)|_{x'_1=x_1} + \int d^4x \rho(x) \hat{v}(\mathbf{r}) + \int d^4x_1 \int d^4x_2 \frac{D_g^{2[i]}(x_1, x_2; x_1, x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (55)$$

where $\int d^4x \equiv \sum_s \int d^3\mathbf{r}$. Let us apply the local-scaling transformation that casts in **Proposal 3** to the wavefunction $\Phi_g^{[i]}$, precisely to its 1- and 2-matrices and its density. This yields

$$D_\rho^{1[i]}(\mathbf{r}'_1, s_1; \mathbf{r}'_1, s'_1) = [J(\mathbf{f}(\mathbf{r}_1); \mathbf{r}_1) J(\mathbf{f}(\mathbf{r}'_1); \mathbf{r}'_1)]^{1/2} D_g^{1[i]}(\mathbf{f}(\mathbf{r}_1), s_1; \mathbf{f}(\mathbf{r}'_1), s'_1), \quad (56)$$

$$D_\rho^{2[i]}(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2; \mathbf{r}_1, s_1, \mathbf{r}_2, s_2) = J(\mathbf{f}(\mathbf{r}_1); \mathbf{r}_1) J(\mathbf{f}(\mathbf{r}_2); \mathbf{r}_2) D_g^{2[i]}(\mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2; \mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2), \quad (57)$$

and

$$\rho(\mathbf{r}, s) = J(\mathbf{f}(\mathbf{r}); \mathbf{r}) \rho_g(\mathbf{f}(\mathbf{r}), s). \quad (58)$$

Partitioning the 1- and 2-matrices, appearing in the rhs of Eqs. (56) and (57), into their local and non-local components:

$$D_g^{1[i]}(\mathbf{f}(\mathbf{r}_1), s_1; \mathbf{f}(\mathbf{r}'_1), s'_1) = [\rho_g(\mathbf{f}(\mathbf{r}_1), s_1) \rho_g(\mathbf{f}(\mathbf{r}'_1), s'_1)]^{1/2} \tilde{D}_g^{1[i]}(\mathbf{f}(\mathbf{r}_1), s_1; \mathbf{f}(\mathbf{r}'_1), s'_1), \quad (59)$$

$$D_g^{2[i]}(\mathbf{f}(\mathbf{r}_1), s_1; \mathbf{f}(\mathbf{r}_2), s_2; \mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2) = \frac{1}{2} \rho_g(\mathbf{f}(\mathbf{r}_1), s_1) \rho_g(\mathbf{f}(\mathbf{r}_2), s_2) \left(1 + \mathcal{F}_{\text{xc}, g}^{[i]}(\mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2) \right) \quad (60)$$

where $\tilde{D}_g^{1[i]}$ is the non-local part of the 1-matrix and $\mathcal{F}_{\text{xc}, g}^{[i]}$ is the non-local exchange-correlation factor. Therefore, the 1- and 2-matrices of (51) take the appearance:

$$D_\rho^{1[i]}(\mathbf{r}_1, s_1; \mathbf{r}'_1, s'_1) = [\rho(\mathbf{r}_1, s_1) \rho(\mathbf{r}'_1, s'_1)]^{1/2} \tilde{D}_g^{1[i]}(\mathbf{f}(\mathbf{r}_1), s_1; \mathbf{f}(\mathbf{r}'_1), s'_1), \quad (61)$$

and

$$D_{\rho}^{2[i]}(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2; \mathbf{r}_1, s_1, \mathbf{r}_2, s_2) = \frac{1}{2} \rho(\mathbf{r}_1, s_1) \rho(\mathbf{r}_2, s_2) \times \left(1 + \mathcal{F}_{\text{xc}, \text{g}}^{[i]}(\mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2) \right). \quad (62)$$

Finally, we obtain [4]

$$\begin{aligned} E[\Phi_{\rho}^{[i]}] &\equiv \mathcal{E}[\rho(x); \Phi_{\text{g}}^{[i]}] \\ &= \frac{1}{8} \int d^4x \frac{[\nabla_{\mathbf{r}} \rho(x)]^2}{\rho(x)} + \frac{1}{2} \int d^4x \rho(x) \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \bar{D}_{\text{g}}^{1[i]}(\mathbf{f}(\mathbf{r}), s; \mathbf{f}(\mathbf{r}'), s')|_{x'=x} \\ &\quad + \int d^4x \rho(x) v(\mathbf{r}) \\ &\quad + \frac{1}{2} \int d^4x_1 d^4x_2 \frac{\rho(x_1) \rho(x_2) \left(1 + \mathcal{F}_{\text{xc}, \text{g}}^{[i]}(\mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2) \right)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \end{aligned} \quad (63)$$

Few statements can be drawn from Eq. (63):

- (i) The kinetic energy density functional is composed of two components. The first, the von Weizsäcker term, is local and orbit-invariant. The second is non-local, orbit-dependent, and due to the one-third power in Eq. (50), transformed to the modified Thomas–Fermi term within the local density approximation;
- (ii) The exchange-correlation energy density functional is explicitly expressed as

$$\begin{aligned} E_{\text{xc}}[\Phi_{\rho}^{[i]}] &\equiv \mathcal{E}_{\text{xc}}[\rho(x); \Phi_{\text{g}}^{[i]}] : \\ &= \frac{1}{2} \int d^4x_1 d^4x_2 \frac{\rho(x_1) \rho(x_2) \mathcal{F}_{\text{xc}, \text{g}}^{[i]}(\mathbf{f}(\mathbf{r}_1), s_1, \mathbf{f}(\mathbf{r}_2), s_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}; \end{aligned} \quad (64)$$

- (iii) In fact, each density functional $\mathcal{E}[\rho(x); \Phi_{\text{g}}^{[i]}]$ depends on two basic variables: the one-electron density $\rho(x)$ and the generator wavefunction $\Phi_{\text{g}}^{[i]}$. Equation (42) expresses the energy as a functional of the one-electron density $\rho(x)$ within the orbit $\mathcal{O}^{[i]}$. True, Eq. (63) satisfies the condition of N-representability; (iv) One of the orbits in the decomposition (52) of \mathcal{L}_N is actually the orbit that contains the exact ground-state wavefunction. Refer it as the Hohenberg–Kohn orbit $\mathcal{O}^{[\text{HK}]}$ $\subset \mathcal{L}_N$. If a generator wavefunction is chosen to belong to $\mathcal{O}^{[\text{HK}]}$, Eq. (63) then determines the Hohenberg–Kohn energy density functional in the explicit manner.

5.4.2 Orbit Variational Principle and Euler–Lagrange Equation

The variational principle of the energy density functional theory based on the definition (33) is a straightforward consequence of the quantum mechanical variational principle (8) and the “functional mapping” (13). It is clearly orbit-dependent

or, equivalently, it is of the intra-orbit type. Let us consider the energy density functional $\mathcal{E}[\rho(\mathbf{r}, s); \Phi_g^{[i]}]$ given by Eq. (63) and defined within the $\mathcal{O}^{[i]}$ only. In this functional, $\rho(\mathbf{r}, s)$ stands for the density variable resulted from the initial density $\rho_g(\mathbf{r}, s)$ associated with the generator wavefunction $\Phi_g^{[i]}$. The extremum of $\mathcal{E}[\rho(\mathbf{r}, s); \Phi_g^{[i]}]$ on \mathcal{D}_N is attained at the i -th-optimal density $\rho_{\text{opt}}^{[i]}(\mathbf{r}, s)$ which is obtained by varying the following auxiliary functional:

$$\mathcal{E}[\rho(\mathbf{r}, s); \Phi_g^{[i]}] - \mu^{[i]} \left(\int d^4x \rho(\mathbf{r}, s) - N \right), \quad (65)$$

where $\mu^{[i]}$ is the Lagrange multiplier that accounts for the normalization of the density and that actually plays the role of a chemical potential on the orbit $\mathcal{O}^{[i]}$. Therefore, the stationary ground-state variational principle for the energy density functional $\mathcal{E}[\rho(\mathbf{r}, s); \Phi_g^{[i]}]$ is given by

$$\frac{\delta}{\delta \rho(\mathbf{r}, s)} \left\{ \mathcal{E}[\rho(\mathbf{r}, s); \Phi_g^{[i]}] - \mu^{[i]} \left(\int d^4x \rho(\mathbf{r}, s) - N \right) \right\} = 0, \rho(\mathbf{r}, s) \in \mathcal{D}_N, \quad (66)$$

we obtain the following integro-differential equation for the one-electron density [4]:

$$\begin{aligned} \frac{1}{8} \left[\frac{\nabla \rho(\mathbf{r}, s)}{\rho(\mathbf{r}, s)} \right]^2 - \frac{1}{r} \frac{\nabla^2 \rho(\mathbf{r}, s)}{\rho(\mathbf{r}, s)} + v_{\text{T},g}^{[i]}([\rho(\mathbf{r}, s)]; \mathbf{r}, s) + v(\mathbf{r}) + v_{\text{H}}([\rho(\mathbf{r}, s)]; \mathbf{r}) + \\ v_{\text{xc},g}^{[i]}([\rho(\mathbf{r}, s)]; \mathbf{r}, s) = \mu^{[i]}, \end{aligned} \quad (67)$$

where $v_{\text{H}}([\rho(\mathbf{r}, s)]; \mathbf{r}) = \int d^4x \rho(\mathbf{r}, s) |\mathbf{r} - \mathbf{r}'|^{-1}$ is the Hartree potential,

$$\begin{aligned} v_{\text{T},g}^{[i]}([\rho(\mathbf{r}, s)]; \mathbf{r}, s) = \frac{1}{2} \left\{ [\nabla_{\mathbf{r}} \nabla_{\mathbf{r}'}, \tilde{D}_g^{1[i]}(\mathbf{f}(\mathbf{r}), s; \mathbf{f}(\mathbf{r}'), s')]_{\mathbf{r}'=\mathbf{r}, s'=s} \right. \\ \left. + \rho(\mathbf{r}, s) \frac{\delta}{\delta \rho(\mathbf{r}, s)} ([\nabla_{\mathbf{r}} \nabla_{\mathbf{r}'}, \tilde{D}_g^{1[i]}(\mathbf{f}(\mathbf{r}), s; \mathbf{f}(\mathbf{r}'), s')]_{\mathbf{r}'=\mathbf{r}, s'=s}) \right\} \end{aligned} \quad (68)$$

is the potential originated from the non-local component of the kinetic energy in (63), and,

$$v_{\text{xc},g}^{[i]}([\rho(\mathbf{r}, s)]; \mathbf{r}, s) = \mathcal{E}_{\text{xc},g}^{[i]}([\rho(\mathbf{r}, s); \Phi_g^{[i]}]; \mathbf{r}, s) + \rho(\mathbf{r}, s) \frac{d\mathcal{E}_{\text{xc},g}^{[i]}([\rho(\mathbf{r}, s); \Phi_g^{[i]}]; \mathbf{r}, s)}{d\rho(\mathbf{r}, s)} \quad (69)$$

the exchange-correlation potential resulted from the non-local part of the electron–electron interaction where

$$\mathcal{E}_{\text{xc},g}^{[i]}([\rho(\mathbf{r}_1, s_1); \Phi_g^{[i]}; \mathbf{r}_1, s_1) = \frac{1}{2} \int d^4x_2 \frac{\rho(\mathbf{r}_2, s_2) \mathcal{F}_{\text{xc},g}^{[i]}(\mathbf{f}(\mathbf{r}_1), s_1; \mathbf{f}(\mathbf{r}_2), s_2)}{|\mathbf{r}_1 - \mathbf{r}|}. \quad (70)$$

Solving Eq. (67) for the given generator wavefunction $\Phi_g^{[i]}$, we obtain the i -th optimal or i -th approximate ground-state density $\rho_0^{[i]}(\mathbf{r}, s) \in \mathcal{D}_N$ and the i -th optimal or i -th ground-state energy

$$E_0^{[i]} \equiv \mathcal{E}_i[\rho_0(\mathbf{r})] \quad (71)$$

that simply casts as the i -th orbit variational principle:

$$E_0^{[i]} \equiv \inf_{\Phi \in \mathcal{O}^{[i]} \subset \mathcal{L}_N} \{E[\Phi]\} = E[\Phi]|_{\Phi = \Psi_0^{[i]} \in \mathcal{O}^{[i]} \subset \mathcal{L}_N} = \inf_{\rho_\Phi \rightarrow \Phi \in \mathcal{O}^{[i]}} \{\mathcal{E}_i[\rho_\Phi]\}. \quad (72)$$

The next step is to substitute the densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ by $\rho_g^{[i]}(\mathbf{r})$ and $\rho_0^{[i]}(\mathbf{r})$ in Eq. (46) correspondingly and to solve the latter. The solution is the i -th optimal local-scaling transformation $\mathbf{f}_0^{[i]}(\mathbf{r}) \in \mathcal{F}$ which is further applied to $\Phi_g^{[i]}$ to get, via Eq. (51), the i -th optimal, ground-state wavefunction $\Phi_0^{[i]} \in \mathcal{L}_N$. True, generally speaking, the latter is the approximate ground-state wavefunction that yields an upper bound to the exact ground-state energy E_0 which is attained, by definition, only at the Hohenberg–Kohn orbit $\mathcal{O}^{[\text{HK}]}$, that is, $E_0^{[\text{HK}]} = E_0$.

5.4.3 Global Variational Principle: The Concept of Local-Scaling Self-Consistent Field

The orbit variational principle (65) deduced in Sect. 5.4.2 is solely defined on a particular orbit. The reason is trivial: this is precisely that orbit where the energy density functional is defined according to Eq. (54). In contrast, the global ground-state quantum mechanical variational principle (8) is carried out over the whole Hilbert space \mathcal{L}_N . Within the local-scaling formulation of the density functional approach is achieved due to the fact that the energy density functional in fact depends on two basic variables of theory: one—the one-electron density—is the key variable of the density functional theory and the other is the generator wavefunction that determines an orbit. Hence, the orbit partitioning (52) of \mathcal{L}_N is governed by the orbit generators. Therefore,

$$E_0 = \inf_{\substack{\text{over} \\ \text{all orbits} \\ \mathcal{O}^{[i]} \subset \mathcal{L}_N}} \left\{ \inf_{\rho(\mathbf{r}) \in \mathcal{D}_N} \{\mathcal{E}[\rho(\mathbf{r}); \Phi_g^{[i]}]\} \right\}. \quad (73)$$

Equation (73) implies that the search for the exact ground-state wavefunction must be carried out by a combined intra-orbit and inter-orbit minimization [7]. The former reflects the charge consistency variational principle, whereas the latter the

inter-orbit one, the orbit consistency. The latter is actually the variational principle of the “inter-orbit” self-consistent field that resembles the Kohn–Sham self-consistent field approach and results in inter-orbit “jumps” that finally leads to the exact, Hohenberg–Kohn orbit.

6 Overlook

All of what is scientific in chemistry is physics—the rest is cooking.
L. D. Landau [187]

I have a feeling that a success in the adequate description of dispersion interactions within the DFT has been achieved. Again what we have at our current disposal is a number of D-DFT functionals among which choosing the best still remains a challenge that leaves a feeling of certain yet-imperfectness in this DFT area and, on the other hand, shows the ways to improve it. This was in fact the key goal undertaken in the present review which has definitely been achieved, I believe.

Acknowledgments Thanks are due first to all friends and colleagues with whom I shared the ideas of the density functional theory during the last three decades, in particular Ivan Zh. Petkov, Mario V. Stoitsov, Eduardo V. Ludeña, Toshi Koga, Jean-Lois Calais, Per-Olov Löwdin, Julian Schwinger, B. M. Deb, Enrico Clementi, Bob Parr, and Erkki Brändas, and Stefan Grimme. Mihai V. Putz and D. Michael P. Mingos are gratefully acknowledged for their kind invitation.

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Applications of Density Functional Theory to Biological
and Bioinorganic Chemistry

Putz, M.V.; Mingos, M.D.P. (Eds.)

2013, XII, 236 p. 107 illus., 41 illus. in color., Hardcover

ISBN: 978-3-642-32749-0