

Electronegativity in Quantum Chemistry

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Abstract—The possibility is discussed for determination of chemical potential (electronegativity) of an electron–nucleus system in terms of the quantum-mechanical density functional theory (DFT). The principle of complete leveling of chemical potentials of natural orbitals, formulated in the framework of DFT, cannot be regarded now as justified. The calculation of electronic chemical potential via difference schemes still remains the only procedure suitable for estimation of this quantity by quantum-chemical methods.

Electronegativity (EN) is one of the oldest terms of theoretical chemistry. However, up to now, it has not received a clear and unequivocal interpretation. We previously [1, 2] made an attempt to follow the development of the concepts of atom and group ENs and, by summarizing the available data, isolated two approaches to determination of ENs of substituents, which were arbitrarily referred to as formal and quantum-chemical. The calculation schemes [2–4] of the formal approach are based on postulates of the theory of chemical structure, and the orbital EN of a substituent is expressed through valence state parameters of the atoms constituting that substituent, namely through their orbital chemical potentials (CP) and orbital hardnesses, using the principle of leveling of orbital CPs of a bond. In these schemes, the equilibrium orbital CPs of different bonds of a substituent and the orbital CP of its unsaturated bond (which is the same as group EN) do not coincide with each other. The calculation schemes [5–8] utilizing the Sanderson principle [9] of complete leveling of atom ENs upon formation of covalent bonds are considered separately, for they are based on the “atom in a molecule” model which has nothing in common with the concept of valence states of atoms within the theory of chemical structure. Here, each atom of a substituent has a fractional charge and is characterized by electron CP, while equilibrium electron CPs of fictitious atoms are similar to each other and are equal to the group EN taken with the opposite sign. It should be noted that the authors of the above schemes use the term *EN* and speak about leveling of atom ENs, which distorts the sense of the term *atom EN* formerly introduced by Pauling [10]. As we stated in [2], both theoretical and practical values of such schemes are more than

doubtful. In the present work we shall turn back to the discussion of this problem.

In the framework of quantum-chemical approach, the orbital EN of a substituent (χ) is equated to CP of its electron subsystem (μ):

$$\chi = -\mu, \quad \mu = (\partial E / \partial N)_v. \quad (1)$$

Here, E is the energy of the ground electronic state, N is the number of electrons, and $v(\mathbf{r})$ is the electrostatic nuclear potential which depends on the charges and geometry of the stationary nuclear subsystem [2, 11]. The electron CP, which can be calculated by variational quantum-chemical methods, characterizes the ground electronic state of an atom, molecule, or radical at a specified (but not necessarily equilibrium) geometric configuration of nuclei. Therefore, non-empirical calculation of group ENs is implicitly based on the assumption that valence state of a substituent can be simulated through the ground electronic state of the same group of atoms at a nonequilibrium configuration of nuclei, which reproduces the standard substituent geometry in various molecules. Definition (1) still does not provide an algorithm for calculation of electron CP of a system. For this purpose, it is necessary to formulate rules of formal energy differentiation with respect to the number of electrons or to develop calculation schemes which do not involve such differentiation in the explicit form. At present, this quantity is usually estimated by interpolation using formula (2) [2, 12]:

$$\mu = 1/2[E(N + 1) - E(N - 1)]. \quad (2)$$

In the present article we consider possible ways of estimating the electron CP in terms of the density

functional theory. This theory was introduced in 1964 by Hohenberg and Kohn [13]. The authors proved that there exists a correspondence rule which relates any ν -representable density function,* normalized with respect to N , to a unique energy value which characterizes the ground state of a system with the given N and $\nu(\mathbf{r})$. This rule is written as $E_{\text{HK}}[\rho]$ functional which, at fixed N and $\nu(\mathbf{r})$, has the lowest value with the density function of the ground state of a system with the given N and $\nu(\mathbf{r})$:

$$E_0(N, \nu) = \inf_{\rho \in N_{\text{HK}}} E_{\text{HK}}[\rho]. \quad (3)$$

Here, the set N_{HK} is limited by those test functions $\nu(\mathbf{r})$ which are normalized with respect to N and are ν -representable. It should be noted that the Hohenberg–Kohn theorems were proved for a family of Hamiltonians which differ only by external (nuclear) potentials $\nu(\mathbf{r})$ and have nondegenerate ground states whose wave functions belong to a single antisymmetric Gilbert space. Search for a constrained extremum of the energy functional $E_{\text{HK}}[\rho]$ is performed by the Lagrange undetermined multiplier procedure. Thus practical application of the Hohenberg–Kohn variational principle (3) requires that the N_{HK} set be defined and precise mathematical expression for $E_{\text{HK}}[\rho]$ be found. Up to now, both these problems have not been solved in explicit form; therefore, approximated functionals (which may be represented in an analytical form) are always used in practice, and only normalization requirement is imposed on a class of variable $\nu(\mathbf{r})$ while deducing Euler–Lagrange equation for one or another approximation. Such variational procedure underlies the approximate density functional theory formulated first by Hohenberg and Kohn for heterogeneous electron gas [13]. The main purpose of this theory is to develop approximations for $E_{\text{HK}}[\rho]$ which could ensure physically meaningful description of complex molecular systems. The energy and density of the ground state for each approximation can be determined by solving the Euler–Lagrange equation

$$\frac{\partial}{\partial \rho(\mathbf{r})} \left[E_{\text{HK}}[\rho] + \mu \left\{ N - \int \partial \mathbf{r} \rho(\mathbf{r}) \right\} \right] = 0$$

* Density function derived from antisymmetric N -electron wave function by the formula

$$\rho(\mathbf{r}_1) = N \sum_{s_1, \dots, s_N} \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \delta \mathbf{r}_2 \dots \delta \mathbf{r}_N$$

is referred to as an N -representable function. An N -representable function is also a ν -representable one provided that it originates from an antisymmetric N -electron wave function of the ground state of an adiabatic Hamiltonian with some $\nu(\mathbf{r})$.

with the constraint

$$\int \rho(\mathbf{r}) \partial \mathbf{r} = N. \quad (4)$$

The Lagrange multiplier μ at normalization requirement (4) is equated to the electron CP of the ground state of a system [14].

In 1978, Donnelly and Parr [15] generalized the Hohenberg–Kohn theorem and formulated a variational principle for energy functional from the generalized density function or reduced first-order density matrix $\gamma_1(\mathbf{x}; \mathbf{x}')$. The principal postulates of this concept were analyzed by Valone [16, 17] who reformulated the Donnelly–Parr theory without resorting to the presently unknown ν -representability condition. While operating with the finite molecular orbital basis, a conclusion was drawn [15–17] that the ground state of a molecule with closed electron shells is described by a set of canonical orbitals $\phi_k(\mathbf{r})$ which are defined by Eqs. (5):

$$(h \rho_1) \phi_k = \varepsilon_k \phi_k, \quad \varepsilon_k = \mu f_k, \quad 0 < f_k < 2, \quad k = 1, 2, \dots, n. \quad (5)$$

Here, ρ_1 is the Hermitean density operator with the kernel $\rho_1(\mathbf{r}; \mathbf{r}')$, f_k are the eigenvalues of ρ_1 (assuming fractional), and h is the Hermitean operator with the kernel $h(\mathbf{r}; \mathbf{r}')$, which is defined as variational derivative of energy with respect to $\rho_1(\mathbf{r}; \mathbf{r}')$. By definition, operator h has degenerate eigenvalues μ_k which are equal to the electron CP of the ground state of a molecule. This may be rewritten as follows:

$$\mu_k \equiv \frac{\partial E}{\partial f_k} \equiv \mu, \quad k = 1, 2, \dots, n. \quad (6)$$

Identity (6) demonstrates leveling of the orbital electron CPs μ_k in the ground state of a molecule. This result was interpreted in [15] as a physical substantiation of the principle of leveling of atom ENs, which was postulated by Sanderson [9], and as a support for calculation schemes utilizing that principle. Some other extensions of Eqs. (5) and (6) were discussed by Donnelly [18].

However, it should be noted that physical sense of the Donnelly–Parr theory cannot be regarded as acceptable unless the validity of Eqs. (5) and (6) is confirmed. Up to now, the question as to whether physically admissible solutions of these equations exist has no answer. In the present article we discuss this problem in terms of the functional N -representability condition [19, 20]. The article is organized as follows. The first section contains a detailed consideration of Valone's formulation of the Donnelly–

Parr theory with an emphasis given to unproved postulates of that theory and its other weak points. The main of these is parametrization of the two-electron part of the precise energy functional, which violates functional N -representability. In the second section we propose two possible parametrizations for the Donnelly–Parr functional and show, using the simplest molecules with closed shells as examples, that the Euler–Lagrange equations obtained in the framework of the proposed approximations have no solution among N -representable density matrices. This means that the equation of the orbital electron CPs of various molecules implies a nonphysical density matrix and that the corresponding Euler–Lagrange equations cannot be applied to determination of electron CP of a system. Finally, we give some important extensions of the calculation results.

Donnelly–Parr theory. Quantum mechanics of isolated molecules deals with energy functionals (7) which are defined as an anticipated value of the Hamiltonian H_v for a state described by N -electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, which belongs to a continuous set L_N :

$$E = E_v[\Psi] \equiv \frac{\langle \Psi | H_v | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (7)$$

Here, \mathbf{x}_i is a combination of spatial and spin coordinates of an i th electron; the spatial coordinates $\mathbf{r} = (x, y, z)$ are continuous, while the spin coordinate has only two possible values, $1/2$ and $-1/2$. The Hamilton operator looks as follows:

$$H_v = \sum_{i=1} h_v(\mathbf{r}_i) + \sum_{i=1} \sum_{j=i+1} g(\mathbf{r}_i, \mathbf{r}_j); \quad (8)$$

$$h_v(\mathbf{r}) = -1/2\nabla^2(\mathbf{r}) + v(\mathbf{r}); \quad (9)$$

$$g(\mathbf{r}_i, \mathbf{r}_j) = |\mathbf{r}_i - \mathbf{r}_j|^{-1}. \quad (10)$$

The operator $v(\mathbf{r})$ is an external Coulomb potential created by fixed nuclei. The subscript “ v ” in H_v and h_v indicates that two N -electron systems can differ only by external potentials. For the sake of simplicity, let us presume that $v(\mathbf{r})$ has no space symmetry. Then, stationary states are unambiguously defined by the energy E and spin quantum numbers S and M which determine the spin symmetry. The ground state of a molecule is described by nondegenerate eigenfunction of operators H_v , S^2 , and S_z ; it conforms to the variational principle represented by Eq. (11):

$$E_0 \equiv \frac{\langle \Psi | H_v | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \inf_{\Psi \in L_N} E_v[\Psi]. \quad (11)$$

Here, the set L_N is limited by those test functions Ψ which are antisymmetric with respect to permutation of the coordinates (both spatial and spin) of any two electrons and which have a spin symmetry corresponding to the ground state being defined. In practice, Eq. (11) is solved by the linear variational method with the use of molecular orbitals.

Let $\{\varphi_k(\mathbf{r})\}_{k=1}^n$ with $n \gg N$ be a finite set of orthonormal molecular orbitals which constitute an n -dimensional Cartesian space E_n . By setting E_n we can built up the direct sum $E_{2n} = E_n \oplus E_n$

$$E_{2n} \equiv \{ \chi(\mathbf{x}) | \chi(\mathbf{r}, 1/2) \equiv \chi_1^\alpha(\mathbf{r}); \chi(\mathbf{r}, -1/2) \equiv \chi_2^\beta(\mathbf{r}) \}, \\ \chi_1^\alpha(\mathbf{r}), \chi_2^\beta(\mathbf{r}) \in E_n,$$

and define spin-orbitals which form the basis in E_{2n} :

$$\varphi_k^\alpha(\mathbf{r}) \equiv \varphi_k(\mathbf{r}) \alpha(s) \in E_{2n}, \quad k = 1, \dots, n;$$

$$\varphi_k^\beta(\mathbf{r}) \equiv \varphi_k(\mathbf{r}) \beta(s) \in E_{2n}, \quad k = 1, \dots, n.$$

Next, let us built up a complete set of orthonormal N -electron configurations $\Phi_k(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ having the same spin symmetry as that of the ground state. Each of these configurations is a linear combination of Slater’s determinants [21]. The number of Φ_k configurations depends upon n and required spin symmetry. Suppose that all possible N -electron configurations have been obtained. The set $\{\Phi_k\}_{k=1}^M$ constitutes a finite subspace of an antisymmetric Gilbert space of N -electron wave functions; this subspace is identified as the set of test wave functions L_N [Eq. (12)]:

$$L_N \equiv \{ \Psi | \Psi = \sum_{k=1}^M C_k \Phi_k \}. \quad (12)$$

The linear variational method based on the above definition of L_N reduces Eq. (11) to linear algebraic system (13):

$$\sum_{j=1}^M \langle \Phi_i | H_v - E | \Phi_j \rangle C_j = 0, \quad i = 1, \dots, M. \quad (13)$$

System (13) defines the complete set of stationary states Ψ_k in L_N , which follow in the order of increasing energy. The set $\{\Phi_k\}_{k=0}^M$ is complete from the viewpoint implying that there is an unambiguous correspondence between the stationary points of $E_v[\Psi]$ functional in the L_N space and wave functions which conform to Eqs. (13). Insofar as L_N is equated to a finite subspace of the antisymmetric Gilbert space, the linear variational procedure gives the upper limit of the precise energy of the ground state and provides

the possibility for systematic approximation refinement through extension of the molecular orbital basis and hence of the set of possible N -electron configurations. Solutions of Eqs. (13) can be regarded as precise eigenfunctions of a hypothetical N -electron system with a Hamiltonian H_v^M defined as an M -rank projection of the H_v operator onto the L_N space:

$$H_v^M = \sum_{i=1}^M \sum_{j=1}^M \langle \Phi_i | H_v | \Phi_j \rangle | \Phi_i \rangle \langle \Phi_j |.$$

Once the molecular orbital basis has been selected, functional (7) may be written in the form

$$E = E_v^M[\Psi] \equiv \frac{\langle \Psi | H_v^M | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad \forall \Psi \in L_N.$$

Then, Eqs. (13) become equivalent to variational principle (14):

$$E_0 \equiv \frac{\langle \Psi_0 | H_v^M | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \inf_{\Psi \in L_N} E_v^M[\Psi]. \quad (14)$$

In this context, precise Hamiltonian (8)–(10) may be represented as the limit

$$H_v = \lim_{M \rightarrow \infty} H_v^M.$$

A fundamental postulate of the Donnelly–Parr theory [15] is the existence of such energy functional from the first-order density matrix $\gamma_1(\mathbf{x}; \mathbf{x}') \in N_N$ that

$$E_0 = \inf_{\Psi \in L_N} E_v^M[\Psi] = \inf_{\gamma_1 \in N_N} E_{\text{DP}}^n[\gamma_1] \quad (15)$$

for any finite molecular orbital basis. Here, N_N is the set of physically admissible first-order density matrices, and n is the dimensionality of the orbital basis set. This statement was clearly formulated by Valone [16, 17] using density matrices of mixed states (which are also referred to as ensembles). Following Valone, let us consider a hypothetical N -electron system with a Hamiltonian H_v^M . Stationary state of a system is called *pure*, if it is an eigenfunction of H_v^M , and *mixed*, if it is described by a density matrix Γ belonging to the set D_N [Eq. (16)]:

$$D_N \equiv \left\{ \Gamma \mid \Gamma = \sum_{k=0}^{M-1} w_k \Psi_k(\mathbf{x}_1, \dots, \mathbf{x}_N) \Psi_k^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N) \right\},$$

$$w_k \geq 0, \quad \sum_{k=0}^{M-1} w_k = 1. \quad (16)$$

By definition, Γ is an antisymmetric kernel of a positive Hermitean operator acting in L_N ; w_k and Ψ_k are eigenvalues and eigenfunctions of Γ . According to Eq. (16), the mixed state is determined by the probabilities for the system to exist in the pure states. From the geometric viewpoint, the density matrix Γ is a point with the coordinates w_0, w_1, \dots, w_{M-1} , which belongs to an M -dimensional Cartesian space U_M , and the set $D_N \subset U_M$ is a convex polyhedron whose apices coincide with the points of pure states [22]. The energy of the ensemble $\Gamma(w_k) \in D_N$ is defined by the expression

$$E \equiv \text{tr}(H_v^M \Gamma) = \sum_{k=0}^{M-1} E_k w_k, \quad \forall \Gamma \in D_N, \quad (17)$$

where E_0, E_1, \dots, E_{M-1} are the energies of the pure states. Equation (17) sets a hyperplane Π_E in the space U_M ; the intersection

$$D_N(E) = \Pi_E \cap D_N$$

is a limited convex polyhedron containing ensembles with the same energy E . Thus the set D_N is divided into nonintersecting subsets

$$D_N = \bigcup_E D_N(E),$$

where E monotonically increases from E_0 to the maximal value E_{M-1} . Assuming that the mixed states described by Eq. (16) are feasible from the physical viewpoint, the subset $D_N(E)$ represents the energy level E of the system. It should be noted that the energy level of the ground state (E_0) is not degenerate, while any higher energy level $E_0 + \partial E$ is represented by an infinite set of ensembles (except for the E_{M-1} level). Taking into account that the Hamiltonian H_v [Eqs. (8)–(10)] contains only one- and two-electron operators, the energy of the ensemble $\Gamma \in D_N$ can be expressed through reduced density matrices γ_1 and γ_2 , derived from Γ . This may be written as follows:

$$E \equiv \text{tr}(H_v^M \Gamma) = \text{tr}(H_v \Gamma) = \text{tr}(h_v \gamma_1) + \text{tr}(g \gamma_2), \quad \forall \Gamma \in D_N; \quad (18)$$

$$\text{tr}(h_v \gamma_1) = \sum_s \int \partial \mathbf{r} [h_v(\mathbf{r}) \gamma_1(\mathbf{x}; \mathbf{x}')]_{s'=s; \mathbf{r}'=\mathbf{r}}; \quad (19)$$

$$\text{tr}(g \gamma_2) = \sum_{s_1} \int \partial \mathbf{r}_1 \sum_{s_2} \int \partial \mathbf{r}_2 [g(\mathbf{r}_1, \mathbf{r}_2) \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)]. \quad (20)$$

Here,

$$\gamma_1(\mathbf{x}; \mathbf{x}') = N \sum_{s_2, \dots, s_N} \int \partial \mathbf{r}_2 \dots \partial \mathbf{r}_N \Gamma(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N) \quad (21)$$

(which is called a first-order density matrix or 1-matrix) is the Hermitean kernel of one-electron density operator acting on E_{2n} , and

$$\gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \binom{N}{s_2, \dots, s_N} \int \partial \mathbf{r}_3 \dots \partial \mathbf{r}_N \times \Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N; \mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3, \dots, \mathbf{x}'_N) \quad (22)$$

(called a second-order density matrix or 2-matrix) is the antisymmetric Hermitean kernel of two-electron density operator acting in $E_{2n} \otimes E_{2n}$. The γ_1 and γ_2 matrices derived from a single $\Gamma \in D_N$ are related to each other through expression (23):

$$\gamma_1(\mathbf{x}; \mathbf{x}') = \frac{2}{N-1} \sum_{s_2} \int \partial \mathbf{r}_2 \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2). \quad (23)$$

Using the Fock expression for S^2 operator [23]

$$S^2 = 3/4 N - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \{1/2 - [s_i, s_j]\}, \quad (24)$$

we obtain [Eqs. (25a), (25b)] that the spin symmetry of the $\Gamma \in D_N$ ensemble is also determined by the reduced density matrices γ_1 and γ_2 derived from Γ :

$$\langle S^2 \rangle \equiv S(S+1) = 3/4 \text{tr}(\gamma_1) - \text{tr}(\{1/2 - [s_1, s_2]\} \gamma_2); \quad (25a)$$

$$\langle S_z \rangle \equiv M = \text{tr}(s_z \gamma_1). \quad (25b)$$

Here, $[s_i, s_j]$ denotes transposition of the spin variables s_i and s_j . As follows from Eqs. (18)–(25), the ground state of a system is unambiguously described by the 2-matrix γ_2 which originates from $\Gamma_0 \in D_N$. This matrix can be determined by minimization of the functional

$$E = E_v^n[\gamma_1, \gamma_2] = \text{tr}(h_v \gamma_1) + \text{tr}(g \gamma_2), \quad (26)$$

which depends on two variables γ_1 and γ_2 interrelated through Eq. (23). In fact, either of these variables can be regarded as independent; therefore, minimization of the functional can be performed in two ways.

The γ_2 matrix is an N -representable ensemble if at least one $\Gamma \in D_N$ ensemble conforms to Eq. (22). Let P_N be a convex set of such 2-matrices. The mapping of D_N onto P_N , specified by Eq. (22), is multivalued, so that D_N can be divided into nonintersecting equivalence classes

$$D_N = \cup_{\gamma_2 \in P_N} D_N(\gamma_2), \quad (27)$$

where $D_N(\gamma_2)$ is a class of ensembles generating one 2-matrix γ_2 . By definition of $D_N(\gamma_2) \subseteq D_N(E)$ with an energy E , obtained with γ_2 by Eqs. (18)–(23), the equivalence class of the Γ_0 matrix contains no other elements but Γ_0 . However, generally speaking, equivalence classes of the other pure states of a system are infinite (except for the equivalence class of Γ_{M-1}). It should be noted once more that two ensembles belonging to a single equivalence class differ by the probabilities w_k , but, taking into account their equal energies and the same spin symmetry, they are indetical in terms of the variational procedure under consideration.

Likewise, the γ_1 matrix is an N -representable ensemble provided that there exists at least one $\Gamma \in D_N$ ensemble which conforms to Eq. (21). Let N_N be a convex set of such 1-matrices. A multivalued mapping of P_N onto N_N , specified by Eq. (23), generates division of P_N into nonintersecting equivalence classes

$$P_N = \cup_{\gamma_1 \in N_N} P_N(\gamma_1), \quad (28)$$

where $P_N(\gamma_1)$ is a class of 2-matrices (N -representable ensembles) giving rise to one 1-matrix γ_1 . It is important that equivalence class of 2-matrix of the ground state can contain other elements in addition to that matrix. In other words, 1-matrix γ_1 , being an N -representable matrix Γ_0 , can also be obtained from the other ensembles belonging to D_N . This is consistent with the fact that 1-matrix itself determines neither energy nor spin symmetry of a state. Comparison of Eqs. (27) and (28) gives

$$D_N = \cup_{\gamma_1 \in N_N} \cup_{\gamma_2 \in P_N(\gamma_1)} D_N(\gamma_2).$$

Equations (27) and (28) make it possible to search for the minimal value of functional $E_v^n[\gamma_1, \gamma_2]$, which is set by Eq. (26), in two ways. The first of these is based on variational principle (29):

$$E_0 = \inf_{\gamma_1 \in N_N} E_v^n[\gamma_1, \gamma_2] = \inf_{\gamma_2 \in P_N} \{ \text{tr}(h_v \gamma_1) + \text{tr}(g \gamma_2) \}. \quad (29)$$

Here, γ_1 is calculated by Eq. (23) for each γ_2 belonging to P_N . The use of γ_2 as independent variable implies that the conditions for N -representability of the γ_2 ensemble are formulated in the explicit form. This complex problem has not been solved so far [24–26]. The second approach utilizes the Levy–Lieb two-step variational principle [27, 28] in the form proposed by Valone [16, 17]:

$$E_0 = \inf_{\gamma_1 \in N_N} \inf_{\gamma_2 \in P_N(\gamma_1)} E_v^n[\gamma_1, \gamma_2]$$

$$= \inf_{\gamma_1 \in N_N} \{tr(h_v \gamma_1) + \inf_{\gamma_2 \in P_N(\gamma_1)} tr(g \gamma_2)\}. \quad (30)$$

In this case, the main difficulty is to conserve the functional N -representability at the stage of γ_2 variation [29, 30], i.e., search for the minimal value of $tr(\gamma_2)$ should be performed within the equivalence class $P_N(\gamma_1 + \delta\gamma_1)$ for each $\gamma_1 + \delta\gamma_1$ belonging to N_N . Such a constraint is improbable to be set at all. The Levy–Lieb–Valone variational principle (30) underlies the density matrix functional theory, and the Donnelly–Parr theory [15] can be regarded as its approximate version. The problem of functional N -representability is solved by introducing the approximation

$$\inf_{\gamma_2 \in P_N(\gamma_1)} tr(g \gamma_2) = Q_{DP}[\gamma_1], \quad \forall \gamma_1 = \tilde{\gamma}_1 + \delta\gamma_1, \quad (31)$$

which is assumed to be valid at least in an infinitesimal neighborhood of the energy minimum

$$E_0 = \inf_{\gamma_1 \in N_N} E_{DP}^n[\gamma_1] = \inf_{\gamma_1 \in N_N} \{tr(h_v \gamma_1) + Q_{DP}[\gamma_1]\} \quad (32)$$

reached with the matrix $\tilde{\gamma}_1$. It was postulated that variational principle (32) ensures attainment of upper limit (14) with $\tilde{\gamma}_1$ originating from the ground state density matrix Γ_0 provided that the precise functional $Q_{DP}[\gamma_1]$ is used. Equation (31) is assumed to be universal since $Q_{DP}[\gamma_1]$ has only one algebraic form, regardless of the number of electrons and spin symmetry of a system. Thus the Donnelly–Parr theory can be regarded as variational if a “precise” universal functional $Q_{DP}[\gamma_1]$ exists, i.e., if such a parametrization of the two-electron part of precise energy functional (26) can be found, which makes Eq. (31) valid for any N -representable 1-matrix belonging to the range of variation of γ_1 . However, the Donnelly–Parr theory implies no recipes for searching for such a functional. Moreover, its existence does not follow from any theorem of the density matrix functional theory, i.e., it cannot be proved rigorously. At present, numerous parametrizations for the Donnelly–Parr functional are known, whose quality can be estimated by the trial-and-error method.

Before deducing the Euler–Lagrange equations for systems with open and closed shells, one should remember that γ_1 is determined by two spin components:

$$\gamma_1(\mathbf{r}, 1/2; \mathbf{r}', 1/2) = \rho_1^{\alpha\alpha}(\mathbf{r}; \mathbf{r}')$$

and

$$\gamma_1(\mathbf{r}, -1/2; \mathbf{r}', -1/2) = \rho_1^{\beta\beta}(\mathbf{r}; \mathbf{r}'),$$

which are equated to Hermitean kernels of one-electron density operators ρ_1^α and ρ_1^β active in E_n . The eigenfunctions and eigenvalues of these operators can be determined from Eqs. (33):

$$[\rho_1^{\sigma\sigma}(\mathbf{r}; \mathbf{r}') \phi_i^\sigma(\mathbf{r}') \partial \mathbf{r}' = f_i^\sigma \phi_i^\sigma(\mathbf{r}), \quad i = 1, \dots, n, \quad \sigma = \alpha, \beta. \quad (33)$$

By setting an orthonormal basis in E_n , we obtain matrix representations of the operators ρ_1^α and ρ_1^β

$$\rho_1^{\sigma\sigma}(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^n \sum_{j=1}^n P_{ij}^\sigma \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}'), \quad \sigma = \alpha, \beta,$$

with Hermitean matrices (34):

$$\mathbf{P}^\alpha = [P_{ij}^\alpha] = [\langle i | \rho_1^\alpha | j \rangle]; \quad (34a)$$

$$\mathbf{P}^\beta = [P_{ij}^\beta] = [\langle i | \rho_1^\beta | j \rangle]. \quad (34b)$$

Provided that a basis in E_n has been set, γ_1 is unambiguously specified by matrices (34), and the $E_{DP}^n[\gamma_1]$ functional becomes a function of \mathbf{P}^α and \mathbf{P}^β , regardless of the $Q_{DP}[\gamma_1]$ form used. Then, the variational derivatives of $E_{DP}^n[\gamma_1]$ with respect to $\rho_1^{\alpha\alpha}$ and $\rho_1^{\beta\beta}$ can be expressed through kernels of the Hermitean operators h^α and h^β acting in E_n . These kernels are given by the equations

$$h^\sigma(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^n \sum_{j=1}^n H_{ij}^\sigma \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}'), \quad \sigma = \alpha, \beta,$$

with Hermitean matrices (35):

$$\mathbf{H}^\alpha = [H_{ij}^\alpha] = [\langle i | h_1^\alpha | j \rangle], \quad \langle i | h_1^\alpha | j \rangle \equiv \left(\frac{\partial E}{\partial P_{ij}^\alpha} \right)_{\gamma_1 = \tilde{\gamma}_1}; \quad (35a)$$

$$\mathbf{H}^\beta = [H_{ij}^\beta] = [\langle i | h_1^\beta | j \rangle], \quad \langle i | h_1^\beta | j \rangle \equiv \left(\frac{\partial E}{\partial P_{ij}^\beta} \right)_{\gamma_1 = \tilde{\gamma}_1}. \quad (35b)$$

The conditions for N -representability of γ_1 by an ensemble are written as follows [24, 31]:

$$0 \leq f_i^\sigma \leq 1, \quad i = 1, \dots, n, \quad \sigma = \alpha, \beta. \quad (36)$$

In addition, normalization requirement (37) and spin purity condition (38) must be set:

$$tr(\rho_1^{\alpha\alpha}) + tr(\rho_1^{\beta\beta}) = N; \quad (37)$$

$$tr(\rho_1^{\alpha\alpha}) - tr(\rho_1^{\beta\beta}) = 2M. \quad (38)$$

Constraint (38) follows from Eq. (25b), and it is necessary for the spin projection value (M) to remain constant upon variation. It should be noted that this constraint was not taken into account by Donnelly and Parr [15]; therefore, the Euler–Lagrange equation obtained by these authors and expressed through γ_1 itself is applicable only to systems with closed shells, for which constraint (38) becomes redundant.

In keeping with [15], let us suppose that all eigenvalues of the 1-matrix $\tilde{\gamma}_1$ corresponding to the minimum of $E_{\text{DP}}^n[\gamma_1]$ are fractional, i.e., they belong to open interval $(0, 1)$. This unproved but quite reasonable assumption becomes very important in the Donnelly–Parr theory [15–17]. First, it ensures the existence of a continuously differentiable function of matrix elements of the operators ρ_1^α and ρ_1^β at the minimum point. Second, it provides the possibility for deducing Euler–Lagrange equations without taking into account constraints (36); the latter should be met by themselves if $E_{\text{DP}}^n[\gamma_1]$ has a minimum on the set N_N . By applying normalization requirement (37) with the Lagrange multiplier μ (which is equated to the electron CP of the ground state of a system) and spin purity condition (38) with the Lagrange multiplier λ (which makes no physical sense in the framework of the density functional theory), we obtain Euler–Lagrange equations (39):

$$h^\alpha \chi^\alpha(\mathbf{r}) = \mu^\alpha \chi^\alpha(\mathbf{r}), \quad \forall \chi^\alpha(\mathbf{r}) \in E_n; \quad (39a)$$

$$h^\beta \chi^\beta(\mathbf{r}) = \mu^\beta \chi^\beta(\mathbf{r}), \quad \forall \chi^\beta(\mathbf{r}) \in E_n. \quad (39b)$$

Here,

$$\mu = 1/2(\mu^\alpha + \mu^\beta), \quad \lambda = 1/2(\mu^\alpha - \mu^\beta).$$

Equations (39) directly follow from the matrix equations

$$\mathbf{H}^\sigma = \mu^\sigma \mathbf{I}, \quad I_{ij} = \delta_{ij}, \quad \sigma = \alpha, \beta, \quad (40)$$

which were derived from the condition

$$\delta \Omega(\mathbf{P}^\alpha, \mathbf{P}^\beta) = \sum_{\sigma} \sum_{k,l} \frac{\partial \Omega}{\partial P_{kl}^\sigma} \delta P_{kl}^\sigma = 0, \quad \sigma = \alpha, \beta,$$

for the auxiliary function

$$\begin{aligned} \Omega(\mathbf{P}^\alpha, \mathbf{P}^\beta) = & E_{\text{DP}}^n(\mathbf{P}^\alpha, \mathbf{P}^\beta) + \mu \left(N - \sum_{k,l} (P_{kl}^\alpha + P_{kl}^\beta) \langle l | k \rangle \right) \\ & + \lambda \left(2M - \sum_{k,l} (P_{kl}^\alpha - P_{kl}^\beta) \langle l | k \rangle \right). \end{aligned}$$

Each of the matrices \mathbf{H}^α and \mathbf{H}^β is a function of \mathbf{P}^α and \mathbf{P}^β ; the optimal \mathbf{P}^α and \mathbf{P}^β (which correspond

to $\gamma_1 = \tilde{\gamma}_1$) satisfy Eqs. (40). Thus variational problem (32) is reduced to iterative solution of two matrix equations (40) with respect to \mathbf{P}^α and \mathbf{P}^β . Canonical orbitals of an open-shell system are defined by the following equations:

$$(h^\alpha \rho_1^\alpha) \phi_i^\alpha(\mathbf{r}) = \varepsilon_i^\alpha \phi_i^\alpha(\mathbf{r}), \quad \varepsilon_i^\alpha = \mu^\alpha f_i^\alpha, \quad i = 1, \dots, n;$$

$$(h^\beta \rho_1^\beta) \phi_i^\beta(\mathbf{r}) = \varepsilon_i^\beta \phi_i^\beta(\mathbf{r}), \quad \varepsilon_i^\beta = \mu^\beta f_i^\beta, \quad i = 1, \dots, n.$$

These equations should be regarded as extension of Eqs. (5) obtained by Donnelly and Parr [15] for the case of spin compensation. By identifying degenerate eigenvalues of the operators h^α and h^β with the orbital electron CPs μ_1^α and μ_1^β , respectively, Eq. (6) may be rewritten as

$$\mu_i^\sigma \equiv \frac{\partial E}{\partial f_i^\sigma} \equiv \mu^\sigma, \quad i = 1, \dots, n, \quad \sigma = \alpha, \beta. \quad (41)$$

Expression (41) demonstrates leveling of the orbital electron CPs within each spin subsystem. From the viewpoint of thermodynamics, Eqs. (41) seem to be at least surprising, for it is not clear why there is no equilibrium between the α - and β -electron subsystems. It is also unclear how can Eqs. (41) be coordinated with the concept of group EN, which is based on the principle of leveling of CPs of orbitals forming covalent bonds between atoms [3].

In the case of spin compensation, the spin components of the 1-matrix γ_1 identically coincide with each other; therefore, the Donnelly–Parr energy functional for closed-shell systems is a function of the matrix \mathbf{P} which is a one-electron density operator ρ_1 with the kernel

$$\rho_1(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^n \sum_{j=1}^n P_{ij} \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}')$$

normalized with respect to the number of electrons N . In this case, the Euler–Lagrange equation looks as follows:

$$h \chi(\mathbf{r}) = \mu \chi(\mathbf{r}), \quad \forall \chi(\mathbf{r}) \in E_n, \quad h \in E_n, \quad (42)$$

where h is a Hermitean operator with the matrix

$$\mathbf{H} = [H_{ij}] = [\langle i | h | j \rangle], \quad \langle i | h | j \rangle \equiv \left(\frac{\partial E}{\partial P_{ij}} \right)_{\gamma_1 = \tilde{\gamma}_1},$$

and μ is the electron CP. Obviously, in the case of spin compensation $h = h^\alpha = h^\beta$ and $\mu = \mu^\alpha = \mu^\beta$. The operator h matrix fits the equation

$$\mathbf{H} = \mu \mathbf{I}, \quad (43)$$

from which optimal \mathbf{P} and electron CP of a system can be determined. Canonical orbitals of a closed-shell system are defined by Eqs. (5).

Determination of the optimal matrix \mathbf{P} and Lagrange multipliers in different approximations.

In this section we consider only closed-shell systems. In the simplest case, the main problem of the Donnelly–Parr theory is reduced to determination of such universal relationship between the 2- and 1-matrices $\rho_2(\mathbf{r}_1; \mathbf{r}_2)$ and $\rho_1(\mathbf{r}; \mathbf{r}')$ of the ground state which would give rise to a reasonable parametrization of two-electron interactions in the system. An analogous problem is solved in terms of the approximate density functional theory which was formulated first for heterogeneous electron gas [13]. Insofar as the density function $\rho(\mathbf{r})$ is a diagonal part of the 1-matrix $\rho_1(\mathbf{r}; \mathbf{r}')$, all energy functionals developed in the framework of the approach described in [13] can be regarded as approximate representations of the Donnelly–Parr functional for systems with closed shells. For instance, in the local density approximation,

$$Q_{\text{DP}}[\rho_1] = \int f(\mathbf{r}, \rho) \rho(\mathbf{r}) \delta \mathbf{r}, \quad (44)$$

where $f(\mathbf{r}, \rho)$ is a function of \mathbf{r} and $\rho(\mathbf{r}) = \rho_1(\mathbf{r}; \mathbf{r})$. Nonlocal approximation (45) is an obvious extension of Eq. (44), which can be used in terms of the density matrix functional theory:

$$Q_{\text{DP}}[\rho_1] = \int \partial \mathbf{r}_2 \int f(\mathbf{r}_1, \mathbf{r}_2, \rho_1) \rho_1(\mathbf{r}_1, \mathbf{r}_2) \delta \mathbf{r}_1. \quad (45)$$

Here, $f(\mathbf{r}_1, \mathbf{r}_2, \rho_1)$ is a function of \mathbf{r}_1 , \mathbf{r}_2 , and $\rho_1(\mathbf{r}_1; \mathbf{r}_2)$. In this section we consider Euler–Lagrange equations for Donnelly–Parr energy functions in the local density approximation (44) and in the Hartree–Fock approximation which is a particular case of nonlocal approximation (45). According to the local density approximation, the energy functional may be given as follows:

$$E = \int_{\mathbf{r}_1=\mathbf{r}_1} f \rho_1(\mathbf{r}_1, \mathbf{r}_1') \delta \mathbf{r}_1; \\ f = -\frac{1}{2} \nabla_1^2 + v(\mathbf{r}_1) + \frac{1}{2} \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta \mathbf{r}_2 + \varepsilon_{\text{xc}}(\rho).$$

The latter term in the expression for one-electron Hermitean operator f is the exchange–correlation energy per electron [32–34]. Using the atomic orbital basis

$$\varphi_k(\mathbf{r}) = \sum_{i=1}^n S_{ik}^{-1/2} \chi_i(\mathbf{r})$$

orthogonalized by symmetrization we obtain matrix representation of the energy functional [Eq. (46)].

$$E = \sum_{k,l}^n P_{kl} \left[\langle k | -\frac{1}{2} \nabla_1^2 + v(\mathbf{r}) + \varepsilon_{\text{xc}}(\rho) | l \rangle + \frac{1}{2} \sum_{i,j}^n P_{ij} \langle ki | lj \rangle \right], \quad (46)$$

$$\langle ki | lj \rangle = \iint \varphi_k^*(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_l(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \delta \mathbf{r}_1 \delta \mathbf{r}_2.$$

Thus matrix representation makes the energy functional a function of matrix elements P_{kl} . Differentiation of Eq. (46) with respect to P_{kl} gives matrix \mathbf{H} in Eq. (43) with the elements defined by Eq. (47):

$$H_{kl} = \langle k | -\frac{1}{2} \nabla_1^2 + v(\mathbf{r}) + \varepsilon_{\text{xc}}(\rho) | l \rangle + \sum_{i,j}^n P_{ij} \left[\langle ki | lj \rangle + \langle ki | \frac{\partial \varepsilon_{\text{xc}}}{\partial \rho} | lj \rangle \right], \quad (47)$$

$$\langle ki | \frac{\partial \varepsilon_{\text{xc}}}{\partial \rho} | lj \rangle = \int \varphi_k^*(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_1) \frac{\partial \varepsilon_{\text{xc}}}{\partial \rho} \varphi_l(\mathbf{r}_1) \varphi_j(\mathbf{r}_1) \delta \mathbf{r}_1.$$

Hence the Donnelly–Parr operator h in the local density approximation is determined by Eq. (48):

$$h = -\frac{1}{2} \nabla_1^2 + v(\mathbf{r}_1) + \varepsilon_{\text{xc}}(\rho) + \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta \mathbf{r}_2 + \rho(\mathbf{r}_1) \frac{\partial \varepsilon_{\text{xc}}(\rho)}{\partial \rho(\mathbf{r}_1)}. \quad (48)$$

When expressed through optimal $\rho(\mathbf{r})$, this operator fits Eq. (42), i.e., it has a single eigenvalue equal to μ . The energy functional with the Hartree–Fock exchange energy may be written as follows:

$$E = \int_{\mathbf{r}_1=\mathbf{r}_1} -\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1; \mathbf{r}_1') \delta \mathbf{r}_1 + \int v(\mathbf{r}_1) \rho(\mathbf{r}_1) \delta \mathbf{r}_1 + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta \mathbf{r}_1 \delta \mathbf{r}_2 - \frac{1}{2} \iint \frac{\rho_1(\mathbf{r}_1; \mathbf{r}_2) \rho_1(\mathbf{r}_2; \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta \mathbf{r}_1 \delta \mathbf{r}_2.$$

In the matrix representation, the energy is given by expression (49):

$$E = \sum_{k,l}^n P_{kl} \left[\langle k | -\frac{1}{2} \nabla^2 + v(\mathbf{r}) | l \rangle + \frac{1}{2} \sum_{i,j}^n P_{ij} \langle ki | lj \rangle - \frac{1}{4} \sum_{i,j}^n P_{ij} \langle ki | jl \rangle \right]. \quad (49)$$

Then, the matrix \mathbf{H} in Eq. (43) consists of elements (50) and is a matrix of nonlocal operator (51):

$$H_{kl} = \langle k | -\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) | l \rangle + \sum_{i,j}^n P_{ij} \left[\langle ki | lj \rangle - \frac{1}{2} \langle ki | jl \rangle \right]; \quad (50)$$

$$h\varphi(\mathbf{r}_1) = \left[-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) + \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta\mathbf{r}_2 \right] \varphi(\mathbf{r}_1) - \frac{1}{2} \int \frac{\rho_1(\mathbf{r}_1; \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi(\mathbf{r}_2) \delta\mathbf{r}_2. \quad (51)$$

Operator (51) expressed through optimal $\rho_1(\mathbf{r}; \mathbf{r}')$ fits Eq. (42), i.e., it has a single eigenvalue equal to μ .

Taking into account that operators (48) and (51) in different bases identically coincide with each other, i.e., they are invariant with respect to basis transformations, Eq. (43) for the basis of nonorthogonal atomic orbitals $\chi_k(\mathbf{r})$ may be written as

$$\mathbf{H} = \mu \mathbf{S}, \quad S_{kl} = \langle k | l \rangle. \quad (52)$$

Using Eq. (52) with the matrices \mathbf{H} defined by Eqs. (47) and (50), we can formulate an algorithm for simultaneous determination of the optimal matrix \mathbf{P} in the atomic orbital basis $\chi_k(\mathbf{r})$ and the Lagrange multiplier μ . In the local density approximation, Eq. (52) supplemented by the normalization requirement with respect to ρ_1 can be regarded as a linear system of $n^2 + 1$ equations

$$\sum_{i,j}^n \left[\langle ki | lj \rangle + \langle ki | \frac{\partial \varepsilon_{xc}}{\partial \rho} | lj \rangle \right] P_{ij} - S_{kl} \mu = \langle k | -\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) + \varepsilon_{xc}(\rho) | l \rangle, \quad k, l = 1, \dots, n; \quad (53a)$$

$$\sum_{i,j}^n S_{ij} P_{ij} = N \quad (53b)$$

with $n^2 + 1$ indeterminates (elements of P_{ij} and μ). It remains only to verify whether this system can be solved with respect to a set of symmetric positively defined density matrices. The symmetry conditions may be applied by assuming $P_{ij} = P_{ji}$ and reducing system (53) to linear equation system (54):

$$\sum_{i \leq j}^n A_{kl,ij} P_{ij} - S_{kl} \mu = -B_{kl}, \quad k \leq l = 1, \dots, n; \quad (54a)$$

$$\sum_{i \leq j}^n (2 - \delta_{ij}) S_{ij} P_{ij} = N. \quad (54b)$$

The coefficients $A_{kl,ij}$ and B_{kl} , which constitute an $[m \times m]$ -dimensional matrix \mathbf{A} and an m -dimensional

column \mathbf{B} with $m = n(n+1)/2$, are determined by the following expressions:

$$A_{kl,ij} = (2 - \delta_{ij}) \left[\langle ki | lj \rangle + \langle ki | \frac{\partial \varepsilon_{xc}}{\partial \rho} | lj \rangle \right];$$

$$B_{kl} = \langle k | -\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) + \varepsilon_{xc}(\rho) | l \rangle.$$

In the Hartree–Fock approximation, system (54) has the following coefficients:

$$A_{kl,ij} = \left[\langle ki | lj \rangle - \frac{1}{2} \langle ki | jl \rangle \right] + (1 - \delta_{ij}) \left[\langle kj | li \rangle - \frac{1}{2} \langle kj | il \rangle \right];$$

$$B_{kl} = \langle k | -\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) | l \rangle.$$

System (54) is a linear system of $m + 1$ equations for determination of m unknown elements P_{ij} ($i \leq j$) and μ . Solutions of this system (if exist) belong to a set of real symmetric density matrices, where positively defined density matrix constitutes a subset. System (54) can be solved by numerical methods. In the local density approximation, the matrix \mathbf{A} and the column \mathbf{B} depend on the density function, and system (54) is solved iteratively:

(1) The original density matrix is determined by the formula

$$\mathbf{P} = \mathbf{T} \mathbf{\Lambda} \mathbf{T}',$$

where matrix \mathbf{T} is an $[n \times n]$ -dimensional matrix for transformation of real basis functions to the Kohn–Sham orbitals [14, 35], and diagonal matrix $\mathbf{\Lambda}$ is a matrix consisting of the occupation numbers of the Kohn–Sham orbitals. The choice of matrix $\mathbf{\Lambda}$ is fairly arbitrary. We considered two versions of determination of $\mathbf{\Lambda}$: (a) the original density matrix was calculated with $\mathbf{\Lambda}$ corresponding to the Kohn–Sham one-determinant wave function and (b) all elements of $\mathbf{\Lambda}$ were set equal to N/n . We obtained a test matrix ρ_1 whose eigenvalues belong to the open interval $(0, 2)$.

(2) The coefficients $A_{kl,ij}$ and B_{kl} are calculated with the original density function.

(3) By solving system (54), a new density matrix and μ are found. The coefficients $A_{kl,ij}$ and B_{kl} and H_{kl} are then calculated with the new density function.

(4) The iteration is terminated when the inequality

$$\frac{1}{m-1} \sum_{k \neq l}^n \left(\frac{H_{kl}}{S_{kl}} - \mu \right)^2 < \delta$$

is fulfilled. Otherwise, we turn back to step (3). The proposed algorithm was applied in the framework of the zero two-atom differential overlap approximation on the basis of MOPAC 6.0 semiempirical quantum-chemical program [36], which was supplemented by the Kohn–Sham calculation procedure [14, 35] in the local density approximation [34]. While selecting numerical integrating network for the exchange–correlation part of the Kohn–Sham matrix, we followed the recommendations given in [37]. According to these recommendations, the molecular integrant was divided into atomic contributions by the Becke scheme [38]; for spherical and radial integration of each contribution we used, respectively, improved [37] Lebedev’s network with 434 nodes necessary for precise integration of all spherical harmonics of an order of 35 ($l \leq 35$) and second-genus Chebyshev’s quadrature in combination with M4 mapping (see [37]) onto the standard finite interval ($a = 1$, $\alpha = 0.6$; values of ξ were taken from Table 1 in [37]) with 35 (H, He), 40 (Li–Ne), 45 (Na–Ar), and 50 (K–Kr) radial points. This quadrature ensures an error not exceeding 10^{-8} in the integration of density functions. In the calculations we used molecular geometric parameters optimized by the original version of MOPAC 6.0. The density matrix elements and the Lagrange multiplier μ for one or another molecule were determined in the local density and Hartree–Fock approximation through pseudoinversion of the $[m+1 \times m+1]$ -dimensional matrix of system (54) via singular decomposition [39]. In each case, the only solution was obtained.

The results of calculations for some molecules are presented in table, where E_{HF} and E_{LDA} stand for the electron energies calculated in the zero two-atom differential overlap with the Fock operator and with the Kohn–Sham operator, respectively. The Lagrange multipliers μ and the occupation numbers of natural orbitals, determined in terms of each of the above two approximations, correspond to solutions of system (54). It is seen that some occupation numbers of final 1-matrices ρ_1 have negative values. In other words, in all cases the final density matrix \mathbf{P} is not a positively defined matrix.

Results and discussion. As we already noted in the first section of this paper, the Donnelly–Parr theory is based on the assumption that there exists a universal Q_{DP} functional which fits Eq. (31). The authors gave no indications as to how such a functional can be found. We thought it reasonable to

emphasize once more that the Donnelly–Parr variational principle (32) may be used only when Eq. (31) is fulfilled for any N -representable 1-matrix (by an ensemble) belonging to the range of variation of γ_1 . The latter statement cannot be proved rigorously, and its validity seems to be fairly doubtful. However, it is also impossible to prove that this statement is invalid. Thus the problem concerning the existence of a precise universal functional $Q_{\text{DP}}[\gamma_1]$ remains open.

In this situation, the left part of Eq. (31) should be regarded as unrepresentable by a functional from 1-matrix unless the reverse has been proved. In other words, we believe that any conceivable algebraic form of $Q_{\text{DP}}[\gamma_1]$ is only an approximation of precise energy functional (26). Obviously, the use of approximate functionals in the two-step variational procedure (30) leads to violation of functional N -representability, so that Eq. (15) could not be fulfilled. This means that such a procedure can no longer be regarded as variational, and the calculated energy may be below the precise value [20]. Moreover, one cannot rule out that the functional has no minimum at all in the set of N -representable 1-matrices, regardless of the $Q_{\text{DP}}[\gamma_1]$ used. The probability for such situation may be estimated from the results of our calculations. However, final answer to this question cannot be obtained, for the number of possible $Q_{\text{DP}}[\gamma_1]$ representations is infinite.

It should be emphasized that no acceptable expression for $Q_{\text{DP}}[\gamma_1]$ has been developed as yet, i.e., the validity of Eqs. (5) and (6) has not been proved. Therefore, physical extensions of the Donnelly–Parr theory should be treated with much care. This concerns mainly the concept of orbital CP leveling and the Sanderson principle of leveling of atom ENs, which cannot be substantiated at present in terms of the density functional theory.

To conclude, let us consider briefly possible ways of estimating the electron CP in terms of the density functional theory. First of all we should note the strict variational procedure described in [40–42], according to which electron CP is defined as the Lagrange multiplier at the normalization requirement to the density functions; it can be calculated together with the ground-state density function of a system. Unfortunately, this rigorous theory utilizes extremely complex equations which can be solved only for the simplest atoms [43, 44]. Up to now, all practical calculations of the electronic structure of atoms, molecules, and radicals in terms of the density functional theory are performed by the Kohn–Sham procedure [14, 35]. It is based on the assumption that the ground-state density function of a real system is equal

Results of ZDO calculations

Molecule	E_{LDA}	E_{HF}	μ_{LDA}	μ_{HF}	Occupation numbers in LDA	Occupation numbers in HF
H ₂ O	-514.58	-500.51	36.00	-77.83	-202.89, -59.38, -2.17, 8.32, 88.23, 175.89	-63.78, -14.54, -10.29, 29.33, 30.67, 36.61
H ₂ S	-374.04	-372.03	-9.53	-39.83	-150.62, -9.81, 0.3, 3.31, 79.75, 85.07	-88.82, -27.06, -12.75, 32.22, 52.01, 52.4
H ₃ N	-447.49	-438.08	34.36	-12.27	-216.78, -35.6, -35.6, 4.69, 77.43, 77.43, 136.43	-3.14, 0.69, 0.77, 0.77, 2.96, 2.96, 2.99
H ₃ P	-350.22	-347.12	-9.44	-9.50	-175.36, -0.24, -0.24, 1.44, 28.38, 77.01, 77.01	-2.64, 0.63, 0.63, 0.95, 2.77, 2.83, 2.83

to that of an imaginary system of noninteracting electrons which move in the effective potential field. In the framework of this approach, the ground-state density function of an N -electron system is determined through variation of the form of N one-electron spin-orbitals which met the orthonormality condition (the occupation numbers of spin-orbitals are fixed and are equal to 0 or 1, which ensures N -representability of test density functions). Provided that the orthonormality of spin-orbitals is retained, the stationary condition for the energy functional is ensured by solving N orbital equations. It follows from the above stated that, in terms of the Kohn–Sham procedure, electron CP of a system is not used as Lagrange multiplier and that its identification with eigenvalue of N th orbital [45] is at least questionable [46–50]. Therefore, the calculation of electron CP by interpolation formula (2) still remains the only way to estimate this quantity.

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