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Differential equations for the square root of the electronic density in symmetry-constrained density-functional theory

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A family of equations for the (square root of the) electronic density is constructed and analyzed within the context of density-functional theory.

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INTRODUCTION

Density-functional theory [1], in a form useful for the study of the electronic structure of atoms, molecules, and condensed matter, can be systematically derived and formulated avoiding both practical and formal inconsistencies, even beyond the limitations imposed by working at a Hartree-Fock-like level. Usually the theory is developed, after considering the properties of the density operators, with particular emphasis on three aspects as follows: (a) definitions and existence theorems, (b) rules for constructing density functionals, and (c) methodology.

The traditional presentation of density-functional theory states first that there is a unique functional to compute the total energy for a system with N electrons interacting with an external potential $v(\mathbf{r})$ (in their ground state) [2],

$$E[v,\gamma]=E_v[\gamma]=F[\gamma]+\int v(\mathbf{r})\gamma(\mathbf{r},\mathbf{r})d\mathbf{r} , \tag{1}$$

where γ is the reduced first-order density operator, and $F[\gamma]$ is defined:

$$F[\gamma]=T[\gamma]+V_{e\text{-}e}[\gamma] . \tag{2}$$

$T[\gamma]$ is the kinetic-energy functional and $V_{e\text{-}e}[\gamma]$ is the total electron-electron interaction energy. Both functionals are well defined but unknown. The one density γ can be written within the one-particle approximation, considering that for each particle of the system there is at least one auxiliary function ψ_i, such that [3]

$$\gamma(\mathbf{r},\mathbf{r})=\sum_i n_i|\psi_i(\mathbf{r})\rangle\langle\psi_i(\mathbf{r}')| . \tag{3}$$

In this approximation the total number of electrons can also be expressed as a density functional

$$N=N[\gamma]=\int\gamma(\mathbf{r},\mathbf{r})d\mathbf{r} \tag{4}$$

using the diagonal part of γ.

On the other hand, the second Hohenberg-Kohn theorem states that for whatever other approximated electron density $\gamma'(\mathbf{r})$ the energy functional obeys the following inequality for the exact ground-state density:

$$E_v[\gamma']\geq E_v[\gamma] . \tag{5}$$

A variational procedure can then be proposed to find both γ and E

$$\delta\left[E_v[\gamma]-\mu\left(\int\gamma(\mathbf{r})d\mathbf{r}-N\right)\right]=0 , \tag{6}$$

where μ is a Lagrange multiplier associated with the restriction of having N particles in the system. It has been argued (Parr *et al.* [4]) that this constraint is enough for the development and use of the theory, but recent evidence indicates that other constraints are needed [5].

We can illustrate the use of further constraints with an expression proposed by Keller and Ludeña for the variation function G including auxiliary Lagrange multipliers (μ and the matrix α')

$$G(\Gamma^n)=\mathrm{Tr}(H_0\Gamma^n)-\mu[\mathrm{Tr}(\Gamma^n)-1]-\mathrm{Tr}[\alpha'(L_n^1\Gamma^n-\gamma)] . \tag{7}$$

Here Γ^n is the density-matrix operator, H_0 is the total Hamiltonian operator, that is (in rydberg units),

$$H_0=\hat{T}+\hat{V}_{e\text{-}e}=\sum_i\left[-\nabla_i^2+\sum_{j>i}\frac{2}{r_{ij}}\right] . \tag{8}$$

The last term on the right-hand side of (7) represents the restriction to correctly projecting the density matrix on the one matrix, that is,

$$L_n^1\Gamma^n\rightarrow\gamma(\mathbf{r},\mathbf{r}') ; \tag{9}$$

this we will call a symmetry constraint and the resulting theory a "symmetry-constrained density-functional theory." This last term on the right-hand side of (7) is then added to warrant the first-order matrix being obtained within the set of matrices that will map onto the full density matrix.

$$\Gamma^n\in(L_n^1)^{-1}\gamma(\mathbf{r},\mathbf{r}') . \tag{10}$$

The two constraints that have been introduced in (7) are related to the following two important restrictions: first, the conservation of the total number of particles of the system, the same as in Eq. (6); and, second, the conservation of the internal symmetry of the system, which can be, for example, described by a given shell structure of the electronic cloud.

The first constraint is well known and widely used, whereas the second is only implicitly used or appears explicitly as a part of the methodology (the best known and more widely used example is the so-called Kohn-Sham procedure) where a full set of stationary states can be obtained; however, for stationary states other than the ground state, we do not know how useful it will be to use the exchange-correlation terms as equal to the terms of the ground-state theory. Within the Kohn-sham methodology an ansatz is made so that the one density can be written as in Eq. (3), where the occupation numbers n_i are either fixed beforehand or given in such a way that the total energy is minimized for a given external potential and for a given approximation of the exchange-correlation part of the total electronic energy.

The Kohn-Sham equations are then obtained from (6) if the kinetic-energy contribution to $E_v[\gamma]$ is written with the auxiliary functional

$$\begin{aligned} T[\gamma] &= \int \sum_i n_i [-\nabla^2_{r'}\gamma(\mathbf{r},\mathbf{r}')|_{r\to r'}]d\tau \\ &= \int k(\mathbf{r})\rho(\mathbf{r})d\tau \end{aligned} \tag{11}$$

to obtain the well-known Kohn-Sham equations

$$\hat{h}\psi_i = -\nabla^2\psi_i + V\psi_i + V_{\text{eff}}\psi_i = \varepsilon_i\psi_i \ . \tag{12}$$

As we said above, the internal symmetry of the system within this procedure consists in assigning a set of $\{n_i\}$, which in general are taken to be integers, either 0 or 1.

We can use this idea to include the internal symmetry in the density functional itself. We have discussed this problem before [6,7], stating that "the formal structure of density-functional theory . . . should be stated in at least three theorems.

(1) The total energy of the system, in any stationary state, is a unique functional of its particle density.

(2) There exists a variational principle for the energy functional of a stationary state of the system.

(3) The internal symmetry of the system, through a set of parameters $\{n_{i,N}\}$, is a necessary part of the theory. The variational equations should read

$$\delta\left[E[\{n_{i,N}\}] - \mu\left[\int \rho[\{n_{i,N}\}]dt - N\right]\right] = 0 \ ,$$

and the parameters $n_{i,N}$ included either in the construction of the density function (as in the Kohn-Sham procedure) or in the energy functional itself."

Here we will use the second proposition of Keller's theorem; 3, that is, we will include the occupation parameters or their equivalents in the construction of the energy functional itself. This procedure will allow us to construct an equation for the square root of the electronic density $\rho(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r})$.

EQUATION FOR THE SQUARE ROOT OF ELECTRONIC DENSITY AND CHEMICAL POTENTIAL

Levy, Perdew, and Sahni proposed that within the spirit of density-functional theory, there should exist an eigenvalue equation for the square root of electronic density [8], that is,

$$h_{\text{eff}}\rho^{1/2}(\mathbf{r}) = \mu\rho^{1/2}(\mathbf{r}) \ , \tag{13}$$

where the Hamiltonian h_{eff} is given by the expression,

$$h_{\text{eff}} = -\nabla^2 + v(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}) \ . \tag{14}$$

If $v_{\text{eff}}(\mathbf{r})$ could be properly modeled, it could simplify the methodology of obtaining electronic density, using only two self-consistent equations instead of $N+1$ self-consistent equations as in the Kohn-Sham methodology. One could adapt a Kohn-Sham program [for atoms, as an example, solve for a 1s-like orbital to obtain $\rho^{1/2}(\mathbf{r})$, or for solids systems $\rho^{1/2}(\mathbf{r})$ would satisfy $\mathbf{k}=0$]. Levy and Ou-Yang [9] further discuss how to construct Eq. (13).

Here we will also consider the approximation for the kinetic energy,

$$T_s[\rho] = \int \rho^{1/2}(\mathbf{r})(-\nabla^2)\rho^{1/2}(\mathbf{r}) + T_\theta[\rho] \ , \tag{15}$$

where $T_s[\rho]$ is the kinetic-energy functional for noninteracting particles. $T_\theta[\rho]$ is the correction due to the fact that the first term, a functional using the square root of the density, may not be enough to represent all the kinetic energy, and in our case, may not be enough for the introduction of some of the shell-structure effects. Equation (15) is introduced into the variational procedure, that is,

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} = -\frac{\nabla^2\rho^{1/2}}{\rho^{1/2}} + v_\theta([\rho];\mathbf{r}) + V_{\text{SS}}([\rho];\mathbf{r}) \ , \tag{16}$$

with the variation of $T_\theta[\rho]$,

$$v_\theta([\rho];\mathbf{r}) + V_{\text{SS}}([\rho];\mathbf{r}) = \frac{\delta T_\theta[\rho]}{\delta\rho(\mathbf{r})} \ . \tag{17}$$

If we make a Euler-Lagrange variation for the Kohn-Sham (KS) energy functional we should obtain a functional for the chemical potential,

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + v_{\text{KS}}([\rho];\mathbf{r}) = \varepsilon_M \ . \tag{18}$$

Equations (16)–(18) result in the desired equation

$$\begin{aligned} &-\nabla^2\rho^{1/2} + v_{\text{KS}}([\rho];\mathbf{r})\rho^{1/2} \\ &\qquad + \{v_\theta([\rho];\mathbf{r}) + V_{\text{SS}}([\rho];\mathbf{r})\}\rho^{1/2} = \mu\rho^{1/2} \ . \end{aligned} \tag{19}$$

In (19), there is an effective potential $v_\theta(\mathbf{r}) + V_{\text{SS}}(\mathbf{r})$, which should contain all the information related to the system's structure and the uncertainty principle, and from these considerations it is named the Pauli potential [10].

As discussed above, to obtain a realistic density with (13) we have to define an effective potential that includes the effect of the internal symmetry (shell structure). The possibility discussed below is to define a shell-structure-dependent energy correction

$$\Delta\bar{\varepsilon}(\mathbf{r})\rho(\mathbf{r}) = \sum_i \varepsilon_i|\psi_i(\mathbf{r})|^2 - \bar{\varepsilon}\rho(\mathbf{r}) \ , \tag{20}$$

where $N\bar{\varepsilon} = \sum_i n_i\varepsilon_i$ corresponds to the sum of the Lagrange multipliers ε_i, in the Kohn-Sham procedure, which are associated with each auxiliary function ψ_i.

Then $\Delta\bar{\varepsilon}(\mathbf{r})$ represents the effect of the shell structure of the effective potential, and can be taken as an approximation to $V_{\mathrm{SS}}(\mathbf{r})$ obtained by construction.

We could have written a functional

$$\Omega=E[\rho]-\mu\left[\int\rho(\mathbf{r})d\mathbf{r}-N\right] -\lambda\left[\int\sum_i\varepsilon_i|\psi_i(\mathbf{r})|^2d\mathbf{r}-\int\bar{\varepsilon}\rho(\mathbf{r})d\mathbf{r}\right] , \tag{21}$$

with λ a new Lagrange multiplier associated with the shell structure imposed as an internal symmetry (to be taken as $\lambda=1$ below from our method of construction considerations), performed a variation with respect to $[\rho^{1/2}(\mathbf{r})]^*$, and written the kinetic energy as in (19) above.

Let us now find a valid equation for $\rho^{1/2}$. We can start from the well-known Kohn-Sham equations

$$-\nabla^2\phi_i+[v_{\mathrm{xc}}(\mathbf{r})+v_{\mathrm{Coul}}(\mathbf{r})+v_{\mathrm{ext}}(\mathbf{r})]\phi_i=\varepsilon_i\phi_i \ . \tag{22}$$

As usual, $v_{\mathrm{xc}}(\mathbf{r})$ is a local exchange-correlation potential and v_{Coul} is the Coulombic potential produced by all the electrons. If we multiply (22) by ϕ_i^* on the left and sum over the one-electron-state index, the resulting expression is

$$\sum_i h_i(\mathbf{r})^{\mathrm{KS}}=\sum_i\varepsilon_i|\phi_i|^2 \ , \tag{23}$$

where we have introduced

$$h_i(\mathbf{r})^{\mathrm{KS}}=-\phi_i^*\nabla^2\phi_i+\phi_i^*[v_{\mathrm{xc}}(\mathbf{r})+v_{\mathrm{Coul}}(\mathbf{r})+v_{\mathrm{ext}}(\mathbf{r})]\phi_i \ . \tag{24}$$

We can then add, both on the right and on the left, the two terms $(1/N)\sum\varepsilon_i\rho^{1/2}$ and $-\nabla^2\rho^{1/2}$, where N is again the total particle number, to obtain, cancelling $\rho^{1/2}$ on both sides, the equation

$$-\nabla^2\rho^{1/2}+v^{\mathrm{FK}}(\mathbf{r})\rho^{1/2}=\bar{\varepsilon}\rho^{1/2} \tag{25}$$

(where again $\bar{\varepsilon}$ is the sum of the KS Lagrange multipliers divided by N), and the effective potential

$$v^{\mathrm{FK}}(\mathbf{r})=v_{\mathrm{xc}}(\mathbf{r})+v_{\mathrm{Coul}}(\mathbf{r})+v_{\mathrm{ext}}(\mathbf{r}) +\rho^{-1/2}\nabla^2\rho^{1/2}+k(\mathbf{r})-\Delta\bar{\varepsilon}(\mathbf{r}) \ . \tag{26}$$

In the effective potential appear $k(\mathbf{r})$ and $\Delta\varepsilon(\mathbf{r})$ [see Eqs. (11) and (20)]. These terms contain the proposed KS structure constraint. In particular, we have introduced a new term in the effective potential, the symmetry-constraint potential $\Delta\bar{\varepsilon}$

$$\Delta\bar{\varepsilon}(\mathbf{r})=\sum n_i\varepsilon_i|\phi_i(\mathbf{r})|^2/\rho(\mathbf{r})-\bar{\varepsilon} \ . \tag{27}$$

The procedure we have followed, a summation over Kohn-Sham equations, has been used before to obtain relations for the kinetic energy within density-functional theory, see Bartolotti and Acharya [11]. The possibility of using this procedure to obtain an equation for the square root of the density has been proposed by Levy and Ou-Yang [9]. A term similar to (27) is shown and discussed in those articles. The energy $\bar{\varepsilon}$ can be replaced by other characteristic energies.

This construction procedure, an algebraic sum, can be directly derived from a variational principle starting from (21), when an adequate constraint from our theorem 3 is introduced. Then, behind the construction, there is always the variational principle supporting the Kohn-Sham equations.

We could use Thomas-Fermi theory or similar considerations to approximate these two terms, instead of using, as we have here, the results of the Slater-Gaspar-Kohn-Sham procedure. The results will change with the chosen starting point for the use of density-functional theory.

To show the usefulness of Eq. (25), we have integrated this expression using the KS $\rho(\mathbf{r})^{1/2}$,

$$\int\rho^{1/2}(-\nabla^2\rho^{1/2})d\mathbf{r}+\int\rho^{1/2}v^{\mathrm{FK}}(\mathbf{r})\rho^{1/2}=\sum_i n_i\varepsilon_i \ . \tag{28}$$

The results are presented in Table I.

We have found that a direct numerical integration of (25) is not difficult; we directly obtain the correct eigenvalues and density. There are several algorithm problems, though. First, we have to change the atomic programs in order to introduce the correct boundary conditions for the case of our potential. Second, the extra term arising from the difference of the actual and the pseudokinetic energies can be very large near the origin or at large distances and special care has to be taken to avoid numerical errors in those regions.

The equation proposed originally by Levy, Perdew, and Sahni is different from Eq. (25) (in fact, it is also different from one proposed by us in a previous paper [12]). The problem is that those equations do not include the symmetry constraints.

If we introduce the correct symmetry constraints, we can obtain as a Lagrange multiplier either the chemical potential or quantities like $\bar{\varepsilon}$ because, by construction, there is in fact a family of equations for the square root of electronic density [13],

$$-\nabla^2\rho^{1/2}+v_{\mathrm{eff}}^{\mathrm{FK}}(\mathbf{r})\rho^{1/2}=\varepsilon\rho^{1/2} \ , \tag{29}$$

with $v_{\mathrm{eff}}^{\mathrm{FK}}(\mathbf{r})$;

$$v_{\mathrm{eff}}(\mathbf{r})=v_{\mathrm{xc}}(\mathbf{r})+v_{\mathrm{Coul}}(\mathbf{r})+v_{\mathrm{ext}}(\mathbf{r}) +\frac{1}{\rho^{1/2}}\nabla^2\rho^{1/2}+k(\mathbf{r})-\Delta\varepsilon(\mathbf{r}) \ ;$$

TABLE I. Numerical solution of Eq. (28) (in hartree energy units).

Atom	Sum of eigenvalues (KS)	Left-hand side Eq. (28)
He	−1.1648	−1.1715
Li	−3.8929	−3.8929
Be	−8.1658	−8.1657
B	−14.0060	−14.0165
C	−21.3627	−21.3769
N	−30.2514	−30.2499
O	−40.7088	−40.7092
F	−52.7705	−52.7645
Ne	−66.3759	−66.3730

and the series of possible $\Delta\varepsilon(\mathbf{r})=\sum_i |\phi_i|^2\varepsilon_i n_i/\rho(\mathbf{r})-\varepsilon$, where ε can be given the desired physical meaning. We have tested several possibilities, but none has a special advantage.

CONCLUSIONS

This work shows the necessity of an extra principle to density-functional theory; that is, to include a symmetry constraint for the projection of the density matrix into the one matrix in the variation principle. As a result, we have found that it is indeed possible to construct an equation for the square root of the electronic density, but it is necessary to include an extra term in the effective potential, which imposes a symmetry constraint into the acceptable electronic density. It should be pointed out that our procedure, in its present form, is aimed at obtaining $\rho(\mathbf{r})$ and not at the development of the series of equations needed to obtain wave functions (orbitals) containing the square root of the density of the form

$$f_k=(\rho/N)^{1/2}e^{i\theta_k}, \tag{30}$$

as discussed, for example, by Nyden and Parr [14].

In the work of Nyden and Parr, the variable θ_k contributes to the local orbital kinetic energy $k_k(\mathbf{r})$; each k_k equals a fraction of the total local kinetic energy of the N-electron system. The sum of the "kinetic" energies $k_k(\mathbf{r})$ of the f_k orbitals adds to $k(\mathbf{r})$, then those orbitals could be used to construct the $v_{\text{eff}}^{\text{FK}}(\mathbf{r})$ potential in the same form as in our Eq. (29). The energy term $\Delta\varepsilon(\mathbf{r})$ integrates to zero; it only produces local variation of the reference energy. Also in our Eq. (29) a pseudokinetic energy is used that needs to be corrected, cancelled, and the $k(\mathbf{r})$ terms of which introduced.

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