

Expression of the exact electron-correlation-energy density functional in terms of first-order density matrices

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The density-functional correlation energy is given in terms of first-order density matrices. These are generated either by switching off the electron-electron interaction, or by a uniform scaling of the density. An expression using Kohn-Sham exchange-only eigenvalues is also given.

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The existence of a universal electron-correlation-energy functional was shown by Kohn and Sham [1]. There are a few variants that define it, the most common one being (see, e.g., [2])

$$E_c[n] = \langle \Psi^{\lambda=1} | \hat{T} + \hat{V}_{ee} | \Psi^{\lambda=1} \rangle - \langle \Psi^{\lambda=0} | \hat{T} + \hat{V}_{ee} | \Psi^{\lambda=0} \rangle, \quad (1)$$

where Ψ^λ is the antisymmetric wave function yielding the electron density n and minimizing $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$, \hat{T} and \hat{V}_{ee} being the operators for the kinetic energy and electron-electron interaction, respectively.

It is well known that E_c can be expressed in terms of the coupling-constant-dependent second-order density matrix $P_2(\mathbf{r}_1, \mathbf{r}_2; \lambda)$ and the one obtained for $\lambda=0$ [3-6]:

$$E_c[n] = \int_0^1 d\lambda \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{1}{r_{12}} [P_2(\mathbf{r}_1, \mathbf{r}_2; \lambda) - P_2(\mathbf{r}_1, \mathbf{r}_2; \lambda=0)]. \quad (2)$$

Following a proof given by Yasuhara [7] it will be shown that the correlation-energy density functional can be expressed by using the first-order density matrices alone.

The constrained-search definition of the universal density functional for scaled electron-electron interaction is

$$F^\lambda[n] = \langle \Psi^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi^\lambda \rangle. \quad (3)$$

The correlation-energy density functional for interaction strength λ can be defined as

$$E_c^\lambda[n] = \langle \Psi^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | \hat{T} + \lambda \hat{V}_{ee} | \Psi^{\lambda=0} \rangle = F^\lambda - \langle \Psi^{\lambda=0} | \hat{T} + \lambda \hat{V}_{ee} | \Psi^{\lambda=0} \rangle. \quad (4)$$

For $\lambda=1$, $E_c^\lambda[n] = E_c[n]$ [cf. Eq. (1)].

The Hellmann-Feynman theorem can be applied to F^λ , as the space of the wave functions Ψ is invariant with λ [8]:

$$\frac{\partial F^\lambda}{\partial \lambda} = \langle \Psi^\lambda | \hat{V}_{ee} | \Psi^\lambda \rangle \quad (5)$$

$$= \frac{1}{\lambda} (F^\lambda - \langle \Psi^\lambda | \hat{T} | \Psi^\lambda \rangle). \quad (6)$$

The second equality follows from Eq. (3). As our interest lies in E_c , F^λ will be eliminated from the preceding equation by the use of Eq. (4). For the left-hand side,

$$\frac{\partial F^\lambda}{\partial \lambda} = \frac{\partial E_c^\lambda}{\partial \lambda} + \langle \Psi^{\lambda=0} | \hat{V}_{ee} | \Psi^{\lambda=0} \rangle \quad (7)$$

is obtained. Equation (6) can be then rewritten as

$$\frac{\partial E_c^\lambda}{\partial \lambda} = \frac{1}{\lambda} (E_c^\lambda + \langle \Psi^{\lambda=0} | \hat{T} | \Psi^{\lambda=0} \rangle - \langle \Psi^\lambda | \hat{T} | \Psi^\lambda \rangle). \quad (8)$$

After division by λ and rearrangement, the above equation is

$$\frac{\partial}{\partial \lambda} \left(\frac{E_c^\lambda}{\lambda} \right) = - \frac{1}{\lambda^2} (\langle \Psi^\lambda | \hat{T} | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | \hat{T} | \Psi^{\lambda=0} \rangle).$$

The integration between $\lambda=0$ and $\lambda=1$ yields

$$E_c[n] = - \int_0^1 \frac{d\lambda}{\lambda^2} (\langle \Psi^\lambda | \hat{T} | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | \hat{T} | \Psi^{\lambda=0} \rangle). \quad (9)$$

To obtain this result, Eqs. (1), (4), (5), and (7) were used, together with

$$\lim_{\lambda \rightarrow 0} \frac{E_c^\lambda}{\lambda} = \lim_{\lambda \rightarrow 0} \frac{\partial E_c^\lambda}{\partial \lambda} = 0. \quad (10)$$

If it happens that for a certain value of λ there is sudden change in Ψ^λ , as long as F^λ remains continuous, the proof can be repeated on each of the intervals, yielding the same final result.

Please note that one has to take care when taking the limit $\lambda \rightarrow 0$ in the case of degeneracy. It may then well happen that only one of the possible combinations of the degenerate $\Psi^{\lambda=0}$ is selected by the limiting process, and this is not a single determinant. This happens, e.g., for the hydrogen molecule at infinite internuclear separation.

As the right-hand side (rhs) of Eq. (9) contains only the mono-electronic operator \hat{T} , it can be rewritten by using the first-order density matrix

$$\gamma_n^\lambda(\mathbf{r}_1, \mathbf{r}'_1) = \sum_{spins} \int d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \Psi^{\lambda*} \times (\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi^\lambda(\mathbf{r}'_1, \dots, \mathbf{r}_N).$$

This gives

$$E_c[n] = \frac{1}{2} \int_0^1 d\lambda \frac{1}{\lambda^2} \int d^3\mathbf{r} \nabla_{\mathbf{r}'}^2 [\gamma_n^\lambda(\mathbf{r}, \mathbf{r}') - \gamma_n^{\lambda=0}(\mathbf{r}, \mathbf{r}')] \Big|_{\mathbf{r}=\mathbf{r}'} \quad (11)$$

The preceding formula shows that the knowledge of $\gamma_n^\lambda(\mathbf{r}, \mathbf{r}')$ is sufficient to obtain E_c . Of course, it would also be possible to work in momentum space, where the momentum density could be replaced by γ_n^λ , and a local operator would substitute for ∇^2 .

Instead of using the first-order density matrices for a fixed density and variable electron-electron interaction, it is possible to consider a series of first-order density matrices, obtained with the full electron-electron interaction, but yielding different electron densities. This can be shown by using the uniform scaling properties (see, e.g., Ref. [2]).

Let Ψ_{n_α} be the antisymmetric wave function obtained by uniform scaling from Ψ^λ :

$$\Psi_{n_\alpha} = \alpha^{3N/2} \Psi^\lambda(\alpha \mathbf{r}_1, \dots, \alpha \mathbf{r}_N). \quad (12)$$

Ψ_{n_α} yields the scaled density

$$n_\alpha(\mathbf{r}) = \alpha^3 n(\alpha \mathbf{r})$$

and minimizes $\langle \hat{T} + \alpha \lambda \hat{V}_{ee} \rangle$ (for all wave functions yielding n_α). Ψ_{n_α} also produces the first-order density matrix

$$\gamma_{n_\alpha}^{\alpha\lambda}(\mathbf{r}, \mathbf{r}') = \alpha^3 \gamma_n^\lambda(\alpha \mathbf{r}, \alpha \mathbf{r}'). \quad (13)$$

An interesting choice for α is $\alpha=1/\lambda$. Then Ψ_{n_α} is minimizing $\langle \hat{T} + \hat{V}_{ee} \rangle$ and is thus the ground state wave function for the system having ground state density n_α . In this specific case, Eq. (13) can be rewritten by using the first-order density matrix of the system with density n_α

$$\gamma_n^\lambda(\mathbf{r}, \mathbf{r}') = \lambda^3 \gamma_{n_{1/\lambda}}^{\lambda=1}(\lambda \mathbf{r}, \lambda \mathbf{r}'). \quad (14)$$

The scaling transformation given in Eq. (12) can also be applied to $\Psi^{\lambda=0}$, which now yields $\Psi_{n_\alpha}^{\lambda=0}$, the antisymmetric wave function yielding n_α and minimizing $\langle \hat{T} \rangle$. The corresponding first-order density matrix will be $\gamma_{n_\alpha}^{\lambda=0}$. Choosing again $\alpha=1/\lambda$, one obtains the equation

$$\gamma_n^{\lambda=0}(\mathbf{r}, \mathbf{r}') = \lambda^3 \gamma_{n_{1/\lambda}}^{\lambda=0}(\lambda \mathbf{r}, \lambda \mathbf{r}'). \quad (15)$$

Using Eqs. (13) and (15) in Eq. (11) one obtains

$$E_c[n] = \frac{1}{2} \int_0^1 d\lambda \int d^3\mathbf{r} \nabla_{\mathbf{r}'}^2 [\gamma_{n_{1/\lambda}}^{\lambda=1}(\mathbf{r}, \mathbf{r}') - \gamma_{n_{1/\lambda}}^{\lambda=0}(\mathbf{r}, \mathbf{r}')] \Big|_{\mathbf{r}=\mathbf{r}'} \quad (16)$$

In this equation λ has the role of producing a family of densities (starting from the reference density n by uniform scaling), but no fictitious interaction is used.

An alternative equation can be obtained by adding and subtracting

$$\int d^3\mathbf{r} v_0(\mathbf{r}) n(\mathbf{r})$$

from the rhs of Eq. (11), where v_0 is a local potential; v_0 should not depend on specific parameters of the molecule or crystal studied, but may depend on the density. Such a potential could be the Kohn-Sham exchange-only potential. One then has

$$E_c[n] = - \int_0^1 \frac{d\lambda}{\lambda^2} (\langle \Psi^\lambda | \hat{T} + \hat{V}_0 | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | \hat{T} + \hat{V}_0 | \Psi^{\lambda=0} \rangle) \quad (17)$$

with

$$\hat{V}_0 = \sum_{i=1}^N v_0(\mathbf{r}_i).$$

Ψ^λ can be written as a sum of Slater determinants, Φ_J , $\Psi^\lambda = \sum_J c_J^\lambda \Phi_J$, each Φ_J being constructed with the eigenfunctions φ_i of

$$(-\frac{1}{2}\nabla^2 + v_0)\varphi_i = e_i \varphi_i, \quad (18)$$

yielding

$$\begin{aligned} \langle \Psi^\lambda | \hat{T} + \hat{V}_0 | \Psi^\lambda \rangle &= \sum_{J,K} c_J^{\lambda*} c_K^\lambda \langle \Phi_J | \hat{T} + \hat{V}_0 | \Phi_K \rangle \\ &= \sum_J |c_J^\lambda|^2 \langle \Phi_J | \hat{T} + \hat{V}_0 | \Phi_J \rangle. \end{aligned}$$

The last equality holds because $\langle \Phi_J | \hat{T} + \hat{V}_0 | \Phi_K \rangle$ becomes zero for $J \neq K$ by using Eq. (18). As

$$\langle \Phi_J | \hat{T} + \hat{V}_0 | \Phi_J \rangle = \sum_i f_{J,i} e_i,$$

where $f_{J,i}$ is the occupation number of the orbital φ_i in Φ_J . Finally, introducing

$$f_i^\lambda = \sum_J |c_J^\lambda|^2 f_{J,i}$$

and

$$v_i = - \int_0^1 \frac{d\lambda}{\lambda^2} (f_i^\lambda - f_i^{\lambda=0}),$$

one gets

$$E_c[n] = \sum_i v_i e_i. \quad (19)$$

A further extension is possible for modified Hamiltonians, such as those used in Ref. [9]. Here one has to replace \hat{T} by $\hat{T} + \hat{W}$ where \hat{W} is a two-body operator. Of course, the obtained formula will not require knowledge of the first-order density matrices alone, but also of that of the second-order density matrices generated by using $\hat{T} + \hat{W}$.

The proof given for Eq. (9) can be extended to ensembles, by replacing $\langle \Psi^\lambda \dots \Psi^\lambda \rangle$ by a sum over the states of the ensemble with corresponding weights. Another extension of

the proof given above is possible for certain classes of wave functions that satisfy the Hellmann-Feynman theorem, allowing another combination of multideterminantal wavefunction methods with density functional methods. One might consider Eq. (11) as justification of the success of one such scheme, which exploits some knowledge about the most important natural orbitals (the orbitals diagonalizing the first-order density matrix) [10].

Traditionally (see, e.g., [5]) the local-density and related approximations are explained as modeling the exchange-correlation hole. Finding a good model for the exchange-correlation hole is made difficult by the fact that N -representability is difficult to satisfy in general [11]. On the other hand, the N -representability conditions for first-order density matrices are easily taken into account (see, e.g., [12]) by using

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i \nu_i \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}'),$$

where $\varphi_i(\mathbf{r})$ are orthonormal (natural) orbitals and ν_i their occupation numbers. One may thus expect that the equations presented in this paper could be useful in modeling $E_c[n]$ via Eq. (11). Another possibility would be to model the distribution of the ν_i in Eq. (19).

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