

An exact second-order expression for the density functional theory correlation potential for molecules

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(Received 5 July 2000; accepted 1 December 2000)

In this communication we present the exact, local, one-electron, second-order correlation potential for molecules, for use in density functional studies. The correlation potential is represented in a basis set, and when combined with the exact exchange potential, it provides an exchange–correlation potential that is derived exclusively from exact, orbital-dependent expressions. In this sense, such potentials provide an *ab initio* density functional theory (DFT) that permits convergence to the exact answer as higher order terms are introduced, just as is the case for *ab initio* correlated methods. Furthermore, this potential includes some dispersion effects that are missing from other DFT potentials. © 2001 American Institute of Physics. [DOI: 10.1063/1.1342809]

Recent advances^{1–5} in developing procedures that use explicit orbital-dependent exchange–correlation functionals and potentials in the Kohn–Sham (KS) formalism^{6–8} of density functional theory (DFT) have demonstrated that present approximations to the exact correlation energy functional, $E_c[n]$, behave poorly with the exact (local) exchange energy treatment obtained from the orbital expression for the exchange energy,^{2–5,9} to generate the optimized exchange potential (OEP), or its approximations such as the Krieger–Li–Iafrate (KLI) approximation.^{9,10} The OEP method for molecules, generated in a basis set, has recently been presented.^{4,5} Since the exchange energy is at least an order of magnitude more important than the correlation energy, once the exchange potential is under control, we can focus on new approximations to the exact correlation energy functional, $E_c[n]$, emphasizing the properties of their corresponding correlation potentials. The objective of this note is to present the second-order correlation potential. By extracting both the exchange and correlation potentials from known orbital-dependent expressions expressed in basis functions, we define an *ab initio* DFT,^{4,11} which shows promise of offering a series of systematically converging DFT approximations to the exact answer, analogous to that in *ab initio* correlated theory.

It has been shown that many widely used approximations to $E_c[n]$ generate potentials with incorrect shape,¹² and do not satisfy certain conditions^{13–15} for the exact correlation potential, $v_c([n]; \mathbf{r}) = \delta E_c[n] / \delta n(\mathbf{r})$, i.e., the first functional derivative of $E_c[n]$ with respect to the electron density $n(\mathbf{r})$. The addition of common approximate correlation functionals to the exact exchange or to the KLI approximation, leads to worsened orbital energies, which are very sensitive to the properties of their corresponding potential.

In the present work, we present the exact form of the correlation potential derived from a second-order correlation functional, for finite densities. The newly derived expression is meant to be included in a self-consistent KS scheme,

which would lead to very accurate orbital energies provided that the perturbation theory approximation is adequate. Since typically $E^{(2)} = \text{MBPT}(2)$ accounts for more than 90% of the correlation energy¹⁶ this is considered a good approximation. The second-order contribution $E_c^{(2)}[n]$,^{17–19} is identified through an asymptotic uniform scaling of $n(\mathbf{r})$.²⁰ Recent connections between $E_c^{(2)}[n]$ and the conventional quantum chemistry $E^{(2)}$ have been established by Ivanov and Levy.²¹ For systems with nondegenerate ground states, $E_c[n]$ satisfies the high-density expansion from Görling–Levy (GL) perturbation theory^{17,18} that keeps the density fixed,

$$E_c[n_\lambda] = E_c^2[n] + \lambda^{-1} E_c^{(3)}[n] + \lambda^{-2} E_c^{(4)}[n] \dots \quad (1)$$

For high enough λ , where the scaled density $n_\lambda(\mathbf{r})$ is

$$n_\lambda(x, y, z) \equiv \lambda^3 n(\lambda x, \lambda y, \lambda z), \quad (2)$$

it follows that as $\lambda \rightarrow \infty$, $E_c[n_\lambda]$ is bounded, and is equal to $E_c^{(2)}[n]$. Besides accounting for most of the correlation energy in molecules, the quantity $2E_c^{(2)}[n]$ is also the initial slope in the adiabatic connection method (coupling-constant integration formula) for $E_c[n]$,^{22–24} which would provide the remainder of the correlation.

The exact correlation energy functional, $E_c[n]$, is given by

$$E_c[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{\text{ee}} | \Psi[n] \rangle - \langle \Phi_0[n] | \hat{T} + \hat{V}_{\text{ee}} | \Phi_0[n] \rangle, \quad (3)$$

where \hat{T} is the kinetic energy operator, \hat{V}_{ee} the electron–electron repulsion operator, and $\Psi[n]$ is the antisymmetric wave function that minimizes $\langle \hat{T} + \hat{V}_{\text{ee}} \rangle$ and yields the density $n(\mathbf{r})$.²⁵ $\Phi_0[n]$ is the KS noninteracting wave function, i.e., the wave function that minimizes $\langle \hat{T} \rangle$, and yields the density $n(\mathbf{r})$.²⁵ Except for certain degenerate cases, $\Phi_0[n]$ is a single determinant,²⁶ and is built from the lowest energy occupied one-particle solutions to the noninteracting KS problem. We assume that form. The respective KS equations are

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$$\begin{aligned} \hat{H}_0[n]\Phi_k[n] &= \left\{ \hat{T} + \sum_{i=1}^N v_s([n];\mathbf{r}_i) \right\} \Phi_k[n] \\ &= E_k[n]\Phi_k[n], \\ E_0[n] &< E_1[n] \leq \dots \leq E_k[n] \leq \dots \end{aligned} \quad (4)$$

The KS potential $v_s([n];\mathbf{r})$ is a unique functional of the N -electron density $n(\mathbf{r})$, written as

$$v_s([n];\mathbf{r}) = v(\mathbf{r}) + u([n];\mathbf{r}) + v_x([n];\mathbf{r}) + v_c([n];\mathbf{r}), \quad (5)$$

where $v(\mathbf{r})$ is the physical external potential for the system of interest. The Hartree potential $u([n];\mathbf{r})$ is

$$u([n];\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \quad (6)$$

which is the functional derivative of the Hartree electron-electron repulsion energy $U[n]$ known explicitly in terms of the density by

$$U[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (7)$$

In Eq. (5), the exchange potential $v_x([n];\mathbf{r})$ is the functional derivative of $E_x[n]$, i.e., $v_x([n];\mathbf{r}) = \delta E_x[n] / \delta n(\mathbf{r})$. The exchange energy functional $E_x[n]$ is known explicitly in terms of the noninteracting KS wave function as

$$E_x[n] = \langle \Phi_0[n] | \hat{V}_{ee} | \Phi_0[n] \rangle - U[n]. \quad (8)$$

The last term in Eq. (5) is the correlation potential, i.e., $v_c([n];\mathbf{r}) = \delta E_c[n] / \delta n(\mathbf{r})$, which is our objective.

The present derivation of the second-order contribution, $v_c^{(2)}([n];\mathbf{r})$, to the correlation potential, $v_c([n];\mathbf{r})$, generalizes the two-electron formula of Ivanov, Burke, and Levy (IBL)¹³ to any number of electrons. We consider $v_c^{(2)}([n];\mathbf{r}) = \delta E_c^{(2)}[n] / \delta n(\mathbf{r})$ obtained via the following identity:

$$\begin{aligned} v_c^{(2)}([n];\mathbf{r}) &= \int \frac{\delta E_c^{(2)}[n]}{\delta v_s([n];\mathbf{r}')} \frac{\delta v_s([n];\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}' \\ &= \int \frac{\delta E_c^{(2)}[n]}{\delta v_s([n];\mathbf{r}')} \mathbf{X}_s^{-1}(\mathbf{r}',\mathbf{r}) d\mathbf{r}'. \end{aligned} \quad (9)$$

In Eq. (9), the quantity

$$\frac{\delta v_s([n];\mathbf{r}')}{\delta n(\mathbf{r})} \equiv \mathbf{X}_s^{-1}(\mathbf{r}',\mathbf{r})$$

is the effective inverse of the static KS linear response function given by

$$\begin{aligned} \mathbf{X}_s(\mathbf{r}',\mathbf{r}) &= \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} \\ &= \sum_{i=1}^N \sum_{a=N+1}^{\infty} \frac{\varphi_a(\mathbf{r}')\varphi_a^*(\mathbf{r})\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')}{\epsilon_i - \epsilon_a} + \text{c.c.}, \end{aligned} \quad (10)$$

with $\varphi_p(\mathbf{r})$, ϵ_p being the KS orbitals and energies, i.e., $[-\frac{1}{2}\nabla^2 + v_s([n];\mathbf{r})]\varphi_p(\mathbf{r}) = \epsilon_p\varphi_p(\mathbf{r})$.

Following IBL, $E_c^{(2)}[n]$ may be written as

$$\begin{aligned} E_c^{(2)}[n] &= \frac{1}{2} \langle \tilde{\Psi}^{(1)}[n] | E_0[n] - \hat{H}_0[n] | \Psi^{(1)}[n] \rangle \\ &\quad + \frac{1}{2} \langle \Psi^{(1)}[n] | E_0[n] - \hat{H}_0[n] | \tilde{\Psi}^{(1)}[n] \rangle. \end{aligned} \quad (11)$$

In Eq. (11), $\Psi^{(1)}[n]$, $\tilde{\Psi}^{(1)}[n]$, $E_0[n]$, and $\hat{H}_0[n]$ are explicit or implicit functionals of the density. According to GL perturbation theory, when the density is kept fixed,^{17,18} $\Psi^{(1)}[n]$ is the solution to

$$\{\hat{H}_0[n] - E_0[n]\}\Psi^{(1)}[n] = \{E^{(1)}[n] - \hat{H}^{(1)}[n]\}\Phi_0[n], \quad (12)$$

where $\hat{H}^{(1)}[n]$ is a perturbation given by

$$\begin{aligned} \hat{H}^{(1)}[n] &= \hat{V}_{ee} - \sum_{i=1}^N \{u([n];\mathbf{r}_i) + v_x([n];\mathbf{r}_i)\} \\ &\equiv \hat{V}_{ee} - \sum_{i=1}^N v_{xu}([n];\mathbf{r}_i). \end{aligned} \quad (13)$$

The wave function $\tilde{\Psi}^{(1)}[n] (\neq \Psi^{(1)}[n])$ in Eq. (11) is the solution to another first-order perturbation problem, which arises from the perturbation \hat{V}_{ee} only,¹³ namely

$$\{\hat{H}_0[n] - E_0[n]\}\tilde{\Psi}^{(1)}[n] = \{\tilde{E}^{(1)}[n] - \hat{V}_{ee}\}\Phi_0[n]. \quad (14)$$

The advantage of the hybrid form, Eq. (11), is that it manifests the pointwise identity,

$$\langle \Phi_0[n] | - \sum_{i=1}^N v_{xu}([n];\mathbf{r}_i) | \Psi^{(1)}[n] \rangle + \text{c.c.} = 0,$$

because by construction $\langle \Phi_0[n] | \hat{\rho} | \Psi^{(1)}[n] \rangle + \text{c.c.} = 0$, where $\hat{\rho}$ is the density operator, i.e.,

$$\hat{\rho} = \sum_{i=1}^N \delta(\mathbf{r}' - \mathbf{r}_i),$$

and the perturbation $v_{xu}([n];\mathbf{r}_i)$ is a local multiplicative operator.

In order to obtain an analytic expression for $v_c^{(2)}([n];\mathbf{r})$, we shall make use of Eq. (9). Considering a density variation $n(\mathbf{r}) + \delta n(\mathbf{r})$ in all density functionals in Eq. (11), we have several components. First, we account for the contributions coming from

$$S_1[n + \delta n] \equiv \frac{1}{2} \langle \tilde{\Psi}^{(1)}[n] | E_0[n + \delta n] - \hat{H}_0[n + \delta n] | \Psi^{(1)}[n] \rangle + \text{c.c.} \quad (15)$$

In Eq. (15), we consider a variation of the density $\delta n(\mathbf{r})$, which keeps the particle number fixed, i.e., $\int \delta n(\mathbf{r}) d\mathbf{r} = 0$. Only terms with explicitly shown density changes, $n(\mathbf{r}) + \delta n(\mathbf{r})$, are considered. Upon using the explicit form of $\hat{H}_0[n]$ and $E_0[n] \equiv \langle \Phi_0[n] | \hat{H}_0[n] | \Phi_0[n] \rangle$, along with the minimizing nature of $\Phi_0[n]$, Eq. (15) yields

$$\begin{aligned} \frac{\delta S_1[n]}{\delta n(\mathbf{r})} &= \frac{1}{2} \{ \langle \tilde{\Psi}^{(1)}[n] | \Psi^{(1)}[n] \rangle + \text{c.c.} \} \\ &\times \int n(\mathbf{r}') \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ &- \frac{1}{2} \int \{ \langle \tilde{\Psi}^{(1)}[n] | \hat{\rho} | \Psi^{(1)}[n] \rangle + \text{c.c.} \} \\ &\times \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}'. \end{aligned} \quad (16)$$

Next, consider

$$\begin{aligned} S_2[n + \delta n] &\equiv \frac{1}{2} \{ \langle \tilde{\Psi}^{(1)}[n + \delta n] | E_0[n + \delta n] \\ &- \hat{H}_0[n + \delta n] | \Psi^{(1)}[n] \rangle + \text{c.c.} \} \\ &+ \frac{1}{2} \{ \langle \tilde{\Psi}^{(1)}[n] | E_0[n + \delta n] \\ &- \hat{H}_0[n + \delta n] | \Psi^{(1)}[n + \delta n] \rangle + \text{c.c.} \}. \end{aligned} \quad (17)$$

The response of the terms with explicitly shown density variations is obtained by considering the right-hand sides of Eqs. (12) and (14), or their complex conjugate counterparts. The particular choice of grouping terms, Eqs. (15) and (17), eliminates the need for a direct consideration of the response of $\Psi^{(1)}[n]$ and $\tilde{\Psi}^{(1)}[n]$ to small changes in the density, via changes in the KS potential as dictated by Eq. (9). Note that $E_0[n + \delta n] - \hat{H}_0[n + \delta n]$ is considered twice. The response of the KS single determinant $\Phi_0[n]$ to small changes in $v_s([n]; \mathbf{r})$ is found by the standard Rayleigh–Schrödinger perturbation theory (coupled perturbed KS equations). The last term that deserves some attention is the response of $v_{xu}([n]; \mathbf{r}) \equiv u([n]; \mathbf{r}) + v_x([n]; \mathbf{r})$. We note that

$$\frac{\delta v_{xu}(\mathbf{r})}{\delta n(\mathbf{r}')} \equiv f_{xu}(\mathbf{r}, \mathbf{r}') = f_x(\mathbf{r}, \mathbf{r}') + \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad (18)$$

where $f_{xu}(\mathbf{r}, \mathbf{r}')$ is the sum of the Hartree kernel and the static exchange kernel.

Hence,

$$\begin{aligned} \frac{\delta S_2[n]}{\delta n(\mathbf{r})} &= \frac{1}{2} \int \left\{ \sum_{i=1}^N \sum_{a=N+1}^{\infty} \langle \Phi_i^a | \hat{V}_{ee} | \Psi^{(1)}[n] \rangle \right. \\ &\times \frac{\varphi_i(\mathbf{r}') \varphi_a^*(\mathbf{r}')}{\epsilon_i - \epsilon_a} + \text{c.c.} \left. \right\} \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ &+ \frac{1}{2} \int \left\{ \sum_{i=1}^N \sum_{a=N+1}^{\infty} \langle \tilde{\Psi}^{(1)}[n] | \hat{V}_{ee} \right. \\ &- \sum_{i=1}^N v_{xu}([n]; \mathbf{r}_i) | \Phi_i^a \rangle \frac{\varphi_i^*(\mathbf{r}') \varphi_a(\mathbf{r}')}{\epsilon_i - \epsilon_a} + \text{c.c.} \left. \right\} \\ &\times \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' - \frac{1}{2} \int f_{xu}(\mathbf{r}, \mathbf{r}') \delta \tilde{n}(\mathbf{r}') d\mathbf{r}' \end{aligned} \quad (19)$$

with

$$\delta \tilde{n}(\mathbf{r}) = \langle \tilde{\Psi}^{(1)}[n] | \hat{\rho} | \Phi_0[n] \rangle + \langle \Phi_0[n] | \hat{\rho} | \tilde{\Psi}^{(1)}[n] \rangle. \quad (20)$$

In Eq. (19), Φ_i^a corresponds to a singly excited determinant obtained by exciting an electron from initial state i to final state a . Noticing that

$$\begin{aligned} E_c^{(2)}[n + \delta n] &= S_2[n + \delta n] - S_1[n + \delta n] \\ &= \int v_c^{(2)}([n]; \mathbf{r}) \delta n(\mathbf{r}) d\mathbf{r} + O(\delta n^2(\mathbf{r})) \\ &= \int \left\{ \frac{\delta S_2[n]}{\delta n(\mathbf{r})} - \frac{\delta S_1[n]}{\delta n(\mathbf{r})} \right\} \delta n(\mathbf{r}) d\mathbf{r} \\ &+ O(\delta n^2(\mathbf{r})) \end{aligned} \quad (21)$$

because we have *twice* included the variation of $E_0[n + \delta n] - \hat{H}_0[n + \delta n]$ in Eqs. (17) and (19). With Eq. (21) in mind, we obtain our desired result

$$\begin{aligned} v_c^{(2)}([n]; \mathbf{r}) &= \frac{\delta S_2[n]}{\delta n(\mathbf{r})} - \frac{\delta S_1[n]}{\delta n(\mathbf{r})} \\ &= -\frac{1}{2} \int f_{xu}(\mathbf{r}, \mathbf{r}') \delta \tilde{n}(\mathbf{r}') d\mathbf{r}' + \frac{1}{2} \int \left\{ \sum_{i=1}^N \sum_{a=N+1}^{\infty} \langle \Phi_i^a | \hat{V}_{ee} | \Psi^{(1)}[n] \rangle \frac{\varphi_i(\mathbf{r}') \varphi_a^*(\mathbf{r}')}{\epsilon_i - \epsilon_a} + \text{c.c.} \right\} \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ &+ \frac{1}{2} \int \left\{ \sum_{i=1}^N \sum_{a=N+1}^{\infty} \langle \tilde{\Psi}^{(1)}[n] | \hat{V}_{ee} - \sum_{i=1}^N v_{xu}([n]; \mathbf{r}_i) | \Phi_i^a \rangle \frac{\varphi_i^*(\mathbf{r}') \varphi_a(\mathbf{r}')}{\epsilon_i - \epsilon_a} + \text{c.c.} \right\} \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ &\cdot \frac{1}{2} \{ \langle \tilde{\Psi}^{(1)}[n] | \Psi^{(1)}[n] \rangle + \text{c.c.} \} \int n(\mathbf{r}') \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' + \frac{1}{2} \int \{ \langle \tilde{\Psi}^{(1)}[n] | \hat{\rho} | \Psi^{(1)}[n] \rangle + \text{c.c.} \} \mathbf{X}_s^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}'. \end{aligned} \quad (22)$$

Equation (22) is an analytic expression for the second-order component of the correlation potential for finite, many-electron densities. It is capable of introducing the second-order dispersion for weakly bound molecules, a failure of most DFT methods. It is easy to implement in the basis set formulation of the exact exchange treatment.^{4,5} It requires two first-order wave functions, the solutions to Eqs. (12) and (14). In other words, MBPT(2) is needed at each self-consistent field iteration. Note that the difference between $\Psi^{(1)}[n]$ and $\tilde{\Psi}^{(1)}[n]$ is in the summation over single excitations, if $\Psi^{(1)}[n]$ and $\tilde{\Psi}^{(1)}[n]$ are expanded in terms of eigenfunctions and eigenvalues of $\hat{H}_0[n]$. Given its rather complicated structure, the exact $v_c^{(2)}([n];\mathbf{r})$ can be readily approximated starting from Eq. (22). A natural approach for developing less computationally demanding approximations would be the replacement of the exact $\Psi^{(1)}[n]$ and $\tilde{\Psi}^{(1)}[n]$ by approximations featuring, for example, an average denominator in their expansions in terms of eigenfunctions and eigenvalues of $\hat{H}_0[n]$ (note that the KLI approximation is based on such an approach). The practical implementation of the exact $v_c^{(2)}([n];\mathbf{r})$ is in progress and will be presented elsewhere.

Last but not least, Eq. (22) is an important link among different elements in GL perturbation theory. It reveals useful connections between the KS formalism as a model one-particle theory and the conventional many-body wave function approach. Moreover, Eq. (22) is an identity connecting $v_c^{(2)}([n];\mathbf{r})$, $v_{xu}([n];\mathbf{r})$, and $f_{xu}(\mathbf{r},\mathbf{r}')$. When time-dependent KS theory is considered, especially in the zero-frequency limit, Eq. (22) leads to results closely related to ones by Gonze and Scheffler.²⁷ Our expression for $v_c^{(2)}([n];\mathbf{r})$ can be multiplied by different functions and integrated over all space to generate different constraints for $v_c^{(2)}([n];\mathbf{r})$. For two-electron densities, when formula (22) is multiplied by $n(\mathbf{r})$ and integrated over all space it recovers some previous results.^{12,13} Equation (22) is the most general result from GL perturbation theory through second order. It

should prove valuable in designing better explicit orbital-dependent functionals, when used in conjunction with the adiabatic integration formula to arrive at an approximation to $E_c[n]$ starting from $E_c^{(2)}[n]$.

The authors thank Professor Mel Levy for helpful comments. This work was sponsored by AFOSR grant F49620-98-1-0166.

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