

ARTICLES

Connections between second-order Görling–Levy and many-body perturbation approaches in density functional theoryStanislav Ivanov^{a)} and So Hirata^{b)}*Quantum Theory Project, University of Florida, Gainesville, Florida 32611*

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Formal connections between the high-density scaling limit of the correlation energy functional $E_c[n]$ in density functional theory and second-order energy expressions from different perturbation theory formulations are presented. It is demonstrated that the second-order correlation potential considered by Grabowski *et al.* [J. Chem. Phys. **116**, 4415 (2002)] is equivalent to the high-density limit of the exact correlation potential, and thus provides the first self-consistent finite-basis-set implementation of a Kohn–Sham (KS) potential correct through second-order. A different second-order correlation functional based on the exchange-only KS approach is introduced. It is shown that this second-order correlation functional leads to the same self-consistent KS realization as the one derived from the second-order component of $E_c[n]$. © 2003 American Institute of Physics. [DOI: 10.1063/1.1522570]

INTRODUCTION AND DEFINITIONS

Very recently Grabowski *et al.* (GHIB) (Ref. 1) have presented exciting new results from computational schemes based on the optimized effective potential (OEP) (Refs. 2–14) method with an inclusion of correlation potentials derived from a second-order many-body perturbation theory (MBPT) energy expression. Approximate second-order implementations have been considered and excellent numerical results have been reported.¹ The explicit orbital-dependent correlation potentials proposed in Ref. 1 present an enormous improvement over the widely-used potentials derived from explicit density approximations to the correlation energy functional. However, because these potentials are obtained from somewhat different viewpoint, the question has arisen about how the GHIB approach relates to the PT introduced by Görling and Levy (GL).^{6,15}

Here, we shall establish some connections between the specific choices of the second-order correlation energy functionals considered in Ref. 1, and the second-order component $E_c^{(2)}[n]$ (Refs. 15–19) of the exact correlation energy functional $E_c[n]$ (Refs. 16, 20–26) in density functional theory (DFT). We shall prove that second-order energy $E_c^{(2),PT}$ from the conventional PT provides a lower bound for $E_c^{(2)}[n]$. In that, $E_c^{(2),PT}$ is more negative than $E_c^{(2)}[n]$ for the same set of Kohn–Sham (KS) orbitals. Previous connections between

the high- Z limit of the common quantum chemistry correlation energy and different DFT correlation energy functionals have been made by Perdew, McMullen, and Zunger,²⁷ by Chakravorty and Davidson,²⁸ and by Ivanov and Levy.^{29,30} The importance of PT considerations in DFT has been recently demonstrated by Engel³¹ in his work on van der Waals interactions.

Also of interest is the second-order energy $E_c^{(2),PT-x}$ derived by means of PT within the exchange-only OEP method. It will be shown that the potential derived from $E_c^{(2),PT-x}$ can be a convenient choice for self-consistent KS calculations. The potential derived from $E_c^{(2),PT-x}$ has been considered by Ivanov and Levy³² in their integral equation formulation of density functional perturbation theory. This formulation enables one to derive correlation potentials without explicitly taking functional derivatives. Their approach is an extension of previous work by GL (Ref. 6) in which the integral equation treatment was initially applied to the zero-order Hamiltonian in GLPT, whereas in Ref. 32 the integral equation perturbation formalism is applied to any appropriate zero-order Hamiltonian.

We shall demonstrate that certain second-order approximations considered in Ref. 1, can lead to the finite-basis-set realizations of exact KS schemes through second order. In particular, we shall compare the computational scheme by GHIB with the one developed by GL (Ref. 6) based on their adiabatic perturbation theory.^{6,15,33} We shall prove that the second-order correlation potential given by Eq. (36) in Ref. 1, GHIB, is the finite-basis-set analog of the high-density

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scaling limit of the correlation potential in DFT. We will show that $E_c^{(2),PT-x}$ and $E_c^{(2)}[n]$ have the same functional form and thus lead to the same final results when their respective potentials are included in self-consistent KS schemes.

We briefly review the KS scheme based on the OEP method²⁻¹⁴ which, in turn, allows one to include explicit orbital-dependent functionals and potentials in self-consistent KS calculations. In atomic units, define the Hamiltonian operator $\hat{H}[n]$ as

$$\begin{aligned} \hat{H}[n] &= \sum_{i=1}^N \left\{ -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}([n]; \mathbf{r}_i) \right\} \\ &+ \sum_{j=i+1}^N \sum_{i=1}^{N-1} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} \\ &= \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \sum_{j=i+1}^N \sum_{i=1}^{N-1} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|}, \end{aligned} \quad (1)$$

where $\hat{h}(\mathbf{r}) \equiv -\frac{1}{2} \nabla^2 + v_{\text{ext}}([n]; \mathbf{r})$, and $v_{\text{ext}}([n]; \mathbf{r})$ is the external spin-independent potential for the N -electron system of interest. According to the Hohenberg–Kohn theorem,²⁰ the potential $v_{\text{ext}}([n]; \mathbf{r})$ is a unique functional of the ground-state density $n(\mathbf{r})$.^{20,34,35}

The ground-state energy of $\hat{H}[n]$, $E_{\text{GS}}[n]$, is given by

$$\begin{aligned} E_{\text{GS}}[n] &= \langle \Phi_n^{\text{KS}} | \hat{H}[n] | \Phi_n^{\text{KS}} \rangle + E_c[n] \\ &= \sum_{\sigma=\uparrow, \downarrow} \sum_{i=1}^{N_\sigma} \left\{ \langle \varphi_{i\sigma} | \hat{h} | \varphi_{i\sigma} \rangle + \frac{1}{2} \langle \varphi_{i\sigma} | \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right. \\ &\quad \left. + \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) | \varphi_{i\sigma} \rangle \right\} + E_c[n], \end{aligned} \quad (2)$$

where Φ_n^{KS} is the single determinant obtained through the KS method. Here, Φ_n^{KS} is the wave function that minimizes the expectation value of the kinetic energy operator and yields the true ground-state density $n(\mathbf{r})$.³⁴ In other words, Φ_n^{KS} is built from the N lowest energy solutions to the one-particle KS equations,

$$\begin{aligned} &\left\{ \hat{h}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{x\sigma}([n_\sigma]; \mathbf{r}) + v_{c\sigma}([n]; \mathbf{r}) \right\} \varphi_{p\sigma}(\mathbf{r}) \\ &\equiv \hat{h}_{s\sigma}([n]; \mathbf{r}) \varphi_p(\mathbf{r}) = \epsilon_{p\sigma} \varphi_p(\mathbf{r}), \quad \sigma = \uparrow, \downarrow, \end{aligned} \quad (3)$$

where $\hat{h}_{s\sigma}([n]; \mathbf{r})$ is the one-particle KS operator defined as the sum of the operators in the curly parentheses, and σ denotes the spin orientation. Pure state v -representability³⁵ is assumed throughout our consideration.

In the above equation, $v_{x\sigma}([n_\sigma]; \mathbf{r})$ is the solution to the following Fredholm linear integral equation of first kind,

$$\begin{aligned} &\int X_\sigma(\mathbf{r}', \mathbf{r}) v_{x\sigma}([n_\sigma]; \mathbf{r}') d\mathbf{r}' \\ &= \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) | \varphi_{a\sigma} \rangle \\ &\quad \times \frac{\varphi_{a\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.}, \end{aligned} \quad (4)$$

where $\hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r})$ is the nonlocal spin-dependent HF exchange operator built from the N_σ occupied KS orbitals, and where $n_\sigma(\mathbf{r})$ is the spin density. The kernel of the integral equation (4) is given by

$$X_\sigma(\mathbf{r}', \mathbf{r}) = \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{a\sigma}(\mathbf{r}') \varphi_{a\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \quad (5)$$

The correlation energy functional $E_c[n]$ in Eq. (2) is defined by

$$\begin{aligned} E_c[n] &= \langle \Psi_n | \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \hat{V}_{ee} | \Psi_n \rangle \\ &\quad - \langle \Phi_n^{\text{KS}} | \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \hat{V}_{ee} | \Phi_n^{\text{KS}} \rangle \\ &= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n^{\text{KS}} | \hat{T} + \hat{V}_{ee} | \Phi_n^{\text{KS}} \rangle, \end{aligned} \quad (6)$$

where Ψ_n is the true ground-state wave function of the interacting Hamiltonian $\hat{H}[n]$, and Φ_n^{KS} is the KS single determinant. The operator \hat{V}_{ee} is the electron–electron interaction operator, i.e., $\hat{V}_{ee} \equiv \sum_{j=i+1}^N \sum_{i=1}^{N-1} 1/|\mathbf{r}_j - \mathbf{r}_i|$, and \hat{T} is the kinetic energy operator, i.e., $\hat{T} \equiv \sum_{i=1}^N -\frac{1}{2} \nabla_i^2$. The right-hand side of Eq. (6) follows from the fact that Φ_n^{KS} is constructed to yield the same density as the one obtained from Ψ_n .³⁴ In other words, Φ_n^{KS} and Ψ_n yield the ground-state density

$$\begin{aligned} n(\mathbf{r}) &= \langle \Psi_n | \hat{\rho} | \Psi_n \rangle \\ &= \langle \Phi_n^{\text{KS}} | \hat{\rho} | \Phi_n^{\text{KS}} \rangle \\ &= n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \\ &= \sum_{i=1}^{N_\uparrow} |\varphi_{i\uparrow}(\mathbf{r})|^2 + \sum_{i=1}^{N_\downarrow} |\varphi_{i\downarrow}(\mathbf{r})|^2, \end{aligned} \quad (7)$$

where $\hat{\rho}$ is the density operator. In Eq. (3), the correlation potential $v_{c\sigma}([n]; \mathbf{r})$ is formally defined as the functional derivative of $E_c[n]$, i.e., $v_{c\sigma}([n]; \mathbf{r}) = \delta E_c[n] / \delta n_\sigma(\mathbf{r})$.

SECOND-ORDER CORRELATION ENERGY FUNCTIONALS

Since the exact form of $E_c[n]$ is intractable in practice, $E_c[n]$ must be approximated. Hence, we can consider an initial approximation to $E_c[n]$ derived from a conventional PT due to

$$\hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \left\{ \int \frac{n(\mathbf{r}')}{|\mathbf{r}_1 - \mathbf{r}'|} d\mathbf{r}' + v_{x\sigma}([n_\sigma]; \mathbf{r}_i) + v_{c\sigma}([n]; \mathbf{r}_i) \right\} = \hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} v_{uxc\sigma}([n]; \mathbf{r}_i), \quad (8)$$

where $v_{uxc\sigma}(\mathbf{r})$ is a short-hand notation for the sum of the

three components in the curly parentheses. Each subscript u , x , and c represents the Hartree, the exchange, and the correlation potentials, respectively. We note that Eq. (8) might be a typical choice for a perturbation treatment when the KS Hamiltonian is chosen as zero-order approximation.

By assuming that all components of $v_{uxc\sigma}(\mathbf{r})$ are of the same order, we consider

$$\begin{aligned} E_c^{(2),PT} &= \sum_{k=1}^{\infty} \frac{|\langle \Phi_k | \hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} v_{uxc\sigma}([n]; \mathbf{r}_i) | \Phi_0 \rangle|^2}{E_o - E_k} \\ &= \sum_{\substack{k=1 \\ \text{D.E.}}}^{\infty} \frac{|\langle \Phi_k | \hat{V}_{ee} | \Phi_0 \rangle|^2}{E_o - E_k} + \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) - v_{c\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \\ &= E_{c,D}^{(2),PT} + \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{f}_\sigma([\varphi_{\text{occ}}]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}, \end{aligned} \quad (9)$$

where $E_{c,D}^{(2),PT}$ denotes the sum over all doubly-excited (DE) states in the second line of Eq. (9). The one body-operator $\hat{f}_\sigma([\varphi_{\text{occ}}]; \mathbf{r})$ is given by

$$\hat{f}_\sigma([\varphi_{\text{occ}}]; \mathbf{r}) = \hat{h}(\mathbf{r}) + \hat{v}_{ux\sigma}^{\text{HF}}([\varphi_{\text{occ}}]; \mathbf{r}). \quad (10)$$

In Eq. (10), we have made use of Eq. (3) along with the fact that

$$\begin{aligned} \hat{f}_\sigma([\varphi_{\text{occ}}]; \mathbf{r}) &= \hat{h}_{s\sigma}([n]; \mathbf{r}) + \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}]; \mathbf{r}) \\ &\quad - v_{x\sigma}([n_\sigma]; \mathbf{r}) - v_{c\sigma}([n]; \mathbf{r}). \end{aligned} \quad (11)$$

By considering Eqs. (10) and (11), and by noticing that $\langle \varphi_{i\sigma} | \hat{h}_{s\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle = 0$, the last line of Eq. (9) is readily obtained. The subscripts i and a denote occupied and unoccupied KS orbitals, respectively.

Since the approximations proposed in Ref. 1 are second-order, we also consider the second-order expression from a specific type of PT advanced by GL.^{6,15,33} Their adiabatic PT, which keeps the density fixed at each order of perturbation, enables one to establish connections between the fully interacting Hamiltonian of the system of interest, and the respective KS Hamiltonian. In addition, the second-order energy in GLPT can be identified with the high-density scaling limit of the full $E_c[n]$.^{6,15–17,22,33}

By considering a *different* first-order perturbation,

$$\begin{aligned} \hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \left\{ \int \frac{n(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' + v_{x\sigma}([n_\sigma]; \mathbf{r}_i) \right\} \\ = \hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} v_{ux\sigma}([n]; \mathbf{r}_i), \end{aligned} \quad (12)$$

GL arrived¹⁵ at

$$\begin{aligned} \lim_{\gamma \rightarrow \infty} E_c[n_\gamma] &= E_c^{(2)}[n] = \sum_{k=1}^{\infty} \frac{|\langle \Phi_k | \hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} v_{ux\sigma}([n]; \mathbf{r}_i) | \Phi_0 \rangle|^2}{E_o - E_k} \\ &= E_{c,D}^{(2)} + \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}, \end{aligned} \quad (13)$$

where the scaled density $n_\gamma(x, y, z)$ is defined²² as

$$n_\gamma(x, y, z) = \gamma^3 n(\gamma x, \gamma y, \gamma z). \quad (14)$$

In order to establish some connections between $E_c^{(2),PT}$ and $E_c^{(2)}[n]$, we shall make use of the fact that $E_{c,D}^{(2),PT} = E_{c,D}^{(2)}$, and of Eq. (4) re-expressed as

$$\begin{aligned} n_\sigma^{(1),GL}(\mathbf{r}) &\equiv \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{HF}([\varphi_{occ\sigma}]; \mathbf{r}) \\ &- v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle \frac{\varphi_{a\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} = 0, \end{aligned} \quad (15)$$

or for any one-body multiplicative operator $g(\mathbf{r})$,

$$\begin{aligned} &\sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{HF}([\varphi_{occ\sigma}]; \mathbf{r}) \\ &- v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle \frac{\langle \varphi_{a\sigma} | g(\mathbf{r}) | \varphi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \\ &= \int n_\sigma^{(1),GL}(\mathbf{r}) g(\mathbf{r}) d\mathbf{r} = 0. \end{aligned} \quad (16)$$

As shown by Eq. (15), its left-hand side can be readily identified as the first-order spin-density $n_\sigma^{(1),GL}(\mathbf{r})$ resulting from the perturbation given by Eq. (12).

First, we note that

$$\begin{aligned} &\sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{HF}([\varphi_{occ\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) - v_{c\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \\ &= \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{HF}([\varphi_{occ\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | v_{c\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \\ &- \left\{ \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{HF}([\varphi_{occ\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle \frac{\langle \varphi_{a\sigma} | v_{c\sigma}([n]; \mathbf{r}) | \varphi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \right\}. \end{aligned} \quad (17)$$

The expression in the curly parentheses in Eq. (17) is zero because of Eq. (16). Hence, by combining Eqs. (9), (13), and (17) we obtain

$$\begin{aligned} E_c^{(2),PT} &= E_c^{(2)}[n] \\ &+ \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | v_{c\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}. \end{aligned} \quad (18)$$

Equation (18) implies

$$E_c^{(2),PT} \leq E_c^{(2)}[n]. \quad (19)$$

Further, according to Eq. (15), the first-order spin-density $n_\sigma^{(1),GL}(\mathbf{r})$ in GLPT is zero at each point of space, and thus $E_c^{(2)}[n]$ is a unique functional of $n(\mathbf{r})$. However, the perturbation given by Eq. (8) does not keep the density fixed since the corresponding first-order density becomes

$$\begin{aligned} n_\sigma^{(1),PT}(\mathbf{r}) &= - \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \langle \varphi_{i\sigma} | v_{c\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle \\ &\times \frac{\varphi_{a\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.}, \end{aligned} \quad (20)$$

and therefore $E_c^{(2),PT}$ is not a functional of $n(\mathbf{r})$ only. In fact, $E_c^{(2),PT}$ is a functional of $n(\mathbf{r}) + n^{(1),PT}(\mathbf{r})$.

However, GHIB noted that the correlation potential $v_{c\sigma}([n]; \mathbf{r})$ is at least one order higher than $\hat{V}_{ee} - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} v_{ux\sigma}([n]; \mathbf{r}_i)$, so in order to get a consistent

second-order approximation, the second term on the right-hand side of Eq. (18) is effectively a higher-order energy contribution.

We point out some inferior features of $E_c^{(2),PT}$ to $E_c^{(2)}[n]$ as possible approximations to $E_c[n]$. The second-order energy $E_c^{(2),PT}$ is not a functional of the ground-state density $n(\mathbf{r})$ only and, in general, the highest occupied KS orbital corresponding to the potential derived from $E_c^{(2),PT}$ will no longer bear a rigorous connection to the ionization potential.^{36,37} For example, the converged self-consistent density is not exactly $n(\mathbf{r})$, if the system of interest is in the high-density limit. For such a system, $E_c^{(2)}[n]$ becomes the exact correlation functional and its functional derivative leads to the exact correlation potential.

We also note that $E_c^{(2),PT}$ is more negative than $E_c^{(2)}[n]$, which is often already too negative when compared with $E_c[n]$. The latter statement obviously follows from Eqs. (18) and (19) unless $\langle \varphi_{i\sigma} | v_{c\sigma}([n]; \mathbf{r}) | \varphi_{a\sigma} \rangle = 0$ for all pairs of occupied and unoccupied spin-orbitals. Following Hirata *et al.*,¹² Eq. (19) will be equality if and only if $v_{c\sigma}([n]; \mathbf{r})$ is a constant. Since $v_{c\sigma}([n]; \mathbf{r})$ is not generally a constant, the contribution from single excitations involving $v_{c\sigma}([n]; \mathbf{r})$ is not zero and as a result $E_c^{(2),PT} < E_c^{(2)}[n]$, in general. In conclusion, $E_c^{(2),PT}$ would not be a better choice than $E_c^{(2)}[n]$ as an approximation to $E_c[n]$. Even though there are numerical differences, they are expected to be very small, and effectively these differences are one order higher when compared to $E_c^{(2)}[n]$.

If we consider an exchange-only scheme, i.e., $v_{c\sigma}([n];\mathbf{r})=0$ in Eq. (3), we note that the PT approach leads to the same perturbation as in GLPT, Eq. (12). However, in this case $n(\mathbf{r})$ must be replaced by the ground-state density from the exchange-only calculation, namely $n^x(\mathbf{r})$. With this in mind, we define

$$E_c^{(2),PT-x} = E_{c,D}^{(2),PT-x} + \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma}^x | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}^x];\mathbf{r}) - v_{x\sigma}([n_\sigma^x];\mathbf{r}) | \varphi_{a\sigma}^x \rangle|^2}{\epsilon_{i\sigma}^x - \epsilon_{a\sigma}^x}$$

$$= E_{c,D}^{(2),PT-x} + \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma}^x | \hat{f}_\sigma([\varphi_{\text{occ}}^x];\mathbf{r}) | \varphi_{a\sigma}^x \rangle|^2}{\epsilon_{i\sigma}^x - \epsilon_{a\sigma}^x}. \tag{21}$$

The superscript “x” indicates that the one-particle orbitals and energies are associated with the exchange-only KS Hamiltonian. We note that Eq. (21) takes on the same functional form as Eq. (13), but with exchange-only orbitals and energies.

Very recently, Ivanov and Levy³² have considered an exchange-only scheme as one of their choices for a zero-order Hamiltonian used to derive correlation potentials from an integral equation DFT formulation.^{6,32} In this approach, the respective correlation potentials are derived by imposing specific density constraints for each order of perturbation.

GHIB SECOND-ORDER CORRELATION POTENTIAL

In this section, we address some issues associated with different second-order expressions for the correlation potential as discussed and implemented by GHIB. We shall dem-

onstrate that the second-order potential $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$, given by Eq. (36) in Ref. 1, is the same as the second-order potential $v_{c\sigma}^{(2)}([n];\mathbf{r})$ from GLPT. Although the two potentials are derived in quite different ways, they assume the same functional form due to the fact that the first-order density $n^{(1),\text{GL}}(\mathbf{r})$ is zero at each point of space. As a result, the two potentials keep the second-order density zero³⁸ as required by GL adiabatic PT.

In order to establish connections between $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$ and $v_{c\sigma}^{(2)}([n];\mathbf{r})$, we first note that Eq. (36) in Ref. 1 represents the projection of $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$ in an auxiliary basis set needed for the finite-basis-set implementation of $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$. [Formula (36) is the closed-shell analog of the general $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$.]

In the following, we study the specific σ -contribution to the sum over all single excitations in Eq. (13), namely,

$$E_{c\sigma,S}^{(2)}[n] = \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}];\mathbf{r}) - v_{x\sigma}([n_\sigma];\mathbf{r}) | \varphi_{a\sigma} \rangle \langle \varphi_{a\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}];\mathbf{r}) - v_{x\sigma}([n_\sigma];\mathbf{r}) | \varphi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}. \tag{22}$$

We note that the contributions from double excitations in Eq. (36) in Ref. 1 are identical to the components stemming from doubly-excited states in $v_{c\sigma}^{(2)}([n];\mathbf{r})$. Hence, we shall concern ourselves with the terms associated with singly-excited states. We take the functional derivative of Eq. (22) with respect to $n_\sigma(\mathbf{r})$ to obtain

$$v_{c\sigma,S}^{(2)}([n];\mathbf{r}) = - \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}];\mathbf{r}) - v_{x\sigma}([n_\sigma];\mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} \int [|\varphi_{i\sigma}(\mathbf{r}')|^2 - |\varphi_{a\sigma}(\mathbf{r}')|^2] X_{s\sigma}^{-1}(\mathbf{r}',\mathbf{r}) d\mathbf{r}'$$

$$+ \left\{ \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}];\mathbf{r}) - v_{x\sigma}([n_\sigma];\mathbf{r}) | \varphi_{a\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \right.$$

$$\times \left[\sum_{s=1,s \neq a}^{\infty} \frac{\langle \varphi_{s\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}];\mathbf{r}) - v_{x\sigma}([n_\sigma];\mathbf{r}) | \varphi_{i\sigma} \rangle}{\epsilon_{a\sigma} - \epsilon_{s\sigma}} \int \varphi_{s\sigma}(\mathbf{r}') \varphi_{a\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}',\mathbf{r}) d\mathbf{r}' \right.$$

$$+ \sum_{s=1,s \neq i}^{\infty} \frac{\langle \varphi_{a\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}}];\mathbf{r}) - v_{x\sigma}([n_\sigma];\mathbf{r}) | \varphi_{s\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{s\sigma}} \int \varphi_{i\sigma}(\mathbf{r}') \varphi_{s\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}',\mathbf{r}) d\mathbf{r}'$$

$$- \sum_{j=1}^{N_\sigma} \sum_{s=1,s \neq j}^{\infty} \frac{\langle \varphi_{a\sigma} \varphi_{s\sigma} | \varphi_{j\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \int \varphi_{s\sigma}(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}',\mathbf{r}) d\mathbf{r}'$$

$$\left. - \sum_{j=1}^{N_\sigma} \sum_{s=1,s \neq j}^{\infty} \frac{\langle \varphi_{a\sigma} \varphi_{j\sigma} | \varphi_{s\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \int \varphi_{j\sigma}(\mathbf{r}') \varphi_{s\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}',\mathbf{r}) d\mathbf{r}' \right\} + \text{c.c.} - \int n^{(1),\text{GL}}(\mathbf{r}') w_{x\sigma}(\mathbf{r}',\mathbf{r}) d\mathbf{r}', \tag{23}$$

where $w_{x\sigma}(\mathbf{r}', \mathbf{r})$ is the static exchange kernel, i.e., $w_{x\sigma}(\mathbf{r}', \mathbf{r}) \equiv \delta v_{x\sigma}([n_\sigma]; \mathbf{r}') / \delta n_\sigma(\mathbf{r})$. In the above equation, $X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r})$ is the effective inverse of $X_{s\sigma}(\mathbf{r}', \mathbf{r})$. The former is defined on the restricted space excluding all constant functions to ensure proper invertibility.¹² In Eq. (23), c.c. indicates the complex conjugate of the sum in the curly parentheses, and

$$\langle \varphi_{p\sigma} \varphi_{q\sigma} | \varphi_{s\sigma} \varphi_{t\sigma} \rangle = \int \int \frac{\varphi_{p\sigma}^*(\mathbf{r}) \varphi_{q\sigma}^*(\mathbf{r}') \varphi_{s\sigma}(\mathbf{r}) \varphi_{t\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}. \quad (24)$$

In our current notation, the contribution from single excitations in Eq. (36) in Ref. 1 can be readily re-expressed as

$$\begin{aligned} v_{c\sigma, S}^{(2), \text{GHIB}}(\mathbf{r}) = & - \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} \int [|\varphi_{i\sigma}(\mathbf{r}')|^2 - |\varphi_{a\sigma}(\mathbf{r}')|^2] X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & + \left\{ \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{\langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \right. \\ & \times \left[\sum_{s=1, s \neq a}^{\infty} \frac{\langle \varphi_{s\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{i\sigma} \rangle}{\epsilon_{a\sigma} - \epsilon_{s\sigma}} \int \varphi_{s\sigma}(\mathbf{r}') \varphi_{a\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \right. \\ & + \sum_{s=1, s \neq i}^{\infty} \frac{\langle \varphi_{a\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{s\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{s\sigma}} \int \varphi_{i\sigma}(\mathbf{r}') \varphi_{s\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & - \sum_{j=1}^{N_\sigma} \sum_{s=1, s \neq j}^{\infty} \frac{\langle \varphi_{a\sigma} \varphi_{s\sigma} | \varphi_{j\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \int \varphi_{s\sigma}(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & - \sum_{j=1}^{N_\sigma} \sum_{s=1, s \neq j}^{\infty} \frac{\langle \varphi_{a\sigma} \varphi_{j\sigma} | \varphi_{s\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \int \varphi_{j\sigma}(\mathbf{r}') \varphi_{s\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & + 2 \sum_{j=1}^{N_\sigma} \sum_{s=1, s \neq j}^{\infty} \frac{\langle \varphi_{s\sigma} \varphi_{a\sigma} | \varphi_{j\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \int \varphi_{s\sigma}(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & \left. + 2 \sum_{j=1}^{N_\sigma} \sum_{s=1, s \neq j}^{\infty} \frac{\langle \varphi_{j\sigma} \varphi_{a\sigma} | \varphi_{s\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \int \varphi_{j\sigma}(\mathbf{r}') \varphi_{s\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \right\} + \text{c.c.} \quad (25) \end{aligned}$$

To obtain Eq. (25), we have used the following definition:

$$f_{\sigma pq} \equiv \epsilon_{\sigma p} \delta_{pq} + \langle \varphi_{p\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) - v_{c\sigma}([n]; \mathbf{r}) | \varphi_{q\sigma} \rangle, \quad (26)$$

along with the assumption¹ that the correlation potential $v_{c\sigma}([n]; \mathbf{r})$ is at least one order higher than $\hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r})$. In this case, there is no term containing $v_{c\sigma}([n]; \mathbf{r})$ in Eq. (25). We note that all terms in Eqs. (23) and (25) are identical except the last one in Eq. (23), and the terms in the last two lines of Eq. (25). We further note that

$$\begin{aligned} & 2 \sum_{i=1}^{N_\sigma} \sum_{s=1, s \neq j}^{\infty} \frac{\langle \varphi_{s\sigma} \varphi_{a\sigma} | \varphi_{j\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \\ & \times \int \varphi_{s\sigma}(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & + 2 \sum_{j=1}^{N_\sigma} \sum_{s=1, s \neq j}^{\infty} \frac{\langle \varphi_{j\sigma} \varphi_{a\sigma} | \varphi_{s\sigma} \varphi_{i\sigma} \rangle}{\epsilon_{j\sigma} - \epsilon_{s\sigma}} \end{aligned}$$

$$\begin{aligned} & \times \int \varphi_{j\sigma}(\mathbf{r}') \varphi_{s\sigma}^*(\mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \\ & = 2 \int \int \int \frac{\varphi_{a\sigma}^*(\mathbf{r}_2) \varphi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 X_{s\sigma}(\mathbf{r}_1, \mathbf{r}') \\ & \times X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' d\mathbf{r}_1 \\ & = 2 \int \frac{\varphi_{a\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (27) \end{aligned}$$

The third line of Eq. (27) is a consequence of Eq. (5), and the fact that

$$\int X_{s\sigma}(\mathbf{r}_1, \mathbf{r}') X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' = \delta(\mathbf{r}_1 - \mathbf{r}).$$

Formula (27) is further manipulated with the common term in front of the square brackets in Eq. (25) to give rise to

$$\begin{aligned}
 & 2 \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \langle \varphi_{i\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{a\sigma} \rangle \\
 & \times \int \frac{\varphi_{a\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \text{c.c.} \\
 & = 2 \int \frac{n_\sigma^{(1),\text{GL}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \tag{28}
 \end{aligned}$$

In their original contribution, GHIB have introduced

$$\left\{ \frac{\delta}{\delta n_\sigma(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{\infty} \frac{|\langle \varphi_{i\sigma} | \hat{f}_\sigma([\varphi_{\text{occ}}]; \mathbf{r}) | \varphi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \right\} \Big|_{v_{c\sigma}(\mathbf{r})=0} \tag{29}$$

In this case, there is no term containing $w_{x\sigma}(\mathbf{r}, \mathbf{r}')$ whose form is quite involved. The static kernel $w_{x\sigma}(\mathbf{r}, \mathbf{r}')$ is eliminated by making use of

$$\frac{\delta \hat{f}_\sigma(\mathbf{r})}{\delta n_\sigma(\mathbf{r}')} = \frac{\delta}{\delta n_\sigma(\mathbf{r}')} \{ \hat{h}(\mathbf{r}) + \hat{v}_{ux\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) \}$$

and

$$\hat{f}_\sigma(\mathbf{r})|_{v_{c\sigma}(\mathbf{r})=0} = \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}).$$

Similarly, the contributions from single excitations in Eq. (25) can be viewed as derived from $E_{c\sigma,s}^{(2)}[n]$ by replacing the functional derivative that appears in the last two lines of Eq. (23), i.e.,

$$\begin{aligned}
 & \frac{\delta}{\delta n_\sigma(\mathbf{r}')} \{ \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) \} \\
 & = \frac{\delta \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r})}{\delta n_\sigma(\mathbf{r}')} - w_{x\sigma}(\mathbf{r}, \mathbf{r}'), \tag{30}
 \end{aligned}$$

with

$$\begin{aligned}
 & \frac{\delta}{\delta n_\sigma(\mathbf{r}')} \left\{ 2 \sum_{k=1}^{N_\sigma} \int \frac{\varphi_{k\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) \right\} \\
 & = \frac{2}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r})}{\delta n_\sigma(\mathbf{r}')} \tag{31}
 \end{aligned}$$

By noticing the difference between Eqs. (30) and (31), we easily confirm that $-\int n^{(1),\text{GL}}(\mathbf{r}') w_{x\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'$ in Eq. (23) is replaced by $2 \int (n_\sigma^{(1),\text{GL}}(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}'$ in Eq. (25).

Clearly, the response functions $w_{x\sigma}(\mathbf{r}, \mathbf{r}')$ and $2/|\mathbf{r}-\mathbf{r}'|$ are different, and therefore $v_{c\sigma}^{(2)}([n]; \mathbf{r})$ and $v_{c\sigma}^{(2),\text{GHIB}}([n]; \mathbf{r})$ would be different unless the integrals

$$- \int n^{(1),\text{GL}}(\mathbf{r}') w_{x\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'$$

and

$$2 \int (n_\sigma^{(1),\text{GL}}(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}'$$

instead of

$$- \int n^{(1),\text{GL}}(\mathbf{r}') w_{x\sigma}(\mathbf{r}', \mathbf{r}) d\mathbf{r}'.$$

In order to eliminate the possible appearance of $w_{x\sigma}(\mathbf{r}, \mathbf{r}')$, the contribution from single excitations in $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$ is obtained by means of

$$2 \int (n_\sigma^{(1),\text{GL}}(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}'$$

are identical. However, both integrals are equal to zero due to the fact that the first-order density $n_\sigma^{(1),\text{GL}}(\mathbf{r})$ is zero at each point of space according to Eq. (15). As a result, $v_{c\sigma}^{(2),\text{GHIB}}(\mathbf{r})$ is precisely the same as $v_{c\sigma}^{(2)}([n]; \mathbf{r})$, when Eq. (13) is used as a starting point. The implementation of Eq. (36) in Ref. 1 is effectively the first finite-basis-set realization of the potential derived from $E_c^{(2)}[n]$.

Furthermore, unlike the exchange-only OEP, the KS orbitals here are generated in the presence of $v_{c\sigma}^{(2)}([n]; \mathbf{r})$, which is added to the exchange-only KS Hamiltonian. When the second-order energy is evaluated with Eq. (13), then we have an exact correspondence with GLPT(2). Alternatively, if Eq. (9) is used, we can estimate the contribution of the term containing $v_{c\sigma}^{(2)}([n]; \mathbf{r})$ on the right-hand side of Eq. (18). We note that the second-order energies in Eqs. (9) and (13) can be related through $\{E_c^{(2),\text{PT}}\}|_{v_{c\sigma}(\mathbf{r})=0} = E_c^{(2)}[n]$.

In order to demonstrate the validity of Eqs. (18) and (19), we refer to the numerical results in Table I, in Ref. 1. For *any* two-electron diamagnetic density, $E_c^{(2)}[n] = E_{c,D}^{(2),\text{PT}}$,^{29,30} i.e., there is no contribution from single excitations in Eq. (13). As a result, the scheme denoted by OEP-MBPT(2)D corresponds to GLPT(2) in terms of the second-order potential and functional. Note that in Eqs. (23) and (25), $v_{c\sigma,s}^{(2)}([n]; \mathbf{r})=0$ for any two-electron diamagnetic density since $\langle \varphi_{a\sigma} | \hat{v}_{x\sigma}^{\text{HF}}([\varphi_{\text{occ}\sigma}]; \mathbf{r}) - v_{x\sigma}([n_\sigma]; \mathbf{r}) | \varphi_{i\sigma} \rangle = 0$. Further, the scheme OEP-MBPT(2)SD (Ref. 1) uses the same potential, and the converged KS orbitals are the same as the ones associated with the potential from GLPT(2). To numerically support this fact, we point out that the exchange energies corresponding to OEP-MBPT(2)SD and OEP-MBPT(2)D are identical. However, the correlation energies from OEP-MBPT(2)SD and OEP-MBPT(2)D are not the same even though the orbitals are the same. The difference is exactly the contribution stemming from

$$2 \sum_{\alpha=2}^{\infty} \frac{|\langle \varphi_{1\sigma} | v_{c\sigma}([n]; \mathbf{r}) | \varphi_{\alpha\sigma} \rangle|^2}{\epsilon_{1\sigma} - \epsilon_{\alpha\sigma}},$$

as Eq. (18) dictates. Clearly, for the same set of orbitals, the functional $E_c^{(2),PT}$ is more negative than $E_c^{(2)}[n]$.

We emphasize the fact that the potential given in Eq. (36) in Ref. 1, which was the objective of the study, is the finite basis-set realization of the potential associated with $E_c^{(2)}[n]$.

It is worth mentioning that the potential derived from $E_c^{(2),PT-x}$ in Eq. (21) accepts exactly the same form as the one given by Eq. (25), with the KS orbitals and energies being replaced by their exchange-only analogs. If $v_{c\sigma}^{(2),PT-x}(\mathbf{r}) [\equiv \delta E_c^{(2),PT-x} / \delta n_{\sigma}(\mathbf{r})]$ is included in self-consistent calculations, then the final results are identical to those obtained from GLPT(2) since both potentials have the same functional form, and both expressions are evaluated at the converged orbitals. In addition, the implementation of $v_{c\sigma}^{(2),GHIB}(\mathbf{r})$ is equivalent to the second-order computational schemes discussed in Ref. 32. See the potential given by the combination of Eqs. (22)–(24).³² According to Ivanov and Levy,³² one starts with the OEP exchange-only Hamiltonian, and considers a perturbation expansion for the unknown correlation potential. Each correlation potential component in the series is determined by solving an integral equation derived from the constraint that density from the standard PT approach is attainable from a generalized KS Hamiltonian.³² A generalization of the integral equation formulation to infinite order in PT and coupled-cluster theory will be presented elsewhere.³⁸

We also remark that the correlation functional and potential corresponding to OEP-MBPT(2)D (Ref. 1) can be directly included in a generalized KS scheme. In this case, one uses the nonlocal HF exchange potential along with a local correlation potential derived from $E_c^{HF}[n]$,^{15,16,39} or from the integral equation approach.^{6,32} The correlation energy functional $E_c^{HF}[n]$ is defined^{15,16,39} as

$$\begin{aligned} E_c^{HF}[n] &= \langle \Psi_n | \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \hat{V}_{ee} | \Psi_n \rangle \\ &\quad - \langle \Phi_n^{HF} | \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \hat{V}_{ee} | \Phi_n^{HF} \rangle \\ &= \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n^{HF} | \hat{T} + \hat{V}_{ee} | \Phi_n^{HF} \rangle, \end{aligned} \quad (32)$$

where the single determinant Φ_n^{HF} minimizes the expectation value of $\hat{H}[n]$, but it is constrained to yield the true ground-state density $n(\mathbf{r})$. When this generalized KS method is used, one obtains $n(\mathbf{r})$ upon self-consistency. Since $E_c^{HF}[n]$ satisfies the following scaling identity:^{15,29,30}

$$\lim_{\gamma \rightarrow \infty} E_c^{HF}[n_{\gamma}] = E_{c,D}^{(2),PT}, \quad (33)$$

the hybrid scheme based on OEP-MBPT(2)D (Ref. 1) is exact within the high-density scaling limit. This scheme will be the method of choice for ground-state calculations. It is ex-

pected to lead to an easier self-consistent field convergence since it does not require solving for the local exchange potential at each iteration.

Having established some connections between the functionals and the potentials studied by GHIB, and the second-order components of different KS-type schemes, we can pursue further extensions by means of the adiabatic integration formula.^{40,41} In this approach, the full correlation functional $E_c[n]$ can be obtained^{16,42–44} via

$$E_c[n] = \int_0^1 \frac{\partial E_c^{\alpha}[n]}{\partial \alpha} d\alpha, \quad (34)$$

where

$$\lim_{\alpha \rightarrow 0} \left\{ \alpha^{-1} \frac{\partial E_c^{\alpha}[n]}{\partial \alpha} \right\} = 2E_c^{(2)}[n]. \quad (35)$$

The quantity $2E_c^{(2)}[n]$ is especially important because it is the initial slope¹⁵ (slope at zero coupling constant) in the adiabatic connection formula for the correlation energy.^{16,40,41,45–49} Promising results in constructing correlation energy functionals by making use of Eqs. (34) and (35) have been reported by Ernzerhof,⁴⁸ and by Perdew and co-workers.^{49–53}

Expressions similar to Eqs. (34) and (35), hold for $E_c^{HF}[n]$ and $E_c^{QC}[n^{HF}]$.^{30,39} The latter functional is defined^{54–56} as

$$\begin{aligned} E_c^{QC}[n^{HF}] &= \langle \Psi_n | \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \hat{V}_{ee} | \Psi_n \rangle \\ &\quad - \langle \Phi_n^{HF} | \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \hat{V}_{ee} | \Phi_n^{HF} \rangle, \end{aligned} \quad (36)$$

where the single determinant Φ_n^{HF} minimizes the expectation value of $\hat{H}[n]$ without the constraint to yield $n(\mathbf{r})$. In other words, Φ_n^{HF} is the HF single determinant that yields the HF density $n^{HF}(\mathbf{r})$. The functional $E_c^{QC}[n^{HF}]$ is meant to be added to the converged HF energy as a tack-on correlation functional to produce the exact ground-state energy.^{54–58} Formal extensions of the generalized Kohn–Sham and hybrid formulations have been studied in depth in Refs. 59 and 60.

A simple realization of a computational scheme based on the exact second-order contribution might be given by

$$E_c[n] \approx E_c^{(2)}[n] + \{ E_c^{APP}[n] - \lim_{\gamma \rightarrow \infty} E_c^{APP}[n_{\gamma}] \}, \quad (37)$$

where $E_c^{APP}[n]$ is an explicit density approximation with bounded high-density limit. In contrast to Eq. (13), the local-density approximation (LDA) correlation energy diverges as $-\ln \gamma$, as $\gamma \rightarrow \infty$, because of the Gell–Mann and Brueckner contribution to the correlation energy per particle of a uniform electron gas.²⁷ In Eq. (37), the second-order component $E_c^{(2)}[n]$ is calculated by means of Eq. (13). We note that in the finite-basis-set realization of KS schemes, the infinite summation over unoccupied orbitals becomes finite. Similarly, one can construct approximations to $E_c^{HF}[n]$ and $E_c^{QC}[n^{HF}]$ by using $E_{c,D}^{(2),PT}$.

It is expected that Perdew–Burke–Ernzerhof (PBE),⁶¹ or Wilson–Levy (WL) (Ref. 62) functionals would be good choices for using Eq. (37) to generate improved approximations with particular emphasis on their potentials. As previously demonstrated^{29,30} for certain model densities, the second-order components of PBE and WL produce very good results for some exact conditions. As a result, when Eq. (37) is utilized, the new hybrid correlation functionals would lead to substantially improved shapes of their corresponding potentials without worsening the quality of the new functionals as approximations to $E_c[n]$ and $E_c^{\text{HF}}[n]$.

CLOSING REMARKS

New formal connections between the second-order potential advanced by GHIB and the second-order correlation potential from GLPT are established. It is proven that GHIB second-order potential is the same as $v_{c\sigma}^{(2)}([n];\mathbf{r})$ from GLPT, and thus provides the first self-consistent finite-basis-set implementation of a KS Hamiltonian exact in the high-density limit.

Different second-order energy expressions are considered and new relationships are derived. It is demonstrated that for the same set of KS orbitals the second-order expression from common perturbation theory, $E_c^{(2),\text{PT}}$, constitutes a lower bound for the high-density limit of $E_c[n]$, i.e., $E_c^{(2),\text{PT}} < E_c^{(2)}[n]$. It is argued that $E_c^{(2)}[n]$ provides a better choice than $E_c^{(2),\text{PT}}$ as an approximation to $E_c[n]$.

A new type of second-order energy functional $E_c^{(2),\text{PT}-x}$ is introduced. It is defined through second-order PT applied to the exchange-only OEP formalism. The functional $E_c^{(2),\text{PT}-x}$ takes on the same form as $E_c^{(2)}[n]$, but with exchange-only orbitals and energies. When $E_c^{(2),\text{PT}-x}$ and $v_c^{(2),\text{PT}-x}(\mathbf{r})$ are included in self-consistent calculations, the final results are identical to those obtained from GLPT(2) since all expressions are evaluated with the converged KS orbitals. In turn, $v_c^{(2),\text{PT}-x}(\mathbf{r})$ leads to the same KS self-consistent orbitals and energies as the ones from $v_{c\sigma}^{(2)}([n];\mathbf{r})$. The potential $v_c^{(2),\text{PT}-x}(\mathbf{r})$ can be derived without explicitly taking functional derivatives, via an integral equation formulation of density functional PT.^{6,32}

As discussed in Ref. 32, the finite-basis-set implementations of second- and higher-order potentials, eliminate the long-range divergence^{32,63} of the correlation potentials derived from PT approaches. The undesired divergence stems from the fact that the second-order density does not vanish at infinity.³² However, when finite basis sets whose basis functions vanish at infinity are used, the second-order density decays to zero. As a result, the second-order potentials vanish as $|\mathbf{r}| \rightarrow \infty$. In addition, the finite-basis-set implementation of the OEP involves a projection method^{9,10,12,14,32} for solving the required integral equations, and by construction all potentials are expanded in terms of functions that vanish at infinity.

The shapes of the potentials presented by GHIB are in a very good agreement with the highly accurate potentials by Umrigar and co-workers.^{64,65} The finite-basis-set implementation of KS schemes featuring explicit orbital dependent exchange-correlation potentials open new opportunities not

only for very accurate ground-state calculations, but also for developments of improved time-dependent approaches as recently demonstrated by Hirata *et al.*⁶⁶

Different computational schemes based upon an explicit determination of the corresponding second-order energies are discussed. Possible choices for conventional (explicit-density-dependent) correlation energy functionals, which can be combined with orbital dependence second-order energies, are proposed.

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