

***Ab initio* density functional theory: OEP-MBPT(2). A new orbital-dependent correlation functional**

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(Received 23 July 2001; accepted 29 November 2001)

Using the optimized effective potential (OEP) method in conjunction with an orbital-dependent correlation functional developed on the basis of second-order many-body perturbation theory [MBPT(2)], we perform *ab initio* correlated density functional calculations. Unlike other density functional methods, this offers the first correlation approximation in a converging series of approximations analogous to that in wave function theory. The OEP-MBPT(2) correlation potentials of the helium isoelectronic series and the neon atom are in excellent agreement with prior quantum Monte Carlo (QMC) results, while the widely used conventional approximate density functional theory correlation potentials have qualitatively incorrect behavior. Furthermore, the correlation energies, total energies, and the highest occupied orbital energies calculated by the OEP-MBPT(2) method are also remarkably accurate. Unlike QMC, our procedure can be applied to general molecules. © 2002 American Institute of Physics. [DOI: 10.1063/1.1445117]

I. INTRODUCTION

Density functional theory (DFT) based on the Kohn–Sham (KS) scheme^{1,2} is widely used to study the electronic structure of matter in physics and chemistry. Since the quality of the results is determined by the approximations used for the exchange–correlation functionals, the development of more accurate and at the same time relatively simple and practical approximate functionals is of primary importance. The newest approach for developing exchange–correlation functionals might be called *ab initio* DFT,³ since it alleviates the primary failing of DFT, namely, that there is no way to guarantee convergence to the right answer. The basic idea is to take an exchange–correlation energy expression established in the *ab initio* wave function theory and to use it as an explicitly orbital-dependent (and hence implicitly density-dependent) exchange–correlation functional in DFT. This universal and parameter-free methodology allows us to directly exploit knowledge from wave function theory and systematically improve exchange–correlation potentials in the KS DFT scheme.

One of the approaches that substantiates *ab initio* DFT is the optimized effective potential (OEP) method.^{4–6} In this approach, a given total energy functional depending explicitly on single-particle orbitals is minimized under the constraint that these orbitals are the solutions of a single-particle KS equation with a local effective potential. Originally, the exchange-only OEP method was derived by Talman and Shadwick⁴ following the idea of Sharp and Horton⁷ as a method of giving a variationally optimal local potential whose associated single-particle orbitals minimize the Hartree–Fock (HF) energy expression. Later in the context of DFT, the OEP equation was rederived from a different

viewpoint by Sham and Schlüter⁸ and by Görling and Levy.⁹ The solution of the full integral equation of the OEP method is numerically very demanding and has been achieved so far only for systems with spherical symmetry^{4,6} or periodic systems.^{10,11} In practice, an approximation proposed by Krieger, Li, and Iafrate^{6,12,13} (KLI) is frequently used. Recently, the linear-combination-of-atomic-orbital (LCAO) algorithms for the OEP method have been developed recently by our group¹⁴ and by Görling.¹⁵ They permit routine OEP calculations for atoms and molecules with Gaussian-type basis sets, but without any further approximation, and consequently extend the applicability of the OEP method significantly.

The incorporation of electron correlation into the OEP formalism has been the subject of substantial interest since the development of the exchange-only OEP method. In most of the existing applications, the exchange-only OEP functional has been combined with conventional density functionals for the correlation energy,^{10,16,17} i.e., the local density approximation (LDA), the generalized gradient approximation (GGA), or the semiempirical Colle–Salvetti functional.^{18,19} It is well known, however, that the success of LDA- or GGA-type functionals relies to some extent on a cancellation of errors between the exchange and correlation, which is no longer maintained if a highly accurate exchange functional such as exchange-only OEP is used. Several approaches to derive approximate correlation energy functionals suitable for the OEP method have been reported in the literature. Görling and Levy^{9,20} proposed a series of orbital-dependent correlation functionals from the coupling-constant perturbation expansion, which converges to a formally exact representation of the correlation functional. Such a development has also been studied by Ivanov and Bartlett.²¹ Casida²² considered including correlation effects in the OEP method with the aid of the Sham–Schlüter equation and second-order perturbative approximation to Dyson’s self-energy.

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Grabo *et al.*⁵ offered another scheme to derive a correlation functional using a particular perturbative expansion for the interacting Hamiltonian, and derived equations involving the Green's functions for the exchange-correlation potential and energy. Unfortunately, there are no numerical examples or practical applications based on any of the proposed formalisms. Recently, however, Engel and co-workers^{23,24} evaluated correlation energies of the Görling–Levy (GL) perturbation theory, although they neglected the single-excitation contribution, and used the converged exchange-only OEP results. They did not achieve self-consistency between the exchange-correlation potential and orbitals because the rigorous solution of the corresponding correlated OEP equation was too complicated.

In this paper, we perform correlated self-consistent OEP calculations for some atoms for which there exist essentially exact correlation energies and potentials.^{25,26} The OEP correlation energy and potential expressions are based on the simplest *ab initio* wave function theory correlation energy expression, namely second-order many-body perturbation theory [MBPT(2)], and hence we call this new orbital-dependent correlation functional treatment OEP-MBPT(2). In this OEP-MBPT(2) correlated calculations, we solve the OEP integral equation for a given MBPT(2) correlation functional within the basis set without any further approximation, and we achieve self-consistency between the potential and orbitals. To test our new correlation functional, we compare the correlation potentials obtained from our MBPT(2) correlation functional with the exact correlation potential^{25,26} and also with the potentials obtained from widely used local and gradient-corrected correlation functionals. We find that, although the total, exchange, or correlation energies calculated with the standard DFT functionals can be reasonable, the corresponding correlation potentials show incorrect behavior. In contrast, our OEP-MBPT(2) correlation potentials are in qualitatively good agreement in both shape and magnitude with the exact ones, and are a dramatic improvement over previously developed correlation functionals. As a consequence, our OEP-MBPT(2) correlation functional can perform well for total and correlation energies, for which conventional explicit correlation density functionals work well, but also accurately reproduces the correlation potentials and orbital energies, for which the latter functionals fail. These results clearly indicate that not only the exchange-correlation energy but also the potential should be employed as a criterion in developing functionals.

II. OEP METHOD AND OEP-MBPT(2) CORRELATION POTENTIAL

A. The OEP method

In the KS DFT method,^{27,28} we express the total energy of the system as a sum of the kinetic energy of a system of noninteracting particles, the Coulombic interaction energy of these particles, and interaction energy between the electrons and the external potential $v(\mathbf{r})$ and the exchange-correlation energy,

$$E[\rho_\alpha, \rho_\beta] = \sum_{\sigma}^{\alpha, \beta} \sum_i^{N_\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_{i\sigma}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} \rho(\mathbf{r})v(\mathbf{r}) + E_{xc}[\rho_\alpha, \rho_\beta], \quad (1)$$

where $\rho(\mathbf{r})$ is the electron density and N_σ is the number of σ -spin electrons. The spin densities $\rho_\alpha(\mathbf{r})$, $\rho_\beta(\mathbf{r})$, and the KS orbitals $\{\phi_{p\sigma}\}$ are obtained by self-consistently solving the KS equation⁷

$$\left\{ -\frac{1}{2} \nabla^2 + v_{s\sigma}[\rho_\alpha, \rho_\beta](\mathbf{r}) \right\} \phi_{p\sigma}(\mathbf{r}) = \epsilon_{p\sigma} \phi_{p\sigma}(\mathbf{r}), \quad \sigma = \alpha, \beta \quad (2)$$

where

$$\rho_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\phi_{i\sigma}(\mathbf{r})|^2. \quad (3)$$

The local effective or KS potential $v_{s\sigma}[\rho_\alpha, \rho_\beta](\mathbf{r})$ in Eq. (2) can be written as

$$v_{s\sigma}[\rho_\alpha, \rho_\beta](\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{xc\sigma}[\rho_\alpha, \rho_\beta](\mathbf{r}), \quad (4)$$

where

$$V_{xc\sigma}[\rho_\alpha, \rho_\beta](\mathbf{r}) = \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma(\mathbf{r})} \quad (5)$$

is the local exchange-correlation potential formally defined as the functional derivative of the exchange-correlation energy with respect to the electron density, $\rho_\sigma(\mathbf{r})$.

The exchange spin components of the exchange-correlation functional $E_{xc}[\rho_\alpha, \rho_\beta]$, where $E_{xc}[\rho_\alpha, \rho_\beta] = E_{x,\alpha}[\rho_\alpha] + E_{x,\beta}[\rho_\beta] + E_c[\rho_\alpha, \rho_\beta]$, are defined via

$$\sum_{\sigma}^{\alpha, \beta} E_{x,\sigma}[\rho_\sigma] = \langle \Phi_0 | \hat{V}_{ee} | \Phi_0 \rangle - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \quad (6)$$

where \hat{V}_{ee} is the electron-electron interaction operator. In Eq. (6) Φ_0 is the KS single determinant built from the N_σ , $\sigma = \alpha, \beta$, lowest-energy solutions to Eq. (2). The correlation energy functional $E_c[\rho_\alpha, \rho_\beta]$ is given by

$$E_c[\rho_\alpha, \rho_\beta] = \langle \Psi_{\rho_\alpha, \rho_\beta} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_\alpha, \rho_\beta} \rangle - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_{\sigma}^{\alpha, \beta} \left\{ E_{x,\sigma}[\rho_\sigma] - \frac{1}{2} \sum_{i=1}^{N_\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \nabla^2 \phi_{i\sigma}(\mathbf{r}) \right\}, \quad (7)$$

where \hat{T} is the kinetic energy operator and $\Psi_{\rho_\alpha, \rho_\beta}$ is the true ground-state wave function of the interacting system that yields the ground-state density $\rho(\mathbf{r})$, which is a sum of the spin densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$, i.e., $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})$. By construction the KS single determinant Φ_0 yields $\rho_\sigma(\mathbf{r})$ for $\sigma = \alpha, \beta$. Pure-state v representability is assumed.²⁹

In the OEP method, where we do not restrict ourselves to exchange-only OEP of Talman and Shadwick⁴ but also “correlated OEP,” the exchange-correlation functional is an explicit, usually approximate, functional of spin orbitals $E_{xc}^{\text{OEP}}[\{\phi_{p\sigma}\}]$ and thus only an implicit functional of the spin densities ρ_α and ρ_β , in contrast to the conventional explicitly density-dependent exchange-correlation functionals. The superscript OEP indicates that the functionals and potentials are now explicitly orbital dependent. The spin orbitals $\{\phi_{p\sigma}\}$ are the solutions to the single-particle KS equation (2) with a local effective OEP potential $v_{s\sigma}^{\text{OEP}}(\mathbf{r})$. This is equivalent to requiring $v_{s\sigma}^{\text{OEP}}(\mathbf{r})$ to be a local potential determined by the condition that its corresponding orbitals be the ones that minimize the energy functional (1).⁴ The stationarity condition

$$\left. \frac{\delta E^{\text{OEP}}[\{\phi_{p\sigma}\}]}{\delta v_{s\sigma}(\mathbf{r})} \right|_{v_{s\sigma}=v_{s\sigma}^{\text{OEP}}} = 0 \quad (8)$$

leads to the following by virtue of the chain rule for functional derivatives:

$$\sum_{\sigma'} \sum_{\beta} \int d\mathbf{r}' \left\{ \frac{\delta E^{\text{OEP}}[\{\phi_{q\tau}\}]}{\delta \phi_{p\sigma'}(\mathbf{r}')} \frac{\delta \phi_{p\sigma'}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r})} \right\}_{v_{s\sigma}=v_{s\sigma}^{\text{OEP}}} + \text{c.c.} \Bigg\} = 0. \quad (9)$$

In the above equations and in the following, we use the convention that i, j, k label occupied orbitals, a, b, c label virtual orbitals, and p, q, r label either. For a given approximation of $E_{xc}^{\text{OEP}}[\{\phi_{p\sigma}\}]$, the first factor in the integrand in Eq. (9) is easily derived. The second factor requires the standard first-order perturbation theory for an infinitesimal perturbation potential $\delta v_{s\sigma}$,

$$\frac{\delta \phi_{p\sigma'}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r})} = \delta_{\sigma, \sigma'} \sum_{q \neq p} \frac{\phi_{p\sigma}(\mathbf{r}) \phi_{q\sigma}^*(\mathbf{r}')}{\epsilon_{p\sigma} - \epsilon_{q\sigma}} \phi_{q\sigma}(\mathbf{r}'). \quad (10)$$

Inserting the functional derivative of Eq. (1) and using Eq. (10) into Eq. (9), we obtain

$$\sum_p \sum_{q \neq p} \left\{ \frac{\phi_{q\sigma}^*(\mathbf{r}) \phi_{p\sigma}(\mathbf{r})}{\epsilon_{p\sigma} - \epsilon_{q\sigma}} \int d\mathbf{r}' \phi_{p\sigma}^*(\mathbf{r}') \times \left[-\frac{1}{2} \nabla^2 + \int d\mathbf{r}'' \frac{\rho(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} + v(\mathbf{r}') + \frac{1}{\phi_{p\sigma}^*(\mathbf{r}') \delta \phi_{p\sigma}(\mathbf{r}')} \frac{\delta E_{xc}^{\text{OEP}}}{\delta \phi_{p\sigma}(\mathbf{r}')} \right] \times \phi_{q\sigma}(\mathbf{r}') + \text{c.c.} \right\} = 0. \quad (11)$$

Using Eq. (2), we can rewrite the above equation in terms of $v_{s\sigma}^{\text{OEP}}$,

$$\sum_p \int d\mathbf{r}' \left\{ v_{s\sigma}^{\text{OEP}}(\mathbf{r}') - \int d\mathbf{r}'' \frac{\rho(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} - v(\mathbf{r}') - \frac{1}{\phi_{p\sigma}^*(\mathbf{r}') \delta \phi_{p\sigma}(\mathbf{r}')} \frac{\delta E_{xc}^{\text{OEP}}}{\delta \phi_{p\sigma}(\mathbf{r}')} \right\} \times \sum_{q \neq p} \frac{\phi_{q\sigma}^*(\mathbf{r}) \phi_{q\sigma}(\mathbf{r}')}{\epsilon_{p\sigma} - \epsilon_{q\sigma}} \phi_{p\sigma}^*(\mathbf{r}') \phi_{p\sigma}(\mathbf{r}) + \text{c.c.} \Bigg\} = 0, \quad (12)$$

and identifying

$$V_{xc\sigma}^{\text{OEP}}(\mathbf{r}) = v_{s\sigma}^{\text{OEP}}(\mathbf{r}) - \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - v(\mathbf{r}), \quad (13)$$

we can rewrite Eq. (12) in the standard form of the OEP equation

$$\sum_p \int d\mathbf{r}' \left[\phi_{p\sigma}^*(\mathbf{r}') \left\{ V_{xc\sigma}^{\text{OEP}}(\mathbf{r}') - \frac{1}{\phi_{p\sigma}^*(\mathbf{r}') \delta \phi_{p\sigma}(\mathbf{r}')} \frac{\delta E_{xc}^{\text{OEP}}}{\delta \phi_{p\sigma}(\mathbf{r}')} \right\} G_{p\sigma}(\mathbf{r}, \mathbf{r}') \phi_{p\sigma}(\mathbf{r}) + \text{c.c.} \right] = 0, \quad (14)$$

where

$$G_{p\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{q \neq p} \frac{\phi_{q\sigma}(\mathbf{r}) \phi_{q\sigma}^*(\mathbf{r}')}{\epsilon_{p\sigma} - \epsilon_{q\sigma}}. \quad (15)$$

The OEP integral equation (14) has to be solved for the exchange-correlation potential V_{xc}^{OEP} in each KS (OEP) iteration, and the self-consistency, Eq. (2), must be achieved at the end.

By rewriting Eq. (14), we can formally represent the exchange-correlation potential as

$$V_{xc\sigma}^{\text{OEP}}(\mathbf{r}) = \sum_p \int \left\{ \frac{\delta E_{xc}^{\text{OEP}}[\{\phi_{q\tau}\}]}{\delta \phi_{p\sigma}(\mathbf{r}')} \frac{1}{\phi_{p\sigma}^*(\mathbf{r}')} + \text{c.c.} \right\} X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}', \quad (16)$$

where $X_{s\sigma}^{-1}(\mathbf{r}', \mathbf{r})$ is the inverse of the static KS linear response function of a system of noninteracting particles

$$X_{s\sigma}(\mathbf{r}, \mathbf{r}') = \frac{\delta \rho_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}')} = \sum_i \sum_a \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{a\sigma}(\mathbf{r}) \phi_{a\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}')}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \quad (17)$$

It should be understood that $X_{s\sigma}^{-1}(\mathbf{r}, \mathbf{r}')$ is defined in the domain of the eigenfunctions of $X_{s\sigma}(\mathbf{r}, \mathbf{r}')$ and singularities in $X_{s\sigma}(\mathbf{r}, \mathbf{r}')$ do not pose any formal problem in Eq. (16).³⁰ In the LCAO-OEP procedure, the potential and the response function (17) are represented in a real atomic orbital (AO) basis $\{g_p(\mathbf{r})\}$ as

$$V_{xc\sigma}^{\text{OEP}}(\mathbf{r}) = \sum_p c_p g_p(\mathbf{r}) \quad (18)$$

and

$$X_{s\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{p, q} (\mathbf{X}_{s\sigma})_{pq} g_p(\mathbf{r}) g_q(\mathbf{r}'), \quad (19)$$

where

$$(\mathbf{X}_{s\sigma})_{pq} = \sum_{i, a} \left(\frac{(i_\sigma a_\sigma | p)(i_\sigma a_\sigma | q)^*}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \right) \quad (20)$$

and $(r_\sigma s_\sigma | p)$ is the overlap integral of the orbitals $\phi_{r\sigma}(\mathbf{r})$, $\phi_{s\sigma}(\mathbf{r})$, and the orthonormal auxiliary Gaussian function $g_p(\mathbf{r})$,

$$(r_{\sigma} s_{\sigma} | p) = \int \phi_{r\sigma}^*(\mathbf{r}) \phi_{s\sigma}(\mathbf{r}) g_p(\mathbf{r}) d\mathbf{r}. \quad (21)$$

Hence, $X_{s\sigma}^{-1}(\mathbf{r}, \mathbf{r}')$ can be expanded by the same basis as

$$X_{s\sigma}^{-1}(\mathbf{r}, \mathbf{r}') = \sum_{p,q} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_{p\sigma}^*(\mathbf{r}) g_{q\sigma}(\mathbf{r}'), \quad (22)$$

where the inverse matrix $\mathbf{X}_{s\sigma}^{-1}$ can be obtained by singular value decomposition of $\mathbf{X}_{s\sigma}$.

The exchange-correlation energy functional can be partitioned into the exchange and correlation components, i.e., $E_{xc}^{\text{OEP}}[\{\phi_{p\tau}\}] = E_x^{\text{OEP}}[\{\phi_{p\tau}\}] + E_c^{\text{OEP}}[\{\phi_{p\tau}\}]$, and likewise the exchange and correlation potentials can be separated, as the OEP equation is a linear integral equation. Choosing the HF exchange energy functional in terms of KS orbitals as the exchange functional E_x^{OEP} ,

$$E_x^{\text{OEP}}[\{\phi_{p\tau}\}] = -\frac{1}{2} \sum_{\sigma}^{\alpha, \beta} \sum_{i,j}^{N_{\sigma}} (i_{\sigma} j_{\sigma} | j_{\sigma} i_{\sigma}), \quad (23)$$

we obtain the exchange potential in the following form:^{3,14}

$$V_{x\sigma}^{\text{OEP}}(\mathbf{r}) = -\sum_{p,q} \sum_{i,j,a} \left[\frac{(i_{\sigma} j_{\sigma} | j_{\sigma} a_{\sigma})}{\epsilon_{i_{\sigma}} - \epsilon_{a_{\sigma}}} (a_{\sigma} i_{\sigma} | q) \right] \times (\mathbf{X}_{s\sigma}^{-1})_{qp} g_p(\mathbf{r}) + \text{c.c.} \quad (24)$$

where the *chemical* notation for two-electron integrals is used:

$$(p_{\sigma} q_{\sigma} | r_{\sigma} s_{\sigma}) = \int \phi_{p\sigma}^*(\mathbf{r}) \phi_{q\sigma}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{r\sigma}^*(\mathbf{r}') \phi_{s\sigma}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (25)$$

B. The orbital-dependent correlation functional and potential

In this study, we shall employ an explicitly orbital-dependent correlation energy functional and potential on the basis of the second-order Rayleigh–Schrödinger (RS) perturbation theory expression. We start with the Hamiltonian of a system of interacting electrons in the standard normal order form:³¹

$$H = \sum_{p,q} f_{pq} \{p^{\dagger} q\} + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \{p^{\dagger} q^{\dagger} sr\} + \langle \Phi_0 | H | \Phi_0 \rangle \quad (26)$$

$$= \sum_p f_{pp} \{p^{\dagger} p\} + \sum_{\substack{p,q \\ p \neq q}} f_{pq} \{p^{\dagger} q\} + \hat{W} + \langle \Phi_0 | H | \Phi_0 \rangle, \quad (27)$$

where $\{p^{\dagger} q\}$ and $\{p^{\dagger} q^{\dagger} sr\}$ denotes the normal product of spin orbital second quantized operators and the last term $\langle \Phi_0 | H | \Phi_0 \rangle$ is the expectation value of the Hamiltonian in the KS determinant Φ_0 , which is the single (Slater) determinant built from the $N = N_{\alpha} + N_{\beta}$ lowest-energy spin orbitals, where N is the total number of electrons in system of inter-

est. The fully contracted part of the Hamiltonian is the expectation value. In the second term we use following notation for two electron integrals:

$$\langle pq || rs \rangle = (pr | qs) - (ps | qr). \quad (28)$$

In Eq. (26) we have introduced the usual Fock matrix elements defined in terms of KS-OEP spin orbitals:

$$f_{pq} = (p | h | q) + \langle p | \sum_j \int \phi_j^*(2) \times \frac{1}{r_{12}} (1 - P_{12}) \phi_j(2) d\tau_2 q \rangle$$

$$= (p | h | q) + \sum_j \{(pq | jj) - (pj | jq)\}, \quad (29)$$

where $(p | h | q)$ is the one-electron integral

$$(p | h | q) = \int \phi_p^*(\mathbf{r}) h(\mathbf{r}) \phi_q(\mathbf{r}) d\mathbf{r}, \quad (30)$$

and h is the *core Hamiltonian* (for a given electron) describing its kinetic energy and potential energy in the field of the nuclei.

In this study we choose the zero-order Hamiltonian H_0 for the perturbation expansion as follows:

$$H_0 = \sum_p \epsilon_p \{p^{\dagger} p\}. \quad (31)$$

From the usual RS perturbation theory, we can write the second-order many-body correlation energy expression [MBPT(2)] in the following form:

$$E_c^{(2)} = \langle \Phi_0 | (\hat{V}_{ee} - \hat{V}_{uxc}) R_0 (\hat{V}_{ee} - \hat{V}_{uxc}) | \Phi_0 \rangle, \quad (32)$$

[$\hat{V}_{uxc} = \sum_{i=1} V_{uxc}(i)$] but with the understanding that

$$V_{uxc} = \lambda V_x + \lambda V_c^{(2)} + \lambda \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (33)$$

which makes all other terms in Eq. (27) part of the perturbation, ordered by λ . It should be apparent that since the correlation potential $V_c^{(2)}$ is formally the functional derivative of $E_c^{(2)}$, it has to arise in second and higher orders of MBPT, while the exchange potential is first order. We temporarily introduce the “order parameter” λ to make this explicit. Hence, the energy functional that is only second-order in λ suppresses the $V_c^{(2)}$, meaning it is exactly the same functional as that in Görling–Levy perturbation theory. This distinction will be important below. The resolvent

$$R_0 = (E_0 - H_0)^{-1} Q, \quad (34)$$

where Q is the projector for the orthogonal complement to Φ_0 (i.e., single and double excitations), and $E_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle$. Henceforth, we use the simplified notation V_x and $V_c^{(2)}$ for the sum of α - and β -spin parts of the local effective exchange and correlation potentials, respectively. The sum of the α and β parts of the left-hand side of Eq. (16) is therefore identified as $V_x + V_c^{(2)}$. We can write this expression in a more explicit well-known spin orbital form:^{32,33}

$$E_c^{(2)} = E_{Dc}^{(2)} + E_{Sc}^{(2)}$$

$$= \frac{1}{2} \sum_{i,j,a,b} \frac{|(ia|jb)|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \frac{1}{2} \sum_{i,j,a,b} \frac{(ia|jb)(aj|bi)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$+ \sum_{i,a} \frac{|f_{ia}|^2}{\epsilon_i - \epsilon_a}, \quad (35)$$

where $E_{Dc}^{(2)}$ and $E_{Sc}^{(2)}$ are the double- and single-excitation parts of the MBPT(2) correlation energy functional. In this expression, it should be understood that $f_{pq} = \epsilon_p \delta_{pq} - \lambda [\sum_k (pk|kp) + \langle p|V_x|p \rangle] - \lambda^2 \langle p|V_c^{(2)}|p \rangle$. Hence, limiting ourselves to consistent orders of perturbation theory, there is no contribution from the correlation potential to the single-excitation, f_{ia} term. Instead, we have the same second-order expression as that in the GL perturbation theory, plus a proper linear equation for V_c as required by Eq. (16). Furthermore, we ensure that the KS density does not change

from its self-consistent, converged value. In a future paper this point will be made explicitly, where we also generalize the theory to infinite order in perturbation theory and to coupled-cluster theory. The second-order solution we obtain, also provides the high-density limit in DFT.

The corresponding σ -spin correlation potential, obtained by taking the derivative of the correlation energy functional (35) with respect to density $V_{c\sigma}^{(2)}(\mathbf{r}) = \delta E_c^{(2)} / \delta \rho_\sigma(\mathbf{r})$, can be readily derived. For the sake of compactness, we only present the expressions for the spin-restricted case, which can be readily implemented for closed-shell systems. Switching to the spatial orbital notation (now i, j, k, l denote occupied spatial orbitals, a, b, c, d virtual spatial orbitals, and s either, and p, q denote orthonormal auxiliary functions) and dropping the spin indices to simplify the expression, we obtain

$$V_{c\sigma}^{(2)}(\mathbf{r}) = V_{Dc\sigma}^{(2)}(\mathbf{r}) + V_{Sc\sigma}^{(2)}(\mathbf{r})$$

$$= \sum_{pq} \left\{ \sum_{ijab} \frac{2(ia|jb) - (aj|bi)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \left[2 \sum_{s \neq i} \frac{(sa|jb)}{\epsilon_i - \epsilon_s} (is|q) + 2 \sum_{s \neq a} \frac{(is|jb)}{\epsilon_a - \epsilon_s} (sa|q) - \frac{1}{2} \frac{(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} [(ii|q) + (jj|q) - (aa|q) - (bb|q)] \right] \right\} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_p(\mathbf{r})$$

$$+ \sum_{pq} \left\{ \sum_{ia} \frac{f_{ia}}{\epsilon_i - \epsilon_a} \left[2 \sum_{s \neq i} \frac{(si|q)}{\epsilon_i - \epsilon_s} f_{sa} + 2 \sum_{s \neq a} \frac{(sa|q)}{\epsilon_a - \epsilon_s} f_{is} \right] + 2 \sum_{kc} \frac{(ck|q)}{\epsilon_k - \epsilon_c} [4(ia|ck) - (ic|ka) - (ik|ca)] - \frac{f_{ia}}{\epsilon_i - \epsilon_a} [(ii|q) - (aa|q)] \right\} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_p(\mathbf{r}), \quad (36)$$

where $V_{Dc\sigma}^{(2)}(\mathbf{r}) = \delta E_{Dc}^{(2)} / \delta \rho_\sigma(\mathbf{r})$ and $V_{Sc\sigma}^{(2)}(\mathbf{r}) = \delta E_{Sc}^{(2)} / \delta \rho_\sigma(\mathbf{r})$.

We can rewrite Eq. (36) in a more explicit way, suppressing the superscript,

$$V_{c\sigma}^{(2)}(\mathbf{r}) = V'_{Dc\sigma}(\mathbf{r}) + V''_{Dc\sigma}(\mathbf{r}) + V'_{Sc\sigma}(\mathbf{r}) + V''_{Sc\sigma}(\mathbf{r}), \quad (37)$$

where

$$V'_{Dc\sigma}(\mathbf{r}) = \sum_{pq} \left\{ \sum_{ijab} \frac{2(ia|jb) - (aj|bi)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \left[2 \sum_c \frac{(ca|jb)}{\epsilon_i - \epsilon_c} (ic|q) + 2 \sum_k \frac{(ik|jb)}{\epsilon_a - \epsilon_k} (ka|q) \right] \right\} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_p(\mathbf{r}), \quad (38)$$

$$V''_{Dc\sigma}(\mathbf{r}) = \sum_{pq} \left\{ \sum_{ijab} \frac{2(ia|jb) - (aj|bi)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \left[2 \sum_{l \neq i} \frac{(la|jb)}{\epsilon_i - \epsilon_l} (il|q) + 2 \sum_{d \neq a} \frac{(id|jb)}{\epsilon_a - \epsilon_d} (da|q) - \frac{1}{2} \frac{(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} [(ii|q) + (ij|q) - (aa|q) - (bb|q)] \right] \right\} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_p(\mathbf{r}), \quad (39)$$

$$V'_{Sc\sigma}(\mathbf{r}) = \sum_{pq} \left\{ \sum_{ia} \frac{f_{ia}}{\epsilon_i - \epsilon_a} \left[2 \sum_c \frac{(ci|q)}{\epsilon_i - \epsilon_c} f_{ca} + 2 \sum_k \frac{(ka|q)}{\epsilon_a - \epsilon_k} f_{ik} + 2 \sum_{kc} \frac{(ck|q)}{\epsilon_k - \epsilon_c} [4(ia|ck) - (ic|ka) - (ik|ca)] \right] \right\} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_p(\mathbf{r}). \quad (40)$$

$$V''_{Sc\sigma}(\mathbf{r}) = \sum_{pq} \left\{ \sum_{ia} \frac{f_{ia}}{\epsilon_i - \epsilon_a} \left[2 \sum_{j \neq i} \frac{(ji|q)}{\epsilon_i - \epsilon_j} f_{ja} + 2 \sum_{b \neq a} \frac{(ba|q)}{\epsilon_a - \epsilon_b} f_{ib} - \frac{f_{ia}}{\epsilon_i - \epsilon_a} [(ii|q) - (aa|q)] \right] \right\} (\mathbf{X}_{s\sigma}^{-1})_{pq} g_p(\mathbf{r}), \quad (41)$$

where we separated terms $V'_{Dc\sigma}(\mathbf{r})$ defined by Eq. (38) and $V'_{Sc\sigma}(\mathbf{r})$ defined by Eq. (40) from the rest, as they maintain the same structure of integral equation for potentials as the exchange-only OEP integral equation (24). The terms $V''_{Dc\sigma}(\mathbf{r})$ defined by Eq. (39) and $V''_{Sc\sigma}(\mathbf{r})$ defined by Eq. (41) result in a more complicated structure for the OEP integral equation.

From the above expressions (38)–(41) for the correlation potential, we can immediately see some possible approximations, which will simplify our OEP-MBPT(2) correlation treatment. First of all, we can neglect terms (40) and (41), which come from the singly excited part of the MBPT(2) energy functional (35). This should not seriously affect our calculated results, because these terms should give a very

small amount to the correlation energy and correlation potential, since the HF and OEP occupied orbitals are similar. We will call this approximation OEP-MBPT(2)D.

Another possible approximation is obtained by neglecting terms (39) and (41), which have a different and more complicated structure than the exchange-only OEP integral equation. We will label it by OEP-MBPT(2)S'D'. We can also use these two types of approximations at the same time, and obtain the simplest expression for the correlation potential, which is Eq. (38) only. We will call it OEP-MBPT(2)D'. The correlated OEP method that contains all terms (38)–(41) will be called OEP-MBPT(2)SD or just OEP-MBPT(2).

In each self-consistent field cycle, we first evaluate the matrix representation of the response function $\mathbf{X}_{s\sigma}$ (17) and then we invert this matrix by the singular value decomposition procedure to ensure that any singularity is excluded from the $\mathbf{X}_{s\sigma}^{-1}$ evaluation. We then evaluate matrix elements of the exchange-correlation potential over atomic orbitals $\{\chi_{\mu}\}$, i.e., $\langle\mu|V_{xc}^{\text{OEP}}|\nu\rangle$, using Eqs. (24) and (36), and proceed to a self-consistent solution that includes the $V_c^{(2)}$ potential. For numerical details applied to V_x see Refs. 14 and 30.

III. RESULTS AND DISCUSSION

A. The helium atom and the helium isoelectronic series

To assess the performance of our correlation functional, we will first concentrate on the helium isoelectronic series, because there exist practically exact solutions²⁵ of the Schrödinger equation for these systems,^{25,34} and they are very useful for benchmark comparisons of various quantities obtained from different (DFT and OEP in our case) methods. For two-electron systems including the helium isoelectronic series, the exact local exchange potential is also known, which makes the discussion of pure correlation effects straightforward.

We start by comparing the results for the helium atom. The OEP-MBPT(2) calculations (full version and different approximations) were performed using the basis set which consisted of even-tempered 20 *s*-type, 10 *p*-type and 2 *d*-type functions.³⁵ We compare them with the DFT results calculated with the conventional exchange-correlation functionals: BLYP is the Becke gradient corrected exchange functional³⁶ (Becke88) and Lee–Yang–Parr correlation functional³⁷ (LYP), and SVWN is the local density approximation to the exchange functional³⁸ (LDA) and Vosko–Wilk–Nusair correlation functional³⁹ (VWN). In our comparison, we also include the results obtained from OEP-KLICs,¹⁹ which is the exchange-only OEP method in conjunction with the semianalytical approximation due to Krieger, Li, and Iafrate⁶ (KLI), plus a correlation contribution from the Colle and Salvetti^{18,40} (CS) correlation functional.

In Fig. 1, we plot the exchange-correlation potential obtained from these approximate functionals and the OEP-MBPT(2)SD method for the helium atom. Since the potentials obtained from a LCAO OEP-MBPT(2) procedure are expanded by Gaussian functions, which do not have the cor-

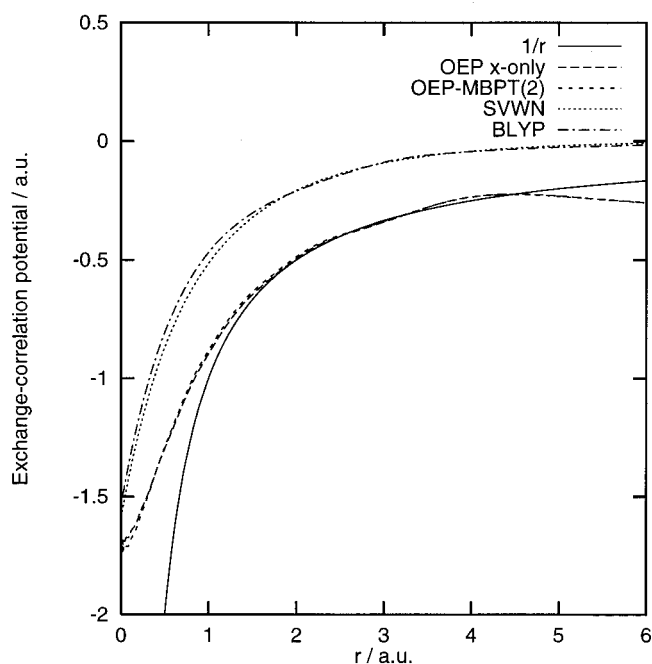


FIG. 1. Comparison of the exchange-correlation potentials of the helium atom obtained from the OEP-MBPT(2), exchange-only OEP, SVWN, and BLYP functionals.

rect ($-1/r$) asymptotic behavior of the potential for large r , although formally correct, the potentials decay too rapidly at very large r . Consequently, the potential obtained from a LCAO OEP-MBPT(2) procedure is displaced from the true solution of Eq. (14), although the shape of the potential is accurately reproduced in the physically important region. In this study, we shift the correlation potential and the magnitude of the shift is determined by a highest occupied molecular orbital (HOMO) condition, analogous to that for exchange-only OEP,⁶ for a correlated OEP-MBPT(2) calculation. For the energy functional (35), we can write this condition as follows:

$$\int \phi_{H\sigma}(\mathbf{r}) V_{xc\sigma}^{\text{OEP}} \phi_{H\sigma}(\mathbf{r}) d\mathbf{r} = - \sum_j (H_{\sigma j\sigma} | j_{\sigma} H_{\sigma}) + \sum_{H\sigma}^{(2)} (\epsilon_{H\sigma}), \quad (42)$$

where $\phi_{H\sigma}(\mathbf{r})$ is the highest occupied orbital. The first term on the right-hand side in Eq. (42) is the expectation value of the nonlocal HF exchange potential constructed for the highest occupied KS orbitals, and $\sum_{pq}^{(2)}(E)$ is a second-order self-energy expression³²

$$\sum_{pq}^{(2)}(E) = \sum_{j,a,b} \frac{(ap|bj)\{2(qa|jb) - (ja|qb)\}}{E + \epsilon_j - \epsilon_a - \epsilon_b} - \sum_{i,j,b} \frac{(ip|jb)\{2(qi|bj) - (bi|qj)\}}{\epsilon_i + \epsilon_j - E - \epsilon_b}, \quad (43)$$

where the summation over spatial orbitals is involved. The orbital energies presented in Tables III and IV are obtained after the exchange-correlation potentials of the LCAO OEP-MBPT(2) are corrected for the displacement. Also the OEP-MBPT(2) exchange-correlation and correlation potentials presented in Figs 1, 2, 3, 5 and 6 are shifted, so that the

TABLE I. Comparison of the total ground-state energies and exchange and correlation energies (in hartrees) for the helium atom obtained from different conventional DFT and OEP calculations. DFT (SVWN, BLYP) and OEP-MBPT(2) calculations were performed using an even-tempered $20s10p2d$ basis set.

| Method | E_{tot} | E_{xc} | E_x | E_c |
|--------------------|------------------|------------|------------|------------|
| SVWN | -2.834 835 | -0.973 320 | -0.861 853 | -0.111 468 |
| BLYP | -2.907 066 | -1.062 048 | -1.018 344 | -0.043 704 |
| KLICS ^a | -2.903 3 | -1.069 1 | -1.027 5 | -0.041 6 |
| OEP-MBPT(2)D | -2.907 800 | -1.069 036 | -1.022 800 | -0.046 236 |
| OEP-MBPT(2)SD | -2.907 923 | -1.069 159 | -1.022 800 | -0.046 359 |
| OEP-MBPT(2)D' | -2.907 773 | -1.071 437 | -1.025 306 | -0.046 131 |
| OEP-MBPT(2)S'D' | -2.907 812 | -1.071 477 | -1.025 306 | -0.046 171 |
| Exact ^b | -2.903 724 | -1.066 676 | -1.024 568 | -0.042 107 |

^aReference 19.

^bReference 26.

HOMO condition is satisfied. The constant shift for the correlation potential has a very small value in comparison to the shift calculated for the exchange potential. For example, for the neon atom for which numerical results are presented in Sec. III B, those shifts are 0.0042 and 0.1570 a.u. for correlation and exchange potentials, respectively.

The total shape and magnitude of the OEP-MBPT(2) potential are almost the same as those of the exchange-only OEP potential. This is expected because the correlation potential is a small fraction of the exchange-correlation one, and correlation hardly affects the overall shape and behavior of the total exchange-correlation potential. However, as is well recognized this small correction is essential in describing chemistry correctly. Note that the OEP-MBPT(2) exchange-correlation potential has the correct $-1/r$ asymptotic behavior for $r < 4.7$ after the correction based on the HOMO condition is made, whereas the SVWN and BLYP potentials do not. The small oscillations of the OEP-MBPT(2) potentials near the nuclei and the deviations from the $-1/r$ curves at large r ($r > 4.7$) are numerical basis-set effects in the LCAO-OEP method, and are discussed in detail in Ref. 30.

In Table I, we show the total ground-state and exchange-correlation energy and also the exchange and correlation contributions to the total energy calculated from different DFT and OEP calculations in comparison with the exact values.²⁵ Despite the fact that the SVWN and BLYP potentials are substantially different from the exact potential, the values of the energy components are reasonable; in particular the BLYP functional provides accurate exchange and correlation energies. Comparing the results with the exact values, it is obvious that the OEP-MBPT(2) and KLICS schemes perform much better than the conventional KS approaches and give qualitatively similar results. Comparing different approximate variants of the OEP-MBPT(2) methods, we can see that there is almost no significant differences in total energies among them. A larger difference in total energies between the OEP-MBPT(2)SD and OEP-MBPT(2)D methods come from different expressions for the energy functional, i.e., an additional (negative) singly excited terms E_{Sc} [Eq. (35)]. In Fig. 2, we compare the exact correlation potential with the OEP-MBPT(2)D', KLICS, and conventional

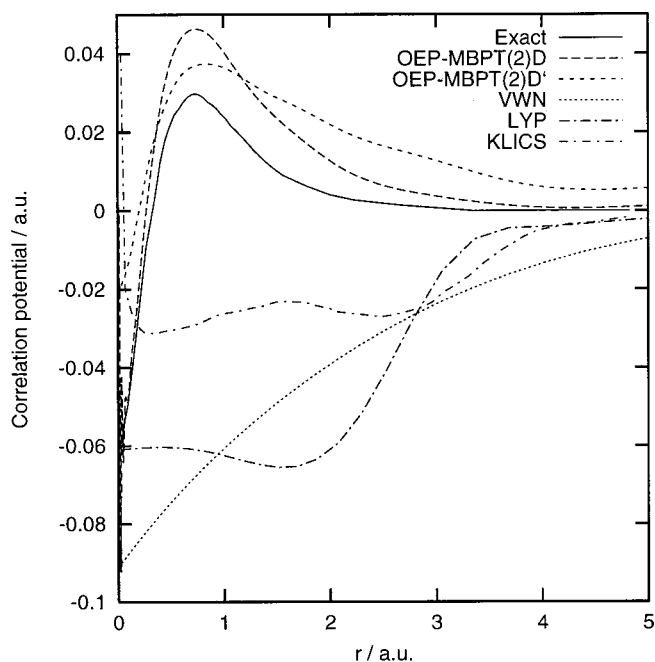


FIG. 2. Comparison of the exact correlation potential of the helium atom with the correlation potentials obtained from the OEP-MBPT(2), KLICS, SVWN, and BLYP functionals. The exact correlation potential from Ref. 25.

DFT correlation potentials, i.e., VWN and LYP. It is evident that, except for the OEP-MBPT(2) correlation potentials, all the approximate correlation potentials show very large deviations from the exact one. In the region with large electron density, these approximate correlation potentials (VWN, LYP, CS) have the wrong sign and qualitatively incorrect shapes. In contrast, our OEP-MBPT(2) correlation potentials are in qualitatively good agreement in shape and magnitude with the exact one. There is a slight difference between the OEP-MBPT(2)D and OEP-MBPT(2)D' potentials, the various approximations to the OEP-MBPT(2) method do not in general cause any qualitative change in the correlation potentials.

In Table II, we compare the total ground-state energies for the helium isoelectronic series obtained from SVWN, BLYP, KLICS, exchange-only OEP, and OEP-MBPT(2) potentials with the exact results.³⁴ The calculations for He, Li^+ , Be^{2+} , and B^{3+} were performed with an even-tempered $20s10p2d$ basis set, and for the other ions we used an uncontracted ROOS-ATZP basis set.⁴⁴ In the last row, the average absolute deviations from the exact values are presented. As we can see from the table, the KLICS and OEP-MBPT(2) total energies are much closer to the exact values than those obtained from the SVWN or BLYP calculations. The average absolute deviation from the exact values is in the same order for both the exchange-only OEP and OEP-MBPT(2) methods, while KLICS results are slightly better. However, for the highly charged two-electron ions, the quality of the KLICS result is worse, while the quality of the OEP-MBPT(2) results becomes better. For Mg^{10+} onwards, the OEP-MBPT(2) total energies are closer to the exact results than the KLICS ones. We would like to mention there are almost no differences in total energies between the

TABLE II. Total ground-state energies (in hartrees, sign reversed) for the helium isoelectronic series from various conventional DFT and OEP-MBPT(2)D calculations. In parenthesis are given the correlation energies obtained from OEP-MBPT(2)D calculations. Basis sets used in DFT (BLYP, SVWN) and OEP-MBPT(2)D calculations are described in the text.

| | BLYP | SVWN | KLICS ^a | OEP-MBPT(2)D | Exact ^b |
|-----------------------|-------------|-------------|--------------------|------------------------|--------------------|
| He | 2.907 066 | 2.834 835 | 2.9033 | 2.907 800(0.046 236) | 2.9037 |
| Li ⁺ | 7.279 429 | 7.142 818 | 7.2803 | 7.281 012(0.044 628) | 7.2799 |
| Be ²⁺ | 13.650 025 | 13.444 694 | 13.6556 | 13.654 044(0.043 108) | 13.6556 |
| B ³⁺ | 22.019 407 | 21.742 617 | 22.0301 | 22.028 263(0.042 047) | 22.0310 |
| C ⁴⁺ | 32.388 272 | 32.038 680 | 32.4045 | 32.402 130(0.041 000) | 32.4062 |
| N ⁵⁺ | 44.758 082 | 44.333 188 | 44.7788 | 44.777 063(0.040 983) | 44.7814 |
| O ⁶⁺ | 59.127 244 | 58.626 541 | 59.1531 | 59.151 432(0.040 967) | 59.1566 |
| F ⁷⁺ | 75.496 340 | 74.918 991 | 75.5274 | 75.526 898(0.040 917) | 75.5317 |
| Ne ⁸⁺ | 93.865 423 | 93.210 726 | 93.9017 | 93.901 800(0.040 855) | 93.9068 |
| Na ⁹⁺ | 114.236 751 | 113.504 042 | 114.2761 | 114.276 651(0.040 894) | 114.2819 |
| Mg ¹⁰⁺ | 136.606 019 | 136.795 111 | 136.6505 | 136.651 638(0.040 909) | 136.6569 |
| Al ¹¹⁺ | 160.975 412 | 160.085 744 | 161.0250 | 161.026 592(0.040 897) | 161.0320 |
| Si ¹²⁺ | 187.344 860 | 186.376 105 | 187.3995 | 187.401 562(0.040 894) | 187.4070 |
| Ar ¹⁶⁺ | 312.822 695 | 311.535 012 | 312.8997 | 312.901 355(0.040 861) | 312.9072 |
| $ \overline{\Delta} $ | 0.032 921 | 0.524 914 | 0.003 736 | 0.004 3 | 0.0 |

^aReference 19.

^bReference 34.

OEP-MBPT(2)D and OEP-MBPT(2)D' methods. Also adding the single excitations in OEP-MBPT(2)SD and OEP-MBPT(2)S'D' do not change the total energies.

To assess the quality of the exchange-correlation potentials, it is informative to look at the highest occupied orbital energies. In the limit of an exact exchange-correlation functional, this value should be equal to the negative of the ionization potential of the system.^{11,41–43} These values are very sensitive to the quality of the exchange-correlation potential. In Table III, we present the highest occupied orbital energies, obtained from various approximate functionals. It is obvious that, once the HOMO condition has been imposed, the OEP-MBPT(2) method has to give very good results. This superior quality is due to the inclusion of the exact exchange through the OEP scheme, leading to the correct asymptotic

behavior in the KS potential, and it is further improved by the OEP-MBPT(2) correlation treatment. In the KLICS results, one might expect similar quality, because the KLI exchange-only potentials are good approximations to the exchange-only OEP. However, as we can see, adding the Colle–Salvetti correlation potentials to the exchange-only KLI potentials deteriorates the results. This is expected since the CS correlation potentials have the wrong sign in the physically relevant regions of space and as has already been confirmed by the plot of the correlation potentials in Fig. 2. As in the total ground-state energy case, the highest occupied orbital energies calculated by the OEP-MBPT(2)D, OEP-MBPT(2)SD, OEP-MBPT(2)D', and OEP-MBPT(2)S'D' methods are almost the same.

TABLE III. The highest occupied orbital energies (in hartrees, signs reversed) for the helium isoelectronic series from various conventional DFT and OEP-MBPT(2)D calculations. Basis sets used in DFT (BLYP, SVWN) and OEP-MBPT(2)D calculations are described in the text.

| | BLYP | SVWN | KLI <i>x</i> only ^b | OEP <i>x</i> only | KLICS ^b | OEP-MBPT(2)D | Exact ^b |
|-----------------------|----------|----------|-----------------------------------|----------------------|--------------------|--------------|--------------------|
| He | 0.5894 | 0.5704 | 0.9180 | 0.9180 | 0.9446 | 0.8904 | 0.9037 |
| Li ⁺ | 2.2312 | 2.1903 | 2.7924 | 2.7924 | 2.8227 | 2.7719 | 2.7799 |
| Be ²⁺ | 4.8760 | 4.8066 | 5.6671 | 5.6671 | 5.6992 | 5.6482 | 5.6556 |
| B ³⁺ | 8.5199 | 8.4206 | 9.5420 | 9.5418 | 9.5751 | 9.5235 | 9.5310 |
| C ⁴⁺ | 13.1634 | 13.0335 | 14.4169 | 14.4166 | 14.4507 | 14.3983 | 14.4062 |
| N ⁵⁺ | 18.8067 | 18.6455 | 20.2918 | 20.2914 | 20.3261 | 20.2738 | 20.2814 |
| O ⁶⁺ | 25.4498 | 25.2567 | 27.1668 | 27.1662 | 27.2014 | 27.1492 | 27.1566 |
| F ⁷⁺ | 33.0928 | 32.8676 | 35.0418 | 35.0410 | 35.0766 | 35.0245 | 35.0317 |
| Ne ⁸⁺ | 41.7357 | 41.4780 | 43.9167 | 43.9158 | 43.9517 | 43.8997 | 43.9068 |
| Na ⁹⁺ | 51.3794 | 51.0890 | 53.7917 | 53.7915 | 53.8269 | 53.7749 | 53.7819 |
| Mg ¹⁰⁺ | 62.0223 | 61.6990 | 64.6667 | 64.6665 | 64.7020 | 64.6500 | 64.6569 |
| Al ¹¹⁺ | 73.6652 | 73.3088 | 76.5417 | 76.5415 | 76.5770 | 76.5251 | 76.5320 |
| Si ¹²⁺ | 86.3081 | 85.9185 | 89.4167 | 89.4165 | 89.4521 | 89.4002 | 89.4071 |
| Ar ¹⁶⁺ | 146.8793 | 146.3556 | 150.9166 | 150.9164 | 150.9523 | 150.9005 | 150.9027 |
| $ \overline{\Delta} $ | 1.8725 | 2.0924 | 0.0110 | 0.0107 | 0.0446 | 0.0074 | 0.0 |

^aReference 19.

^bReference 34.

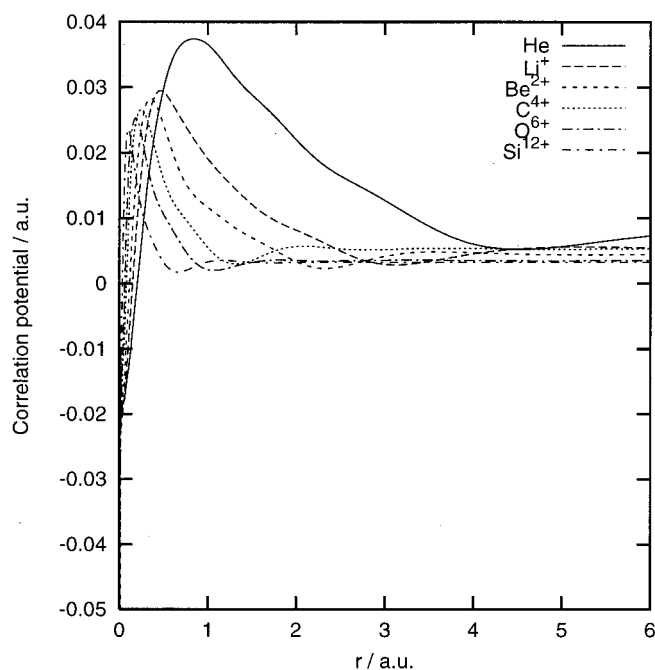


FIG. 3. Correlation potentials of selected members of the helium isoelectronic series obtained from the OEP-MBPT(2)D' calculations.

In Fig. 3, we plot the OEP-MBPT(2)D' correlation potentials of some selected atoms in the helium isoelectronic series. The shapes and magnitudes of the plotted correlation potentials are in good agreement with the exact results presented in Fig. 4 of Ref. 25 (note that the horizontal axes of Fig. 3 are not scaled by the nuclear charge Z , unlike in Fig. 4 of Ref. 25). As we can see in the figure, the position of the maximum of the correlation potential is shifted toward the nucleus for heavier ions. This can be simply explained by the dependence of the correlation potential on the shell structure of the electron density. In Fig. 4, we plot the radial charge density obtained from the OEP-MBPT(2) calculations for a few members of the helium isoelectronic series. The positions of maxima in both figures match very well.

B. Neon atom

As another example, we have performed OEP-MBPT(2) calculations for the neon atom in an uncontracted ROOS-ATZP basis set. In Table IV, we compare the total ground-state energies and highest occupied orbital energies obtained from OEP-MBPT(2), KLICS, SVWN, and BLYP calculations with the exact results.⁴⁵ Again the correlated OEP calculations give much better total energies and highest occupied orbital energies than the conventional DFT method. The approximate KLICS total energies are slightly closer to the exact result than the total energy of the OEP-MBPT(2) method, although the latter result is already highly accurate. The total energies calculated in the OEP-MBPT(2) methods are too negative, because the GL expression for the second-order energy functional that we use in our calculations already gives much lower energies than Hartree-Fock based MBPT(2), e.g. The highest occupied orbital energies obtained from the OEP-MBPT(2) calculations are also of

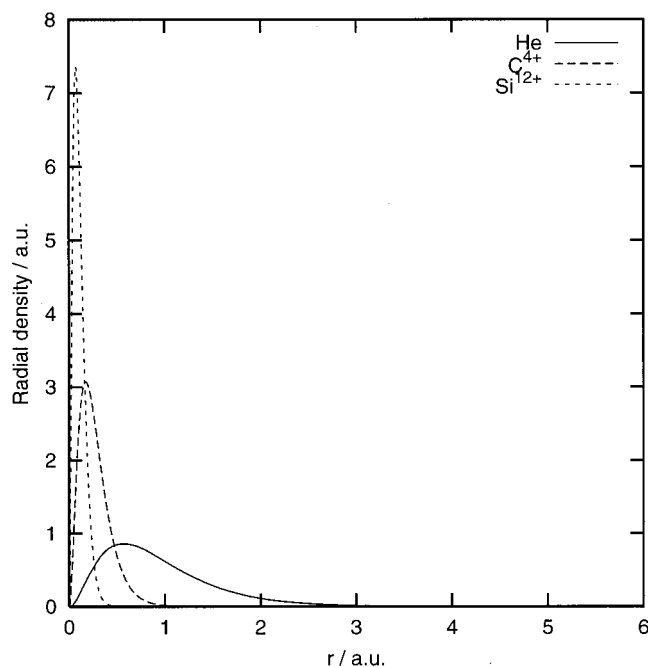


FIG. 4. Radial density of the selected members of the helium isoelectronic series obtained from the OEP-MBPT(2)D' calculations.

slightly poorer quality than those of KLICS. Again, like in the case of the helium atom, adding the CS correlation potential worsens the orbital energy relative to the KLI exchange-only result, again indicating that the CS correlation potential has the wrong sign in the physically relevant region just as for the helium atom. In the OEP-MBPT(2) case, the correlation correction moves in the correct direction because of the qualitatively correct correlation potential (see Fig. 6), but the magnitude of the correction is slightly too large. In Fig. 5, we plot the exchange-correlation potential obtained from the OEP-MBPT(2) calculations and the exchange potential from the exchange-only OEP calculations. As expected, the exchange contribution largely determines the shape of the total exchange-correlation potential, although the effect of correlation is visible near the intershell region and is quantitatively very important. In Fig. 6, we plot the LYP, VWN, and OEP-MBPT(2) correlation potentials. We

TABLE IV. Total ground-state energies and the highest occupied orbital energies ϵ_{HOMO} (in hartrees, signs reversed) for the neon atom. DFT (BLYP, SVWN) and OEP-MBPT(2) were performed using an uncontracted ROOS-ATZP basis set.

| | E_{tot} | ϵ_{HOMO} |
|--------------------|------------------|--------------------------|
| BLYP | 128.972 478 | 0.4914 |
| SVWN | 128.232 975 | 0.4980 |
| KLI x only | 128.545 4 | 0.8494 |
| KLICS ^a | 128.920 2 | 0.8841 |
| OEP-MBPT(2)D | 128.987 017 | 0.6490 |
| OEP-MBPT(2)SD | 129.009 088 | 0.6489 |
| OEP-MBPT(2)D' | 128.985 505 | 0.6546 |
| OEP-MBPT(2)S'D' | 128.995 330 | 0.6545 |
| Exact ^b | 128.937 6 | 0.7945 |

^aReference 19.

^bReference 45.

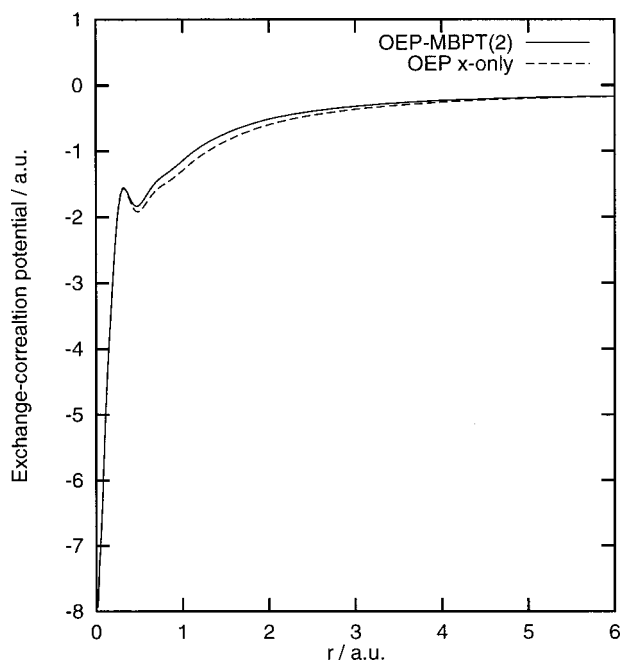


FIG. 5. Comparison of the exchange-correlation potential with exchange potential of the neon atom obtained from the OEP-MBPT(2) and exchange-only OEP calculations, respectively.

compare them with the exact correlation potential²⁶ calculated from very accurate charge density obtained from quantum Monte Carlo calculations (QMC). The conventional DFT correlation potentials have the completely wrong shape as compared to the exact (QMC) one. Our OEP-MBPT(2) correlation potential shows qualitatively the correct shape,

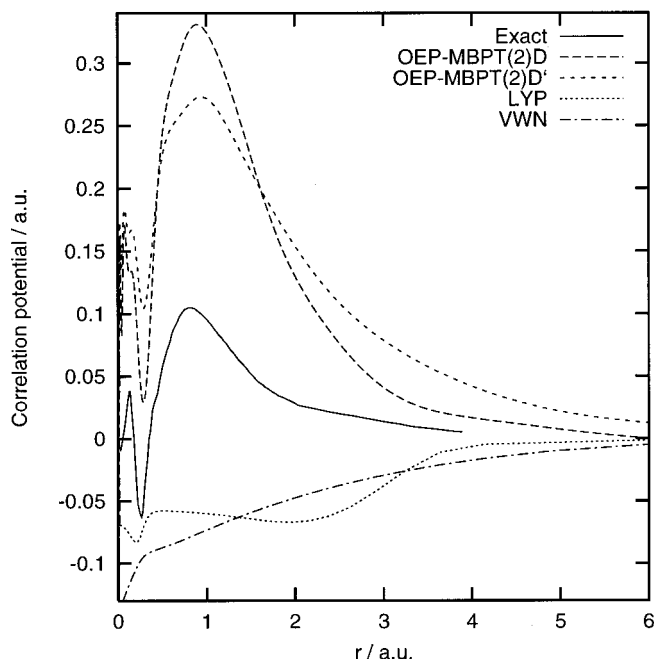


FIG. 6. Comparison of the exact (QMC) correlation potential of the neon atom with the correlation potentials obtained from the OEP-MBPT(2), SVWN, and BLYP functionals. The exact (QMC) correlation potential from Ref. 26.

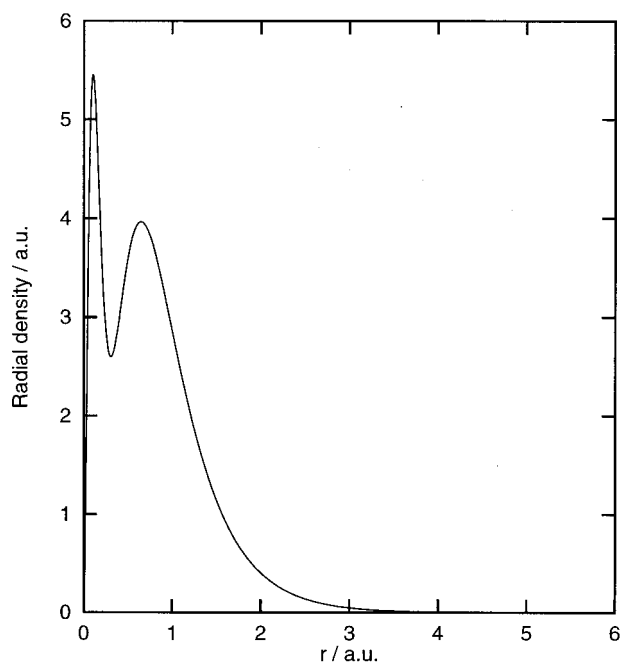


FIG. 7. Radial density of the neon atom obtained from the OEP-MBPT(2)D' calculations.

although the magnitude of the OEP-MBPT(2) correlation potential is almost twice as great as the exact (QMC) one. Overall the OEP-MBPT(2) correlation potential is a striking improvement over those obtained from popular functionals. It may also be noticed that the shape of the correlation potentials reflects the shape of the corresponding radial charge density. This is analogous to the well-known observation that the humps in the exchange potentials occur owing to the intershell structure of the radial charge density. One might expect that a correlation potential will reflect the radial charge density for an atom and allow the electrons to avoid each other. This simple argument appears to be supported by Figs. 2 and 3 for He and by Figs. 6 and 7 for Ne, where we can find that the peaks in the correlation potentials coincide with those in the radial charge densities. A comparison of the radial charge density obtained with accurate orbital-dependent correlation potentials should compare well with those from *ab initio* correlated methods like coupled-cluster theory.

IV. CONCLUSIONS

We have performed an *ab initio* correlated DFT calculation employing the OEP-MBPT(2) correlation functional and obtained accurate exchange-correlation and correlation potentials for some atoms whose exact exchange and correlation potentials are known. We have performed fully self-consistent OEP-MBPT(2) calculations to achieve self-consistency between the exchange-correlation potential and orbitals. The total exchange-correlation potentials, when plotted, are hardly affected by electron correlation as the exchange potentials dominate in the total exchange-correlation potentials. This is expected as the correlation effects are subtler and are at least an order of magnitude

smaller than the exchange. However, the correlation effect is very important in obtaining accurate total energies and orbital energies, and the OEP-MBPT(2) treatment systematically improves the exchange-only OEP results across different properties. These OEP-based methods—exchange-only OEP and OEP-MBPT(2)—give significantly better results than conventional DFT functionals such as SVWN or BLYP. For correlation potentials, only our OEP-MBPT(2) calculations among the other functionals examined in this study can reproduce the correct shape of the correlation potential, and simultaneously give highly accurate results for other quantities such as the total and orbital energies. Additionally we found almost no difference between numerical results obtained from different approximations of the OEP-MBPT(2) methods, though observable in the potential itself. The accurate prediction of potentials and orbital energies achieved by OEP-MBPT(2) is essential in, for example, the calculations of ionization potentials and excitation energies by time-dependent DFT. Our findings also illustrate that not only the exchange-correlation energy, but also the corresponding potential should be employed as a criterion in developing new functionals. We emphasize that our OEP-MBPT(2) correlation potentials are perhaps currently the most accurate ones that can be obtained for general atoms and molecules against which other approximate functionals should be tested and calibrated, and will be instrumental in developing more accurate and systematically improvable exchange-correlation functionals. The natural extension to the higher orders of perturbation theory and to infinite-order coupled-cluster theory should provide a series of converging correlation potentials, analogous to the well known converging *ab initio* correlated approximations, MBPT(2) < CCD < CCSD ~ MBPT(4) < CCSD(T) < CCSDT < ... < full CI.

ACKNOWLEDGMENTS

This work was supported by the U.S. Air Force Office of Scientific Research under Grant No. F49620-98-0116 and the National Science Foundation under Grant No. 990015. We thank Mark Casida for interesting discussions.

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