

Time-dependent density functional theory employing optimized effective potentials

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Exchange-only *ab initio* (parameter-free) time-dependent density functional calculations for the vertical excitation energies of atoms and polyatomic molecules are performed by employing optimized effective potentials (OEP's) and their corresponding adiabatic exchange kernels for the first time. Accurate OEP's are obtained by a novel linear-combination-of-atomic-orbital (LCAO) algorithm [R. Colle and R. K. Nesbet, *J. Phys. B* **34**, 2475 (2001)] in which a potential is represented as a sum of a seed potential having the correct $-1/r$ asymptotic behavior and a small and rapidly decaying correction, the latter being approximated accurately by a linear combination of Gaussian functions. The time-dependent OEP (TDOEP) methods with and without the Tamm–Dancoff approximation are implemented by using a trial-vector algorithm, which allows us to avoid the storage or manipulation of transformed two-electron integrals or the diagonalization of large matrices. No approximation is made to TDOEP, besides the adiabatic approximation to the exchange kernel, the LCAO expansion of the orbitals and potentials, and occasionally the Tamm–Dancoff approximation. The vertical excitation energies of the beryllium atom and the nitrogen and water molecules calculated by TDOEP are compared with those obtained from time-dependent density functional theory (TDDFT) employing conventional local or gradient-corrected functionals, configuration interaction singles (CIS), time-dependent Hartree–Fock (TDHF) theory, similarity-transformed equation-of-motion coupled-cluster with single and double substitutions, and experiments. TDOEP, which neglects electron correlation while treating the exchange contribution rigorously within the Kohn–Sham DFT framework, performs equally well as, or even appreciably better than, CIS or TDHF. The slightly better performance of TDOEP might be attributed to the local nature of the exchange potentials that allows the bare orbital energy differences to approximate excitation energies well. Nevertheless, TDDFT employing local or gradient-corrected functionals outperforms TDOEP for low-lying valence excited states, implying that the former somehow accounts for electron correlation effectively, whereas for high-lying and Rydberg excited states, the latter performs better than the former. By combining the desirable features of OEP and local or gradient-corrected exchange–correlation potentials, we arrive at a simple asymptotic correction scheme to the latter. TDDFT with the asymptotic correction yields uniformly accurate excitation energies for both valence and Rydberg excited states. © 2002 American Institute of Physics.
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I. INTRODUCTION

Time-dependent density functional theory (TDDFT) (Refs. 1–3) has enjoyed increasingly greater popularity recently and has become a standard excited-state density functional method, with the aid of efficient linear-combination-of-atomic-orbital (LCAO) algorithms^{4–13} permitting the applications of the theory to general polyatomic molecules. The initial applications performed by Jamorski, Casida, and Salahub⁴ and by Bauernschmitt and Ahlrichs⁵ have indicated

that TDDFT employing conventional approximate exchange–correlation functionals and the so-called adiabatic approximation performs remarkably well for low-lying valence excited states; much better than Hartree–Fock (HF) theory-based single excitation methods such as configuration interaction singles (CIS) or time-dependent Hartree–Fock (TDHF) theory. A highlight of the initial success of TDDFT for molecular systems might be that it has proven a considerable improvement over CIS or TDHF when applied to low-lying valence excited states of radicals.¹¹ TDDFT can describe the excited states of radicals that have appreciable two-electron character when treated by the HF-based methods as simple one-electron replacement from the ground state, and thereby reproduce their transition energies accurately. Recently, methods that enable the analytical evaluation of geometrical derivatives of TDDFT excitation energies have also been implemented by Van Caillie and Amos.^{14,15}

However, TDDFT with conventional approximate

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exchange-correlation functionals has failed dramatically when applied to high-lying diffuse excited states.^{4,5} Casida *et al.*⁷ identified the origin of this failure as the wrong asymptotic behavior of the corresponding exchange-correlation potentials, which plagued most of the exchange-correlation functionals widely in use. This has been convincingly supported by Tozer and Handy,¹⁰ who reproduced the excitation energies accurately for low- and high-lying excited states by grafting the correct $-1/r$ asymptotic tails to the potentials generated from a conventional exchange-correlation functional. Therefore, the necessity of developing accurate and desirably systematic approximations to the exact exchange-correlation functional is even greater for the excited states than for the ground states. In the development of such approximations, much attention must be paid not only to exchange-correlation energies, which are numbers, but also to exchange-correlation potentials, which are functions of space variables and impose a more severe constraint on the form of the functionals than the former.¹⁶

After several years of pertinent developments by some groups,^{17–42} serious efforts toward using purely *ab initio* quantum chemical expressions to define rigorous exchange-correlation energies and potentials have been realized.^{43–62} The underlying idea of this new “*ab initio* DFT” scheme,⁵¹ in distinction to the conventional “parametrized DFT” scheme, is to employ systematic and parameter-free energy expressions of *ab initio* wave function theory and cast them into the framework of single-particle Kohn–Sham (KS) DFT. The exchange-only model of the scheme amounts to the optimized effective potential (OEP) method of Talman and Shadwick,^{63,64} which possesses many of the analytical features of the KS DFT.²⁵ OEP has the correct $-1/r$ asymptotic behavior, cancels exactly the self-interaction, exhibits an integer derivative discontinuity,^{19,65,66} obeys the exchange virial theorem^{67,68} and the HOMO condition (also called Janak’s theorem),²⁵ and is exact in the homogeneous-electron-gas limit. The OEP method has been implemented into a linear-combination-of-atomic-orbital (LCAO) algorithm by Ivanov, Hirata, and Bartlett⁴³ and by Görling,⁴⁴ on the basis of the finite-basis-set OEP formalism of Görling and Levy,^{29,30} allowing the exchange-only *ab initio* DFT calculations for atomic and molecular systems in an equal footing to conventional DFT or *ab initio* wave function methods. Recently, we⁶² as well as Engel and co-workers^{40,47,59} have also presented correlation potentials evaluated via the *ab initio* DFT. In one of these LCAO algorithms, which we call the *S* algorithm,^{43,58} an OEP is expanded by atom-centered Gaussian functions. Although the *S* algorithm can provide occupied orbitals and exchange energies with a reasonable accuracy when a large basis set is used, the algorithm in its present form is not suitable for excited-state calculations. This is because the exchange potentials obtained by the algorithm tend to exhibit the wrong asymptotic behavior owing to the rapid Gaussian falloff of the expansion basis functions (although formally OEP’s have the correct $-1/r$ asymptotic behavior) and hence the virtual orbitals are not accurately reproduced.⁵⁸ Several schemes have been proposed to ensure the correct $-1/r$ behavior throughout the asymptotic region by virtue of some additional

constraints,^{44,60,61} but such constraints tended to deteriorate the potentials in the physically important regions near nuclei.

In this article, we report for the first time TDDFT employing OEP’s (TDOEP) within a LCAO formalism applicable to general polyatomic molecules (see Refs. 3, 31, 49, 56, 57 for previous efforts in this direction). We overcome the above-mentioned computational difficulty in obtaining accurate OEP’s in the asymptotic region by combining the *S* algorithm and a novel algorithm developed and implemented recently by Colle and Nesbet.⁵⁵ This hybrid algorithm invokes an analytical seed potential having the correct $-1/r$ asymptotic behavior and determines just the difference between the seed potential and an OEP, which is small and rapidly decaying. Hence, the exchange potentials obtained by the hybrid algorithm exhibit the correct $-1/r$ behavior throughout the asymptotic region and satisfy the HOMO condition within a few hundredths of an atomic unit for molecules with the largest basis set we employed in this study. The TDOEP method employing the adiabatic exchange kernel derived by Görling^{38,39} is implemented into an efficient trial-vector algorithm^{69,70} that avoids the storage or manipulation of transformed integrals or the diagonalization of large matrices. No approximation is made to TDOEP, besides the adiabatic approximation to the exchange kernel, the LCAO expansion of the orbitals and potentials, and occasionally the Tamm–Dancoff approximation. We compare the vertical excitation energies of the beryllium atom and the nitrogen and water molecules computed by TDOEP with or without the Tamm–Dancoff approximation¹² against those obtained from TDDFT employing conventional local and gradient-corrected exchange-correlation functionals, CIS, TDHF, similarity-transformed equation-of-motion coupled-cluster with single and double substitutions (STEOM-CCSD),^{71–73} and experiment. We also devise, in the same spirit as Tozer and Handy,¹⁰ an approximate TDOEP by hybridizing conventional local and gradient-corrected exchange-correlation potentials and an analytical potential having the correct $-1/r$ behavior, and discuss its performance.

II. THEORY AND COMPUTER IMPLEMENTATION

A. OEP

The σ -spin component of an OEP (Refs. 63, 64) can be written as

$$V_{\sigma}^{\text{OEP}}(\mathbf{r}_1) = -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{K_{ia\sigma} \psi_{i\sigma}(\mathbf{r}_2) \psi_{a\sigma}(\mathbf{r}_2)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \times X_{\sigma}^{-1}(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_2, \quad (1)$$

where we designate σ -spin canonical OEP orbitals by $\{\psi_{p\sigma}(\mathbf{r})\}$, which we assume to be real for the sake of simplicity, σ -spin one-electron energies by $\{\epsilon_{p\sigma}\}$, and $K_{ia\sigma}$ denotes a HF exchange matrix element defined by

$$K_{ia\sigma} = \sum_j^{\text{occ.}} (i_{\sigma} j_{\sigma} | j_{\sigma} a_{\sigma}), \quad (2)$$

and

$$(p_{\sigma}q_{\sigma}|r_{\sigma}s_{\sigma}) = \int \int \frac{\psi_{p\sigma}(\mathbf{r}_1)\psi_{q\sigma}(\mathbf{r}_1)\psi_{r\sigma}(\mathbf{r}_2)\psi_{s\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (3)$$

In the above equation and in the following, we follow the convention that i, j, k label occupied orbitals, a, b label virtual orbitals, and p, q, r, s label either. It must be understood^{29,30,58} that the inverse of the linear response function $X_{\sigma}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (1) is defined within the domain of eigenfunctions of the corresponding linear response function,

$$X_{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{a\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{a\sigma}(\mathbf{r}_2)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}. \quad (4)$$

The derivation of Eq. (1) is given in the Appendix. We require that the exchange potential $V_{\sigma}^{\text{OEP}}(\mathbf{r})$ satisfy Eq. (1) and the self-consistency condition between the canonical OEP orbitals and the exchange potential, i.e.,

$$\int \psi_{p\sigma}(\mathbf{r})H_{\sigma}\psi_{q\sigma}(\mathbf{r})d\mathbf{r} = \epsilon_{p\sigma}\delta_{pq}, \quad (5a)$$

$$\int \psi_{p\sigma}(\mathbf{r})\psi_{q\sigma}(\mathbf{r})d\mathbf{r} = \delta_{pq}, \quad (5b)$$

where the KS Hamiltonian is

$$H_{\sigma} = -\frac{1}{2}\nabla_1^2 + V_{\text{ext}}(\mathbf{r}_1) + \sum_{\tau}^{\alpha, \beta} \int \frac{\rho_{\tau}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_2 + V_{\sigma}^{\text{OEP}}(\mathbf{r}_1), \quad (6)$$

and $V_{\text{ext}}(\mathbf{r})$ represents an external potential, which is typically an attractive potential produced by nuclei, and $\rho_{\tau}(\mathbf{r})$ is the τ -spin electron density, i.e.,

$$\rho_{\tau}(\mathbf{r}) = \sum_i^{\text{occ.}} \psi_{i\tau}(\mathbf{r})\psi_{i\tau}(\mathbf{r}). \quad (7)$$

In the S algorithm,^{43,58} the $V_{\sigma}^{\text{OEP}}(\mathbf{r})$ contribution to a KS Hamiltonian matrix element can be calculated as

$$V_{pq\sigma}^{\text{OEP}} \equiv \int \psi_{p\sigma}(\mathbf{r})V_{\sigma}^{\text{OEP}}(\mathbf{r})\psi_{q\sigma}(\mathbf{r})d\mathbf{r} = -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{\kappa, \lambda}^{\text{aux.}} \frac{K_{ia\sigma}(i_{\sigma}a_{\sigma}\kappa)(p_{\sigma}q_{\sigma}\lambda)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} (\mathbf{X}_{\sigma}^{-1})_{\kappa\lambda}, \quad (8)$$

with

$$(p_{\sigma}q_{\sigma}\lambda) = \int \psi_{p\sigma}(\mathbf{r})\psi_{q\sigma}(\mathbf{r})\theta_{\lambda}(\mathbf{r})d\mathbf{r}, \quad (9)$$

and $\{\theta_{\kappa}(\mathbf{r})\}$ is a set of orthonormalized auxiliary atom-centered Gaussian functions. The inverse matrix \mathbf{X}_{σ}^{-1} is created by a singular value decomposition of the matrix \mathbf{X}_{σ} , whose elements are in turn given by

$$(\mathbf{X}_{\sigma})_{\kappa\lambda} = 2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{(i_{\sigma}a_{\sigma}\kappa)(i_{\sigma}a_{\sigma}\lambda)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}. \quad (10)$$

Being expanded by Gaussian functions, $V_{\sigma}^{\text{OEP}}(\mathbf{r})$ generated by this algorithm does not exhibit the correct $-1/r$ asymptotic behavior throughout the space. Nevertheless, when a sufficiently large orbital basis set is used, the algorithm is capable of reproducing the occupied orbitals with a reasonable accuracy, as they are hardly effected by the behavior of $V_{\sigma}^{\text{OEP}}(\mathbf{r})$ in the asymptotic regions. Hence, the calculated total energies and orbital energy differences among occupied orbitals are also reasonable, whereas the absolute values of the orbital energies, virtual orbitals, and orbital energy differences between occupied and virtual orbitals and among virtual orbitals are excessively erroneous (see Ref. 58 for more details).

This shortcoming of the S algorithm, which is fatal when an excited-state treatment is considered, can be rectified by a scheme suggested and implemented by Colle and Nesbet⁵⁵ recently for atomic OEP calculations in combination with the S algorithm for polyatomic molecules. The scheme of Colle and Nesbet amounts to employing some analytical seed potential that has the correct $-1/r$ asymptotic decay behavior and determining just the difference between an OEP and the seed potential. Following Colle and Nesbet, we employ the analytical orbital-dependent potential proposed by Slater,⁷⁴ i.e.,

$$V_{\sigma}^S(\mathbf{r}_1) = - \sum_{i,j}^{\text{occ.}} \frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)}{\rho_{\sigma}(\mathbf{r}_1)} \int \frac{\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_2, \quad (11)$$

as the seed potential and determine by the S algorithm the difference from an OEP, which is rapidly decaying and approximated accurately by a linear combination of atom-centered Gaussian functions. Hence, the $V_{\sigma}^{\text{OEP}}(\mathbf{r})$ contribution to a KS Hamiltonian matrix element becomes

$$V_{pq\sigma}^{\text{OEP}} = V_{pq\sigma}^S - 2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{\kappa, \lambda}^{\text{aux.}} \frac{(K_{ia\sigma} + V_{ia\sigma}^S)(i_{\sigma}a_{\sigma}\kappa)(p_{\sigma}q_{\sigma}\lambda)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \times (\mathbf{X}_{\sigma}^{-1})_{\kappa\lambda}, \quad (12)$$

with

$$V_{pq\sigma}^S \equiv \int \psi_{p\sigma}(\mathbf{r})V_{\sigma}^S(\mathbf{r})\psi_{q\sigma}(\mathbf{r})d\mathbf{r}. \quad (13)$$

This algorithm can provide an OEP that has the correct $-1/r$ decay behavior throughout the asymptotic regions and satisfies the following analytical condition (the HOMO condition²⁵), which a true solution of Eq. (1) satisfies, typically within a few hundredths of an atomic unit for molecules with the largest Gaussian basis sets we employed,

$$V_{hh\sigma}^{\text{OEP}} = -K_{hh\sigma}, \quad (14)$$

where $\psi_{h\sigma}(\mathbf{r})$ represents the highest occupied KS orbital of σ -spin symmetry. The Slater potential may be defined once in terms of any convenient set of orbitals and need not be updated in the self-consistent-field (SCF) procedure, insofar as it has the correct $-1/r$ asymptotic behavior.

The novel LCAO OEP algorithm has been implemented in the quantum chemistry computer program POLYMER 1.0.⁷⁵

The two- (which are needed when the bare auxiliary Gaussian functions are orthonormalized via the canonical orthonormalization) and three-center overlap integrals involving the auxiliary Gaussian functions are computed analytically by the Obara–Saika recursion formulas.⁷⁶ The Slater potentials are evaluated at grid points and the associated exchange matrix elements, Eq. (13), are computed by virtue of the three-dimensional quadrature elaborated originally by Becke.⁷⁷ The multicenter numerical grids consist of a second-kind Gauss–Chebyshev radial grid and a 302-point Lebedev angular grid. Exceptionally large grids (90 600 points for the beryllium atom and 30 200 points per nucleus for the nitrogen and water molecules) are used in accordance with very diffuse character of some of the basis functions employed. The integration in Eq. (11) can be performed analytically at grid points by employing the method of Termath and Handy.⁷⁸

B. TDOEP

The vertical excitation energies ω can be obtained by TDOEP as the solutions to the matrix eigenvalue equation (see, e.g., Ref. 2) of the form

$$\sum_j^{\text{occ.}} \sum_b^{\text{virt.}} \sum_\tau^{\alpha,\beta} (A_{ai\sigma}^{bj\tau} x_{bj\tau} + B_{ai\sigma}^{bj\tau} y_{bj\tau}) = \omega x_{ai\sigma}, \quad (15a)$$

$$\sum_j^{\text{occ.}} \sum_b^{\text{virt.}} \sum_\tau^{\alpha,\beta} (B_{ai\sigma}^{bj\tau} x_{bj\tau} + A_{ai\sigma}^{bj\tau} y_{bj\tau}) = -\omega y_{ai\sigma}, \quad (15b)$$

with

$$A_{ai\sigma}^{bj\tau} = \delta_{ij} \delta_{ab} \delta_{\sigma\tau} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) + (a_\sigma i_\sigma | j_\tau b_\tau) + (a_\sigma i_\sigma | f_{\sigma\tau}^{\text{OEP}} | j_\tau b_\tau), \quad (16a)$$

$$B_{ai\sigma}^{bj\tau} = (a_\sigma i_\sigma | b_\tau j_\tau) + (a_\sigma i_\sigma | f_{\sigma\tau}^{\text{OEP}} | b_\tau j_\tau). \quad (16b)$$

The last terms in Eqs. (16) are the two-electron integrals involving the adiabatic exchange kernel $f_{\sigma\tau}^{\text{OEP}}(\mathbf{r}_1, \mathbf{r}_2)$ and are defined by

$$(a_\sigma i_\sigma | f_{\sigma\tau}^{\text{OEP}} | j_\tau b_\tau) = \int \int \psi_{a\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_1) \times f_{\sigma\tau}^{\text{OEP}}(\mathbf{r}_1, \mathbf{r}_2) \psi_{j\tau}(\mathbf{r}_2) \psi_{b\tau}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (17)$$

An explicit expression of the frequency-dependent exchange kernel has been derived by Görling.^{38,39} In this study, we employ the static limit of Görling’s expression, which is

$$f_{\sigma\tau}^{\text{OEP}}(\mathbf{r}_1, \mathbf{r}_2) = \delta_{\sigma\tau} \int \int X_\sigma^{-1}(\mathbf{r}_3, \mathbf{r}_1) h_\sigma(\mathbf{r}_3, \mathbf{r}_4) \times X_\sigma^{-1}(\mathbf{r}_4, \mathbf{r}_2) d\mathbf{r}_3 d\mathbf{r}_4, \quad (18)$$

and

$$\begin{aligned} h_\sigma(\mathbf{r}_3, \mathbf{r}_4) = & -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ba\sigma} + V_{ba\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_4) \psi_{b\sigma}(\mathbf{r}_4) \\ & + 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ij\sigma} + V_{ij\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{i\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_4) \\ & - 2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{b\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_4) \psi_{b\sigma}(\mathbf{r}_4) \\ & - 2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \\ & + 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{i\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_4) \\ & + 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{a\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_4) \\ & - 2 \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{(i_\sigma b_\sigma | j_\sigma a_\sigma)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_4) \psi_{b\sigma}(\mathbf{r}_4) \\ & - 2 \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{(i_\sigma j_\sigma | b_\sigma a_\sigma)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_4) \psi_{b\sigma}(\mathbf{r}_4). \end{aligned} \quad (19)$$

The derivation can be found in the Appendix. With the orthonormal auxiliary Gaussian functions, an explicit expression of the kernel integrals can be written as

$$(a_{\sigma}i_{\sigma}|f_{\sigma\tau}^{\text{OEP}}|j_{\tau}b_{\tau}) = \delta_{\sigma\tau} \sum_{\kappa,\lambda,\mu,\nu}^{\text{aux.}} (a_{\sigma}i_{\sigma}\kappa)(\mathbf{X}_{\sigma}^{-1})_{\kappa\lambda}(\mathbf{h}_{\sigma})_{\lambda\mu}(\mathbf{X}_{\sigma}^{-1})_{\mu\nu}(j_{\tau}b_{\tau}\nu), \quad (20)$$

with

$$\begin{aligned} (\mathbf{h}_{\sigma})_{\lambda\mu} = & -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ba\sigma} + V_{ba\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} (i_{\sigma}a_{\sigma}\lambda)(i_{\sigma}b_{\sigma}\mu) + 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ij\sigma} + V_{ij\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} (i_{\sigma}a_{\sigma}\lambda)(a_{\sigma}j_{\sigma}\mu) \\ & - 2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} (b_{\sigma}a_{\sigma}\lambda)(i_{\sigma}b_{\sigma}\mu) - 2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} (i_{\sigma}b_{\sigma}\lambda)(b_{\sigma}a_{\sigma}\mu) \\ & + 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} (i_{\sigma}j_{\sigma}\lambda)(a_{\sigma}j_{\sigma}\mu) + 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} (a_{\sigma}j_{\sigma}\lambda)(i_{\sigma}j_{\sigma}\mu) \\ & - 2 \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{(i_{\sigma}b_{\sigma}|j_{\sigma}a_{\sigma})}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{b\sigma})} (i_{\sigma}a_{\sigma}\lambda)(j_{\sigma}b_{\sigma}\mu) - 2 \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{(i_{\sigma}j_{\sigma}|b_{\sigma}a_{\sigma})}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{b\sigma})} (i_{\sigma}a_{\sigma}\lambda)(j_{\sigma}b_{\sigma}\mu). \end{aligned} \quad (21)$$

The TDOEP method outlined above was implemented into an LCAO algorithm with or without the Tamm–Dancoff approximation (i.e., with or without neglecting the matrix \mathbf{B}).¹² TDOEP/TD will represent TDOEP employing the Tamm–Dancoff approximation. We invoked Davidson’s trial-vector algorithm⁶⁹ modified by Olsen *et al.*⁷⁰ for the particular form of Eq. (15). By virtue of this algorithm, we avoided the storage or diagonalization of the potentially large \mathbf{A} and \mathbf{B} matrices and also the storage or manipulation of transformed two-electron integrals. The fourfold summations in Eqs. (20) and (21) were carried out stepwise to minimize the scaling of computational cost. The algorithm is analogous to the ones employed in the implementation of the conventional TDDFT method and its detail will not be described here. The interested readers are referred to the literature.^{5,6,9}

We also consider an approximate TDOEP method employing a hybrid of the Slater potential and an exchange-correlation potential generated from a conventional local or gradient-corrected exchange-correlation functional, i.e., the Slater–Vosko–Wilk–Nusair (SVWN) or Becke–Lee–Yang–Parr (BLYP) functional. The Slater potential is used in the asymptotic region, while the SVWN or BLYP potential is used in the vicinity of nuclei, and they both are defined in terms of the converged KS orbitals for the resulting hybrid potential. We shift the SVWN or BLYP potential by a constant, so that we can graft it onto the former potential seamlessly. This constant is determined by insisting that the shifted potential (but before the Slater potential is grafted) satisfy the HOMO condition analogous to Eq. (14). We simply graft the two potentials to each other where they cross, except when the crossing occurs within the Bragg–Slater radius of any of the constituent nuclei. The SVWN or BLYP kernel within the adiabatic approximation is employed in conjunction with the asymptotically-corrected SVWN or BLYP potential in the TDDFT calculations. We shall henceforward call these methods SVWN/AC and BLYP/AC (AC stands for asymptotic correction).

III. RESULTS AND DISCUSSION

The uncontracted Gaussian basis sets employed in the TDOEP calculations are specified in Table I. In each TDOEP calculation, the same set was used as an orbital basis set and also as an auxiliary basis set to expand a potential, a linear response function, and a kernel. Table II compiles the total and highest occupied orbital energies of Be and Tables III and IV list the highest occupied orbital energies of N₂ and H₂O at their respective equilibrium geometries, which are specified in the tables along with the basis sets employed. Observed ionization potentials⁷⁹ are also given in these tables. Tables V–VII summarize the calculated and observed (adopted from Refs. 80–82) vertical excitation energies of Be, N₂, and H₂O, respectively. Figures 1–3 compare the various exchange potentials employed in this study.

As can be seen in Tables II–IV, SVWN and BLYP underestimate excessively the absolute values of the highest occupied orbital energies relative to the experimental ionization potentials. This is attributed to the well-known fact that the exchange-correlation potentials obtained from these functionals decay too rapidly.⁷ Figures 1–3 illustrate this for the SVWN functionals. When the asymptotic correction is made, the SVWN potentials are shifted down and the $-1/r$ tail is grafted to the shifted SVWN potentials. Clearly, the SVWN/AC potentials approximate the OEP’s reasonably well, not exhibiting any visible discontinuity at the seams. Since we employ Eq. (14) to determine the magnitude of the shift, the SVWN/AC and BLYP/AC highest occupied orbital energies become very close to the HF highest occupied orbital energies and are in significantly better agreement with the experimental result. A greater proportion of the errors (from the experimental ionization potentials) in the SVWN and BLYP highest occupied orbital energies is ascribed to the wrong asymptotic decay of the respective potentials, whereas the remainder of the errors has to do with the shape of the SVWN/AC or BLYP/AC potential near the atom or molecule. It may also be noticed from the figures that the characteristic humps in the intershell region of the OEP, which are known to be energetically significant,²² are not repro-

TABLE I. Uncontracted Gaussian basis sets.

Element	Angular momentum	Exponent
H	<i>s</i>	54.0, 18.0, 6.0, 2.0, 0.666667, 0.222222, 0.0733333, 0.0244444, 0.00814815
	<i>p</i>	2.0, 0.666667, 0.222222, 0.0733333, 0.0244444
	<i>d</i> ^a	0.666667
Be	<i>s</i>	13122.0, 4374.0, 1458.0, 486.0, 162.0, 54.0, 18.0, 6.0, 2.0, 0.666667, 0.222222, 0.0733333, 0.0244444, 0.00814815, 0.00271605, 0.000905350
	<i>p</i>	54.0, 18.0, 6.0, 2.0, 0.666667, 0.222222, 0.0733333, 0.0244444, 0.00814815, 0.00271605, 0.000905350
	<i>d</i> ^a	2.0, 0.666667, 0.222222, 0.0733333, 0.0244444, 0.00814815, 0.00271605
N, O	<i>s</i>	13122.0, 4374.0, 1458.0, 486.0, 162.0, 54.0, 18.0, 6.0, 2.0, 0.666667, 0.222222, 0.0733333, 0.0244444, 0.00814815
	<i>p</i>	54.0, 18.0, 6.0, 2.0, 0.666667, 0.222222, 0.0733333, 0.0244444, 0.00814815
	<i>d</i> ^a	2.0, 0.666667, 0.222222

^aCartesian 6*d* components are used.TABLE II. The total (*E*) and highest occupied orbital (ϵ_h) energies (in E_h) of Be calculated with the 16*s*11*p*7*d* basis set given in Table I.

	SVWN	BLYP	SVWN AC	BLYP AC	HF	OEP ^a	OEP ^b	OEP ^c	Expt. ^d
<i>E</i>	-14.4471	-14.6614	-14.4471	-14.6614	-14.5729	-14.5723	-14.5723	-14.5724	...
ϵ_h	-0.2057	-0.2009	-0.3077	-0.3063	-0.3093	-0.3148 ^e	-0.1828 ^f	-0.3092	-0.3426

^aCombined Colle–Nesbet and *S* algorithm.^b*S* algorithm.^cGrid-based numerical algorithm (Ref. 28).^dFrom the observed ionization potential from Ref. 79.^eThe deviation from the HOMO condition [Eq. (14)] is 0.0055 E_h .^fThe deviation from the HOMO condition [Eq. (14)] is -0.1264 E_h .TABLE III. The highest occupied orbital energy (in E_h) of N₂ (1.0980 Å).

SVWN ^a	BLYP ^a	SVWN ^a AC	BLYP ^a AC	HF ^a	OEP ^{b,c}	OEP ^{b,d}	Expt. ^e
-0.3841	-0.3779	-0.6118	-0.6092	-0.6355 ^f	-0.5853 ^g	-0.3644 ^h	-0.5726

^aThe 6-311(3+,3+)G** (6 Cartesian *d* components) basis set is used.^bThe 14*s*9*p*3*d* basis set given in Table I is used.^cCombined Colle–Nesbet and *S* algorithm.^d*S* algorithm.^eFrom the observed ionization potential from Ref. 79.^fThe energy of the 3 σ_g orbital.^gThe deviation from the HOMO condition [Eq. (14)] is -0.0491 E_h .^hThe deviation from the HOMO condition [Eq. (14)] is -0.2700 E_h .TABLE IV. The highest occupied orbital energy (in E_h) of H₂O (0.9584 Å and 104.45°).

SVWN ^a	BLYP ^a	SVWN ^a AC	BLYP ^a AC	HF ^a	OEP ^{b,c}	OEP ^{b,d}	Expt. ^e
-0.2703	-0.2637	-0.5026	-0.5027	-0.5100	-0.5271 ^f	-0.3211 ^g	-0.4638

^aThe 6-311(3+,3+)G** (6 Cartesian *d* components) basis set is used.^bThe 14*s*9*p*3*d* (oxygen) and 9*s*5*p*1*d* (hydrogen) basis sets given in Table I are used.^cCombined Colle–Nesbet and *S* algorithm.^d*S* algorithm.^eFrom the observed ionization potential from Ref. 79.^fThe deviation from the HOMO condition [Eq. (14)] is 0.0184 E_h .^gThe deviation from the HOMO condition [Eq. (14)] is -0.1876 E_h .

TABLE V. Excitation energies (in eV) of Be calculated with the $16s11p7d$ basis set given in Table I.

State	SVWN ^a	BLYP ^a	SVWN AC	BLYP AC	CIS	TDHF ^b	TDOEP TD	TDOEP ^b	STEOM CCSD	Expt. ^c
1S	5.66	5.47	7.20	7.20	7.26	7.26	7.41	7.40	8.11	8.09
3S	5.64	5.43	7.12	7.09	7.10	...	7.24	...	8.01	8.00
1D	7.52	7.47	7.58	7.58	7.77	7.77	...	7.99
3D	5.83	5.55	6.83	6.71	6.84	...	6.92	...	7.76	7.69
1P	5.65	5.43	6.61	6.56	6.77	6.73	6.80	6.76	7.66	7.46
3P	5.79	5.58	7.36	7.47	7.40	...	7.55	...	8.31	7.40
3P	5.65	5.42	6.41	6.30	6.44	...	6.45	...	7.35	7.30
1D	5.83	5.54	6.75	6.67	6.92	6.92	7.02	7.02	7.72	7.05
1S	5.58	5.33	6.02	5.97	6.13	6.12	6.16	6.15	6.87	6.78
3S	5.50	5.28	5.76	5.69	5.53	...	5.54	...	6.51	6.46
1P	4.82	4.81	4.83	4.86	5.05	4.80	5.06	4.82	5.50	5.28
3P	2.36	2.09	2.36	2.09	1.70	...	1.73	...	2.86	2.73
Error ^d	1.45	1.66	0.62	0.69	0.63	0.54	0.57	0.46	0.22	

^aSome high-lying states were not found among the roots, because we sought only the several lowest-lying excited states by the trial-vector algorithm.

^bOwing to the triplet near instability of the ground-state wave function, triplet excited states were not accessible.

^cReference 81.

^dThe mean absolute errors from the experimental data.

duced by the SVWN or SVWN/AC potentials. The Krieger–Li–Iafrate (KLI) potentials,^{23–27,63} which are approximations to OEP's, somewhat recover the intershell humps but they apparently underestimate their magnitude, and consequently they lie in between the SVWN/AC potentials and OEP's.

The OEP method with the new algorithm developed in this study and that with the S algorithm reproduce the accurate total energy of Be (Table II) obtained from the grid-based OEP calculation²⁸ within $0.1 mE_h$, which attests to the fact that they both provide us with reliable occupied orbitals.⁵⁸ However, there is much greater variation in the calculated highest occupied orbital energies depending on the algorithms used. OEP with the S algorithm alone exhibits deviations in excess of $0.1E_h$ from the HOMO condition, which indicates that the virtual orbitals obtained from this algorithm are not reliable. When the new algorithm is used and hence the $-1/r$ asymptotic behavior is imposed, the deviations from the HOMO condition become smaller by an

order of magnitude. The deviations ($0.0055 E_h$ to $-0.0491 E_h$) are sufficiently small that we can perform the calculations of transition energies to the several lowest excited states with a reasonable numerical precision. As the excitation energies approach the first ionization potential, however, we must anticipate the error to grow to roughly the observed deviations from the HOMO condition, but for low-lying excited states, the errors would be much more modest. The apparently good agreement between the experimental ionization potentials and the negative of some of the bare OEP highest occupied orbital energies (see, e.g., Table III) is an artifact arising from the difficulty in computing OEP orbital energies accurately, and must not be overrated. When the deviations from the HOMO condition are added, the OEP highest occupied orbital energies become very close (albeit not necessarily equal) to the HF value, as expected from Eq. (14).

TABLE VI. Vertical excitation energies (in eV) of N_2 (1.0980 Å).

State	SVWN ^a	BLYP ^a	SVWN ^a AC	BLYP ^a AC	CIS ^a	TDHF ^a	TDOEP ^b TD	TDOEP ^b	STEOM ^c CCSD	Expt. ^d
$^1\Sigma_u^+$	10.70	10.49	13.25	13.02	14.37	14.05	13.19	13.17	12.84	12.98
$^1\Pi_u$	10.70	10.50	13.30	13.12	13.24	13.23	12.88	12.88	12.84	12.90
$^1\Sigma_g^+$	10.46	10.19	12.62	12.37	14.04	14.02	12.38	12.36	12.20	12.2
$^3\Sigma_g^+$	10.35	10.03	12.21	11.93	13.14	13.07	11.97	11.94	11.78	12.0
$^3\Pi_u$	10.36	10.32	10.42	10.39	11.81	11.37	10.74	10.46	11.28	11.19
$^1\Delta_u$	10.26	9.89	10.34	9.97	9.04	8.76	9.15	9.04	10.55	10.27
$^1\Sigma_u^-$	9.70	9.60	9.76	9.66	8.47	7.89	10.20	10.20	10.10	9.92
$^3\Sigma_u^-$	9.70	9.60	9.76	9.66	8.47	7.89	10.20	10.20	9.87	9.67
$^1\Pi_g$	9.09	9.10	9.16	9.18	9.98	9.73	10.03	9.93	9.30	9.31
$^3\Delta_u$	8.87	8.29	8.92	8.32	7.32	5.89	7.30	6.18	8.96	8.88
$^3\Pi_g$	7.58	7.46	7.62	7.49	8.02	7.67	8.09	7.81	8.15	8.04
$^3\Sigma_u^+$	7.91	7.49	7.94	7.52	6.20	3.38	5.98	3.42	7.59	7.75
Error ^e	0.82	1.01	0.27	0.28	1.08	1.50	0.58	0.92	0.13	

^aThe 6-311(3+,3+)G** (6 Cartesian d components) basis set is used.

^bThe $14s9p3d$ basis set given in Table I is used.

^cThe 6-311(2+,2+)G** (6 Cartesian d components) basis set is used.

^dReference 82.

^eThe mean absolute errors from the experimental data.

TABLE VII. Vertical excitation energies (in eV) of H₂O (0.9584 Å and 104.45°).

State	SVWN ^a	BLYP ^a	SVWN ^a AC	BLYP ^a AC	CIS ^a	TDHF ^a	TDOEP ^b TD	TDOEP ^b	STEOM ^d CCSD	Expt. ^c
¹ A ₁	8.52	8.27	11.04	10.89	11.49	11.45	11.15	11.10	10.03	10.17
¹ B ₁	7.49	7.30	10.81	10.61	11.26	11.25	10.53	10.53	9.89	10.0
³ B ₁	7.48	7.28	10.77	10.54	11.15	11.11	10.46	10.44	9.85	...
¹ A ₁	7.72	7.46	10.00	9.87	10.88	10.86	10.44	10.43	9.67	9.67
³ A ₁	8.18	7.88	10.71	10.48	10.80	10.67	10.50	10.38	9.65	...
¹ A ₂	7.48	7.24	9.81	9.59	10.32	10.27	10.19	10.18	9.14	9.1
³ A ₂	7.48	7.22	9.60	9.31	9.97	9.86	9.99	9.94	8.97	...
³ A ₁	7.70	7.42	9.47	9.22	10.07	9.85	9.72	9.54	9.34	...
¹ B ₁	6.50	6.18	7.97	7.76	8.64	8.59	8.50	8.49	7.35	7.4
³ B ₁	6.24	5.89	7.53	7.25	7.97	7.85	7.89	7.81	7.02	7.2
Error ^d	1.60	1.87	0.60	0.41	1.17	1.12	0.86	0.83	0.09	

^aThe 6-311(3+,3+)G** (6 Cartesian *d* components) basis set is used.

^bThe 14s9p3d (oxygen) and 9s5p1d (hydrogen) basis sets given in Table I are used.

^cReference 80.

^dThe mean absolute errors from the experimental data.

Owing to the wrong asymptotic behavior of the SVWN and BLYP potentials, the excitation energies (Tables V–VII) obtained with these functionals degrade rapidly as they approach the negative of the highest occupied orbital energies.⁷ The SVWN and BLYP excitation energies deviate more from the experimental excitation energies as they go higher. The mean absolute error from the experimental data can be as great as 1.87 eV for H₂O, whose excited states are dominated by Rydberg excited states. SVWN/AC and BLYP/AC, as we would expect, do not exhibit such pathological behavior. The SVWN/AC and BLYP/AC excitation energies are in proportion to the experimental excitation energies and they also behave in a very similar manner as the CIS, TDHF, TDOEP/TD, and TDOEP excitation energies. For Be, SVWN/AC and BLYP/AC provide the results that are comparable to the results of HF-based single excitation theories, and hence, we consider that the remaining errors between the

SVWN/AC or BLYP/AC results and the experimental data be traced to the electron correlation effect. Although Be has only two valence electrons, owing to the near degeneracy of 2s and 2p orbitals, the effect of electron correlation in the ground state is substantial. For N₂, whose low-lying excited states are characterized as valence excited states, SVWN and BLYP do not break down until the experimental excitation energies reach 11 eV.^{4,5} SVWN/AC and BLYP/AC yield essentially the same excitation energies for those low-lying states and also significantly improve (i.e., raise) the excitation energies to the higher-lying states. They, as a result, achieve impressive mean absolute errors of 0.27 (SVWN/AC) and 0.28 (BLYP/AC) eV, which may be compared with the results obtained by Tozer and Handy¹⁰ with a more elaborate asymptotic correction scheme. The excited states of H₂O are dominated by Rydberg excited states, and as we would expect, the asymptotic correction turns out to be par-

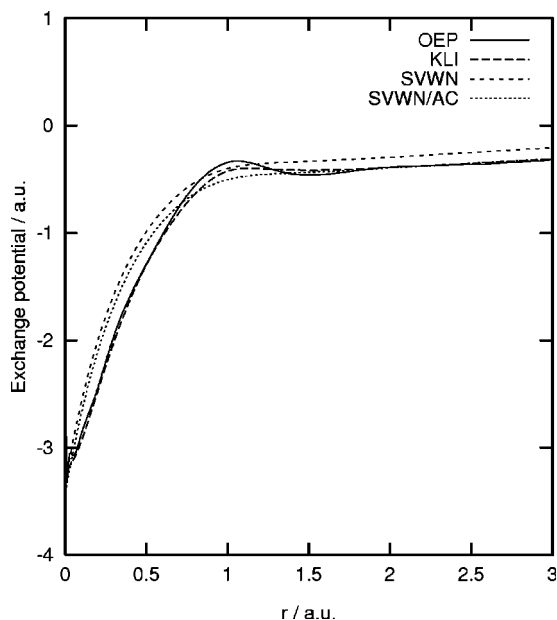


FIG. 1. The exchange potentials of Be as a function of the distance from the nucleus (*r*). For the basis set used, see the caption of Table II.

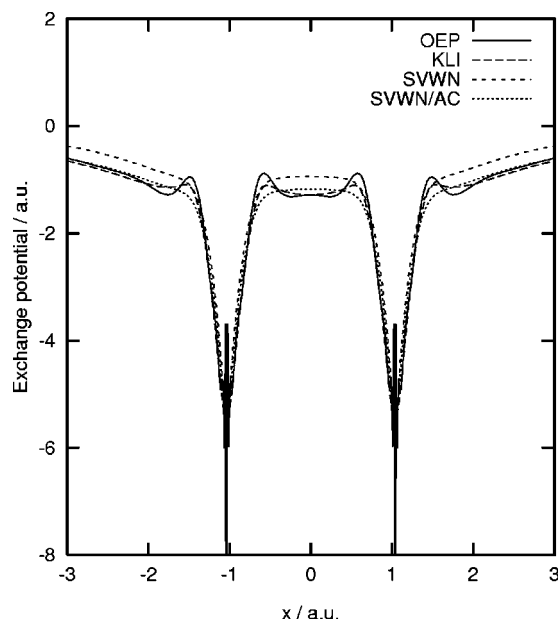


FIG. 2. The exchange potentials of N₂ (1.0980 Å) along the C_∞ axis. For the basis set used, see the caption of Table III.

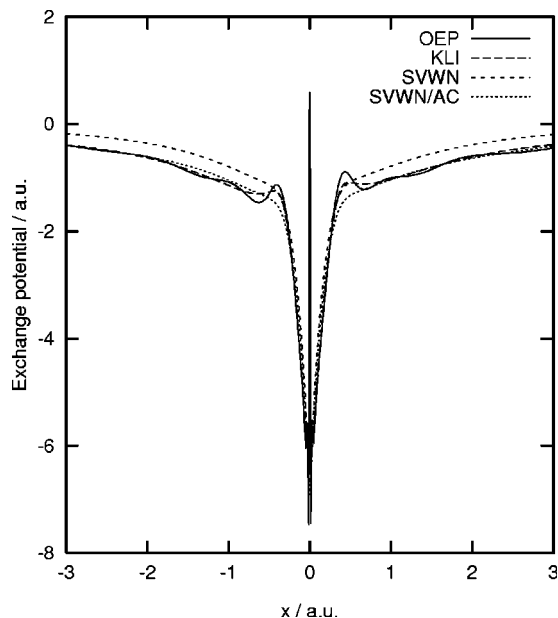


FIG. 3. The exchange potentials of H_2O (0.9584 \AA and 104.45°) along the C_2 axis (the oxygen atom is at the origin and the hydrogen atoms are in the right-hand side). For the basis set used, see the caption of Table IV.

ticularly effective throughout the energy range shown in the table. The fact that SVWN/AC and BLYP/AC perform significantly better than TDOEP might imply that the former potentials effectively account for the electron correlation effects to some extent. The comparison of the SVWN/AC and BLYP/AC potentials and OEP's (see Figs. 1–3) then suggests that correlation would diminish the characteristic inter-shell humps of OEP's. This indeed appears to be supported at least qualitatively by our recent study⁶² of accurate *ab initio* correlation potentials.

Overall, the behavior of TDOEP/TD and TDOEP excitation energies parallels that of CIS and TDHF excitation energies. Remarkably, both TDOEP and TDHF suffer from a near triplet instability problem for Be and N_2 . It may also be noticed that the difference between the TDOEP/TD and TDOEP excitation energies for each transition is similar to the difference between the CIS and TDHF excitation energies; in other words, the Tamm–Dancoff approximation¹² affects TDHF and TDOEP in the same manner. These results are not surprising, in that both the HF and OEP are two closely related exchange-only models employing the identical energy expression. The only difference between the HF and OEP methods is that the latter uses a constraint that the potential be local (multiplicative). Hence, it is not unreasonable to expect that these two methods, which are known to give very close total energies across a variety of chemical systems,⁴³ would exhibit a very similar time-dependent response to any time-dependent perturbation. The present results indicate that this is indeed the case, and the excitation energies obtained from TDOEP (TDOEP/TD) are essentially of the same quality as those obtained from TDHF (CIS). In other words, TDOEP, which neglects electron correlation while treating the exchange contribution rigorously within the KS DFT framework, performs just as well as, but not substantially better than, the HF-based single excitation theo-

ries. This conclusion was foreseen by Ullrich, Gossman, and Gross.³¹ It may be said that we have now added two new members of fundamental single excitation theories, i.e., TDOEP/TD and TDOEP, to the usual members, the CIS and TDHF methods.

The errors between the CIS, TDHF, TDOEP/TD, and TDOEP and experimental data are, therefore, traced to electron correlation. In this light, it is of interest to compare the TDOEP excitation energies of Be obtained in this study and those obtained by Petersilka, Gross, and Burke⁴⁹ from the TDOEP calculations for the same system employing an accurate local (multiplicative) exchange-correlation potential. The addition of correlation potential by Petersilka, Gross, and Burke resulted in eliminating the errors between the TDOEP (exchange-only) results obtained by ourselves and experimental data almost completely. Hence, we are rather optimistic about the prospect of constructing a new hierarchy of excited state theories that systematically approaches the exact solution of the Schrödinger equation by starting from TDOEP (exchange-only) and adding the correlation effects at different levels of theoretical rigor, while maintaining the TDDFT framework. Such a hierarchy is appealing in that it provides an immediate physical interpretation of potentials and orbitals in connection with electronic excitation processes and also suggests possible computational advantages arising from the single excitation theory framework. For the ground states, intensive efforts in this direction have been made.^{40,47,59,62} The table also includes the results of an ultimate correlated single excitation theory, i.e., STEOM-CCSD, and they agree accurately with the experimental excitation energies for all but two states (1D and 3P states) of Be. These exceptions involve simultaneous promotion of two electrons and are beyond the applicability of current single excitation theories including STEOM-CCSD and the correlated TDOEP of Petersilka, Gross, and Burke. Hence, the good agreement between CIS, TDHF, TDOEP/TD, and TDOEP and experimental results for these two states is due to fortuitous cancellation of errors.

The errors in the TDOEP/TD or TDOEP excitation energies are consistently smaller than those of the CIS or TDHF excitation energies. It should be noted, however, that the better agreement between TDOEP (TDOEP/TD) and experimental data for the higher-lying excited states of Be and N_2 than that between TDHF (CIS) and experimental data can be due, at least partly, to the lowering of the numerical accuracy in the occupied and virtual orbital energy differences as they become larger. A unique property of TDOEP that is not present in the HF-based single excitation theories is that the excitation energies are frequently accurately approximated by orbital energy differences (see, e.g., Garza *et al.*^{53,54}). This property arises from the local (multiplicative) nature of exchange(-correlation) potentials, and can also be seen in other TDDFT methods including SVWN/AC and BLYP/AC. This is in striking contrast with the HF-based single excitation theories in which the occupied and virtual orbital energy differences cannot be interpreted as approximations to the excitation energies, but they involve not only the promotion of an electron from one orbital to another but also an increment in the number of electrons. It is possible

that, because of this simple relationship between the orbital energies and the excitation energies in OEP or local (multiplicative) potentials in general, TDOEP can provide an appreciably better balanced description of excitation processes,³ notwithstanding the above-mentioned statement that TDOEP does not lead to a substantial improvement over HF-based single excitation theories in the sense that it also neglects electron correlation.

IV. CONCLUSION

In this article, we have reported the formalisms and initial implementation of the LCAO TDOEP method within the adiabatic approximation applicable to general polyatomic molecules. No approximation besides the LCAO and adiabatic approximations has been made. To achieve this aim, we have first devised a new LCAO OEP algorithm for molecules suitable for a time-dependent linear response treatment, by combining the idea of Colle and Nesbet⁵⁵ and the S algorithm of the LCAO OEP method. The new algorithm has provided OEP's having the correct $-1/r$ asymptotic behavior throughout the space and hence well-balanced spectra of virtual as well as occupied orbital energies, without deteriorating the total energies. We have applied TDOEP to atoms and polyatomic molecules employing this new LCAO OEP algorithm and the adiabatic exchange kernel derived earlier by Görling.^{38,39} Davidson's trial-vector algorithm^{69,70} has been employed to avoid the storage or manipulation of transformed two-electron integrals or the diagonalization of large matrices.

The results of the TDOEP calculations performed for Be, N₂, and H₂O are remarkable in the following respects. TDOEP suffers from a triplet (near) instability problem for Be and N₂ just as TDHF, and the Tamm–Dancoff approximation affects the excitation energies in a very similar manner for both TDHF and TDOEP. Overall, the excitation energies of TDOEP and TDOEP/TD parallel closely those of TDHF and CIS, respectively. These results can be interpreted as indicating that an OEP energy, which closely approximates the corresponding HF energy in time-independent situations, exhibits a similar time-dependent response to time-dependent perturbation as the corresponding HF energy. TDOEP (TDOEP/TD) treats the exchange energy and potential rigorously within the KS DFT framework and hence it works as well as TDHF (CIS), but it does not take into account any correlation contribution and hence it cannot perform substantially better than TDHF (CIS). However, for all the systems studied, the errors from the experimental data are noticeably smaller in TDOEP (TDOEP/TD) than in TDHF (CIS), suggesting that the former may provide a better balanced zeroth-order description of electronic excitation processes, although drawing a definitive conclusion warrants an OEP algorithm that computes the virtual orbital energies for molecules with an even higher accuracy. TDOEP (TDOEP/TD) and TDHF (CIS) are the fundamental single excitation theories in the two main approaches of contemporary computational chemistry, i.e., KS DFT and wave-function theories, to the exact solutions to the Schrödinger equation, and are the bases of more elaborate correlation treatments for excited states in respective approaches. These correlation

treatments can be rather different between the two approaches and hence correlated TDOEP may as well offer some unique computational advantages, which we will investigate in the future. Another important issue that the present TDOEP will open a possibility to tackle is the effect of adiabatic approximation^{38,39} in TDDFT. We will vigorously pursue this direction also in the future.

The local (multiplicative) nature of an OEP also permits straightforward approximations to TDOEP such as SVWN/AC and BLYP/AC proposed in this study. An SVWN/AC or BLYP/AC potential consists of an SVWN or BLYP potential shifted by a constant near the nuclei and a Slater potential in the asymptotic regions. The magnitude of the shift is determined by the HOMO condition. SVWN/AC and BLYP/AC potentials thus obtained do not exhibit any visible discontinuity at the seams and are reasonably good approximations to an OEP. TDDFT employing these functionals in conjunction with the bare SVWN or BLYP kernel shows performance superior to that of TDOEP or of HF-based single excitation theories. The mean absolute errors from the experimental data are in the range of 0.2–0.7 eV and are significantly smaller than those for SVWN or BLYP (0.8–1.9 eV), and hence this simple correction scheme to the conventional functionals is highly recommended for future application of TDDFT. The better performance of SVWN/AC and BLYP/AC over TDOEP implies that the former potentials somehow effectively incorporate the electron correlation effects, which, according to the comparison of the former and latter potentials, may amount to smoothing the intershell humps in OEP's.

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APPENDIX A: DERIVATION OF THE OEP INTEGRAL EQUATION

We start with a σ -spin exchange energy expression of the form,

$$E_{X\sigma} = -\frac{1}{2} \sum_{i,j}^{\text{occ.}} (i_{\sigma} j_{\sigma} | j_{\sigma} i_{\sigma}). \quad (\text{A1})$$

The corresponding KS local (multiplicative) exchange potential is defined by

$$V_{\sigma}^{\text{OEP}}(\mathbf{r}_1) = \frac{\delta E_{X\sigma}}{\delta \rho_{\sigma}(\mathbf{r}_1)} = \int \frac{\delta V_{\sigma}(\mathbf{r}_2)}{\delta \rho_{\sigma}(\mathbf{r}_1)} \frac{\delta E_{X\sigma}}{\delta V_{\sigma}(\mathbf{r}_2)} d\mathbf{r}_2, \quad (\text{A2})$$

where $V_{\sigma}(\mathbf{r})$ is a sum of the external, Coulomb, and exchange potentials, i.e.,

$$V_{\sigma}(\mathbf{r}_1) = V_{\text{ext}}(\mathbf{r}_1) + \sum_{\tau}^{\alpha, \beta} \int \frac{\rho_{\tau}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 + V_{\sigma}^{\text{OEP}}(\mathbf{r}_1). \quad (\text{A3})$$

By applying the first-order perturbation theory to the KS equation,

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\sigma}(\mathbf{r}) \right\} \psi_{p\sigma}(\mathbf{r}) = \epsilon_{p\sigma} \psi_{p\sigma}(\mathbf{r}), \quad (\text{A4})$$

we have

$$\frac{\delta \psi_{p\sigma}(\mathbf{r}_1)}{\delta V_{\sigma}(\mathbf{r}_2)} = \sum_{q \neq p}^{\text{all}} \frac{\psi_{p\sigma}(\mathbf{r}_2) \psi_{q\sigma}(\mathbf{r}_2) \psi_{q\sigma}(\mathbf{r}_1)}{\epsilon_{p\sigma} - \epsilon_{q\sigma}}, \quad (\text{A5a})$$

$$\frac{\delta \epsilon_{p\sigma}}{\delta V_{\sigma}(\mathbf{r}_2)} = \psi_{p\sigma}(\mathbf{r}_2) \psi_{p\sigma}(\mathbf{r}_2). \quad (\text{A5b})$$

Invoking these relationships, we find that the first factor in the integrand of Eq. (A2) is the inverse of the linear response function defined by Eq. (4), i.e.,

$$\begin{aligned} \frac{\delta \rho_{\sigma}(\mathbf{r}_1)}{\delta V_{\sigma}(\mathbf{r}_2)} &= 2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{\psi_{i\sigma}(\mathbf{r}_1) \psi_{a\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \psi_{a\sigma}(\mathbf{r}_2)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \\ &= X_{\sigma}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (\text{A6})$$

The inverse exists within the domain of the eigenfunctions of the linear response function.⁵⁸ Also applying the results of first-order perturbation theory to the second factor, we obtain

$$\frac{\delta E_{X\sigma}}{\delta V_{\sigma}(\mathbf{r}_2)} = -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} \psi_{i\sigma}(\mathbf{r}_2) \psi_{a\sigma}(\mathbf{r}_2)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}. \quad (\text{A7})$$

By substituting Eqs. (A6) and (A7) into Eq. (A2), we arrive at Eq. (1).

APPENDIX B: DERIVATION OF THE ADIABATIC OEP KERNEL

In the adiabatic approximation, the OEP kernel is simply

$$f_{\sigma\tau}^{\text{OEP}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta^2 E_{X\sigma}}{\delta \rho_{\sigma}(\mathbf{r}_1) \delta \rho_{\tau}(\mathbf{r}_2)} = \delta_{\sigma\tau} \frac{\delta V_{\sigma}^{\text{OEP}}(\mathbf{r}_1)}{\delta \rho_{\tau}(\mathbf{r}_2)}. \quad (\text{B1})$$

Using the chain rule and Eqs. (A5), we find

$$\begin{aligned} f_{\sigma\sigma}^{\text{OEP}}(\mathbf{r}_1, \mathbf{r}_2) &= \int \frac{\delta V_{\sigma}(\mathbf{r}_3)}{\delta \rho_{\sigma}(\mathbf{r}_2)} \frac{\delta V_{\sigma}^{\text{OEP}}(\mathbf{r}_1)}{\delta V_{\sigma}(\mathbf{r}_3)} d\mathbf{r}_3 \\ &= -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \frac{\delta}{\delta V_{\sigma}(\mathbf{r}_3)} \left[\sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{(i\sigma j\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 \right] d\mathbf{r}_3 \\ &= -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq i}^{\text{all}} \int \frac{(p\sigma j\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq j}^{\text{all}} \int \frac{(i\sigma p\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq j}^{\text{all}} \int \frac{(i\sigma j\sigma | p\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq a}^{\text{all}} \int \frac{(i\sigma j\sigma | j\sigma p\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{a\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq i}^{\text{all}} \int \frac{(i\sigma j\sigma | j\sigma a\sigma) \psi_{p\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq a}^{\text{all}} \int \frac{(i\sigma j\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{p\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{a\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad + 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{(i\sigma j\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{(i\sigma j\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) d\mathbf{r}_4 d\mathbf{r}_3 \\ &\quad - 2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{(i\sigma j\sigma | j\sigma a\sigma) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \frac{\delta X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1)}{\delta V_{\sigma}(\mathbf{r}_3)} d\mathbf{r}_4 d\mathbf{r}_3. \end{aligned} \quad (\text{B2})$$

Since the functional derivative of the inverse of the linear response²⁹ can be written as

$$\frac{\delta X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1)}{\delta V_{\sigma}(\mathbf{r}_3)} = - \int \int X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_5) \frac{\delta X_{\sigma}(\mathbf{r}_5, \mathbf{r}_6)}{\delta V_{\sigma}(\mathbf{r}_3)} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_5 d\mathbf{r}_6, \quad (\text{B3})$$

the last term of the right-hand side of Eq. (B2) becomes

$$\begin{aligned} & -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{(i_{\sigma} j_{\sigma} | j_{\sigma} a_{\sigma}) \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \frac{\delta X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1)}{\delta V_{\sigma}(\mathbf{r}_3)} d\mathbf{r}_4 d\mathbf{r}_3 \\ & = -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \int \int V_{\sigma}^{\text{OEP}}(\mathbf{r}_5) \frac{\delta}{\delta V_{\sigma}(\mathbf{r}_3)} \left[\frac{\psi_{i\sigma}(\mathbf{r}_5) \psi_{a\sigma}(\mathbf{r}_5) \psi_{i\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_6)}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \right] X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_3 \\ & = -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq i}^{\text{all}} \int \frac{V_{pa\sigma}^{\text{OEP}} \psi_{i\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_6) \psi_{i\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_6 d\mathbf{r}_3 \\ & -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq a}^{\text{all}} \int \frac{V_{ip\sigma}^{\text{OEP}} \psi_{i\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{a\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_6 d\mathbf{r}_3 \\ & -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq i}^{\text{all}} \int \frac{V_{ia\sigma}^{\text{OEP}} \psi_{p\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_6) \psi_{i\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_6 d\mathbf{r}_3 \\ & -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq a}^{\text{all}} \int \frac{V_{ia\sigma}^{\text{OEP}} \psi_{i\sigma}(\mathbf{r}_6) \psi_{p\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{a\sigma} - \epsilon_{p\sigma})} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_6 d\mathbf{r}_3 \\ & +2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{V_{ia\sigma}^{\text{OEP}} \psi_{i\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_6) \psi_{i\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_6 d\mathbf{r}_3 \\ & -2 \int X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \int \frac{V_{ia\sigma}^{\text{OEP}} \psi_{i\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_6) \psi_{a\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3)}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} X_{\sigma}^{-1}(\mathbf{r}_6, \mathbf{r}_1) d\mathbf{r}_6 d\mathbf{r}_3. \end{aligned} \quad (\text{B4})$$

Combining Eqs. (B2) and (B4), we obtain

$$f_{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \int \int X_{\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_1) h_{\sigma}(\mathbf{r}_4, \mathbf{r}_3) X_{\sigma}^{-1}(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 d\mathbf{r}_4, \quad (\text{B5})$$

with

$$h_{\sigma}(\mathbf{r}_4, \mathbf{r}_3) = -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq i}^{\text{all}} \frac{K_{pa\sigma} + V_{pa\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{p\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3) \quad (\text{B6})$$

$$-2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq j}^{\text{all}} \frac{(i_{\sigma} p_{\sigma} | j_{\sigma} a_{\sigma})}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{p\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3) \quad (\text{B7})$$

$$-2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq j}^{\text{all}} \frac{(i_{\sigma} j_{\sigma} | p_{\sigma} a_{\sigma})}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{p\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3) \quad (\text{B8})$$

$$-2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq a}^{\text{all}} \frac{K_{ip\sigma} + V_{ip\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{a\sigma} - \epsilon_{p\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3) \quad (\text{B9})$$

$$-2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq i}^{\text{all}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{p\sigma})} \psi_{p\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3) \quad (\text{B10})$$

$$-2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{p \neq a}^{\text{all}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{a\sigma} - \epsilon_{p\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{p\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{p\sigma}(\mathbf{r}_3) \quad (\text{B11})$$

$$+2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_3) \quad (\text{B12})$$

$$-2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3). \quad (\text{B13})$$

We can further simplify the expression by noticing

$$\begin{aligned}
 \text{(B6)} + \text{(B10)} &= -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ba\sigma} + V_{ba\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{b\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{j \neq i}^{\text{occ.}} \frac{K_{ja\sigma} + V_{ja\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{j\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{j \neq i}^{\text{occ.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{j\sigma})} \psi_{j\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \\
 &= -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ba\sigma} + V_{ba\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{b\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \\
 &\quad +2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \sum_{j \neq i}^{\text{occ.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{j\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \\
 &= -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ba\sigma} + V_{ba\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{b\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{b\sigma}(\mathbf{r}_3) \\
 &\quad +2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{j\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{i\sigma}(\mathbf{r}_3) \psi_{i\sigma}(\mathbf{r}_3), \tag{B14}
 \end{aligned}$$

and similarly

$$\begin{aligned}
 \text{(B9)} + \text{(B11)} &= 2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ij\sigma} + V_{ij\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \\
 &\quad +2 \sum_{i,j}^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{j\sigma} - \epsilon_{a\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{j\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{j\sigma}(\mathbf{r}_3) \\
 &\quad -2 \sum_i^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})(\epsilon_{i\sigma} - \epsilon_{b\sigma})} \psi_{i\sigma}(\mathbf{r}_4) \psi_{b\sigma}(\mathbf{r}_4) \psi_{b\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3) \\
 &\quad +2 \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \frac{K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}}}{(\epsilon_{i\sigma} - \epsilon_{a\sigma})^2} \psi_{i\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_4) \psi_{a\sigma}(\mathbf{r}_3) \psi_{a\sigma}(\mathbf{r}_3). \tag{B15}
 \end{aligned}$$

Using these results, we arrive at Eq. (19). The same expression can be readily obtained by applying the adiabatic approximation to the more general frequency-dependent OEP kernel expression derived by Görling.^{38,39}

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