Multireference Density Functional Theory for Describing Ground and Excited States with Renormalized Singles

Jiachen Li, Zehua Chen, and Weitao Yang

Department of Chemistry, Duke University, Durham, NC 27708, USA

E-mail: weitao.yang@duke.edu

*Jiachen Li and Zehua Chen share the first authorship.
Abstract

We applied renormalized singles (RS) in the multireference density functional theory (DFT) to calculate accurate energies of ground and excited states. The multireference DFT approach determines the total energy of the \(N\)-electron system as the sum of the \((N-2)\)-electron energy from a density functional approximation (DFA) and the two-electron addition energies from the particle-particle Tamm-Dancoff approximation (ppTDA), naturally including multireference description. The ppTDA@RS-DFA approach uses the RS Hamiltonian capturing all singles contributions in calculating two-electron addition energies, and its total energy is optimized with the optimized effective potential method. It significantly improves the original ppTDA@DFA. For ground states, ppTDA@RS-DFA properly describes dissociation curves tested and the double bond rotation of ethylene. For excited states, ppTDA@RS-DFA provides accurate excitation energies and largely eliminates the DFA dependence. ppTDA@RS-DFA thus provides an efficient multireference approach to systems with static correlation.

Graphical TOC Entry
Density functional theory (DFT) has become the most widely used tool in the electronic structure theory. The success of Kohn-Sham DFT (KS-DFT) can be attributed to the accurate and efficient description of complicated many-body effects by density functional approximations (DFAs), including local density approximations (LDAs), generalized gradient approximations (GGAs) and hybrid functionals. In past decades, KS-DFT has been successfully implemented in quantum chemistry packages to predict properties of molecules and solids. However, there are still many challenges in KS-DFT. For example, KS-DFT cannot properly describe systems with a strong static correlation, such as molecules with partially broken bonds. These strong correlated systems with degenerate or nearly degenerate states are multiconfigurational and thus is challenging for the single-determinant-based KS-DFT. It was shown that the errors of KS-DFT for predicting dissociation energies of multiconfigurational systems are from fractional spin errors in the functional approximation. To properly describe the bond breaking problem, multiconfiguration self-consistent field (MC-SCF) methods like the complete active space self-consistent field (CASSCF) method and other multireference methods in the wave function theory (WFT) are commonly used. Extending the traditional Kohn-Sham DFT, multiconfigurational methods have also been developed for describing multireference systems, including multiconfigurational pair-density functional theory (MC-PDFT) and the multistate density functional theory (MSDFT). Developments based on KS-DFT have also been made in past decades. The fractional-spin localized orbital scaling correction (FSLOSC) method corrects fractional spin errors and fractional charge errors within the KS-DFT framework. FSLOSC restores the flat-plane behavior of electronic energy at fractional charges and fractional spins and properly describes the dissociation of ionic species, single bonds, and multiple bonds while maintaining the proper symmetry in spin densities. The spin-restricted ensemble-referenced Kohn-Sham (REKS) method based on the rigorous ensemble representation of the energy and the density provides accurate description for strongly correlated systems. The commonly used time-dependent density functional theory (TDDFT) is known to provide poor accuracy.
for charge transfer and Rydberg excitations.\textsuperscript{29,30} Recently developments including orbital optimized (OO) DFT\textsuperscript{31} and mixed-reference spin-flip (MRSF)-TDDFT\textsuperscript{32} are shown to provide considerable improvements over KS-DFT and TDDFT.

Recently a self-consistent multireference approach has been developed in DFT based on linear response approaches.\textsuperscript{33} In this multireference DFT approach, the physical system is described by a generalized auxiliary system. The total energy of the physical system is divided into two parts: the energy of the auxiliary system determined by the chosen DFA and the excitation energy from a linear response theory. The excitation energy from the linear response theory is used to provide multiconfigurational description for the physical system in a natural way.\textsuperscript{33} In the original work of the multireference DFT approach, two linear response theories are used to provide the multiconfigurational description. In the first approach, the generalized auxiliary system is chosen to be the $(N - 2)$-electron system described with a DFA and the two-electron addition excitation energy is calculated by particle-particle random phase approximation (ppRPA)\textsuperscript{34–36}. The method is denoted here as ppRPA@DFA. This ppRPA@DFA approach can also be viewed as a Fock-Space embedding approach that seamlessly combines the many-body description of the two-electron subsystem with the DFT description of the remaining $(N - 2)$ electrons.\textsuperscript{37} The ppRPA method has also been explored recently by other research groups.\textsuperscript{38,39} In the second approach, the generalized auxiliary system is chosen to be a high-spin state. Then low-spin states are obtained by using spin-flip time-dependent DFT (SF-TDDFT)\textsuperscript{40–43}. This approach is denoted here as SF@DFA. In both cases, the total energy in the multireference DFT approach is an implicit functional of the density of the physical system. The electron density of the physical systems is given by the functional derivative of the total energy with respect to the external field.\textsuperscript{33} It is clearly not equal to the density of the auxiliary reference system, in contrast to the traditional KS theory.\textsuperscript{11} The self-consistent field (SCF) solution, or the minimization of the energy functional was obtained by the generalized optimized effective potential (GOEP) method.\textsuperscript{33,45} It has
been shown that the self-consistency is important for ppRPA@DFA and SF@DFA to predict more accurate dissociation energies than the post-SCF approaches: post-SCF-ppRPA@DFA and post-SCF-SF@FDA. Here post-SCF means the total energy in the multireference DFT approach is evaluated without the self-consistency.

The multireference DFT approach was shown to provide good descriptions for both ground and excited states. The ppRPA@HF approach properly describes bond breaking of small molecules and the the double bond rotation of the C$_2$H$_4$ molecule. The SF@HF provides accurate excitation energies of atomic and molecular systems. However, there are two problems in the original multireference DFT approach. First, as demonstrated in this work, the multireference DFT approach with commonly used DFAs has large errors for predicting energies of both ground states and excited states. The accuracy of the multireference DFT approach has an undesired dependence on the choice of the DFA. Second, the optimization of the GOEP method for multireference DFT with traditional DFAs can produce an unphysical density of the generalized auxiliary system, which has a negative HOMO-LUMO gap, or the switching of the HOMO and LUMO. This unphysical density leads to a failed optimization. Thus, only HF and a designed DFA with a high percentage of exact exchange were used in the original work. The orbital optimization (OO) can also be developed for the energy optimization in multireference DFT, as shown in the Section.S1 of the Supporting Information. Although OO has a better convergence rate than GOEP, it is shown to be equivalent to the optimization of an orbital functional with respect to the GOEP Hamiltonian and is thus expected to have the similar problem as with the GOEP method. Not using the optimal DFA can lead to large error in energies of the generalized auxiliary systems, for example, for the (N-2)-electron system in the case of the ppRPA@DFA approach. Ideally, one would like to use the optimal DFA to describe the (N-2)-electron reference system, because its energy contributes to the major part of the total energy for the N-electron system.
In the present work, to overcome the first challenge, we applied renormalized singles (RS) in the multireference DFT. RS was developed to provide a good starting point in the GW calculations, which is the RS Green’s function. The motivation of the RS Green’s function is to use the form of the Hartree-Fock (HF) self-energy to include all singles contributions. Because of the Brillouin theorem, the HF self-energy captures all the contributions of the single excitations completely. However, the HF Green’s function itself is not a good starting point for GW calculations. Therefore, the HF Hamiltonian is constructed with KS orbitals and diagonalized separately in the occupied and virtual subspaces of the DFA used. This renormalization procedure absorbs all singles contributions into the self-energy to eliminate the dependence on the choice of the DFA. The RS Green’s function constructed with RS eigenvalues is shown to predict accurate quasiparticle energies for valence states in the GW method as well as valence and core states in the T-matrix methods. The RS Green’s function shares a similar thinking as the renormalized single-excitation (rSE) correction in the random phase approximation (RPA) calculations for the correlation energy. The accuracy of RPA with rSE calculations for predicting binding energies of rare-gas dimers is significantly improved. In our work, RS changes the linear response calculation of the multireference DFT approach for ground and excited states, and the renormalization process does not modify the one-electron density matrix of the (N − 2)-electron auxiliary system and consequently its energy from a given DFA. The renormalization process that includes contributions of all one-body perturbations from the auxiliary system is expected to bring a better description for the linear response property and the resulting multireference description for the static correlation, as RS does for improving significantly the GW method and the T-matrix method. Based on the (N − 2)-electron system as the auxiliary system, the two-electron addition energy is obtained from particle-particle Tamm-Dancoff approximation (ppTDA) in the present work, to simplify the calculations without lost of accuracy. The RS Hamiltonian is used in the working equation of ppTDA. We denote this approach as ppTDA@RS-DFA. The corresponding post-SCF approach that calculates the total energy
without the self-consistency is denoted as post-SCF-ppTDA@RS-DFA.

To address the second issue on the failure of the GOEP optimization for multireference DFT when applied with commonly used DFAs, we introduced the optimized effective potential (OEP) method of Yang and Wu\textsuperscript{56} for the total energy optimization in the multireference DFT approach, in contrast to the GOEP method used in the original work.\textsuperscript{33} The Yang and Wu OEP method is an accurate and efficient method for the direct energy optimization for functionals depending on one-particle density matrix. A solution to the inverse problem of calculating a set of orbitals and the density matrix from a given electron density has also been developed similarly.\textsuperscript{57} In the OEP method, the local potential is constructed from the sum of a fixed one-electron potential and a linear combination of potential basis functions. This turns the difficult-to-solve integral equation in OEP to a direct optimization with respect to the coefficients of the potential basis functions, with the correct asymptotic conditions of the potential enforced by the long-range fixed one-electron potential. The OEP method has been implemented for calculating total energies, potentials and geometries for a broad range of systems.\textsuperscript{56-58} In this paper, we explored the optimization of multireference DFT with the OEP method. The gradient of the total energy with respect to the coefficients of the linear expansion in multireference DFT consists of two parts. The gradient of the \((N - 2)\)-electron auxiliary system with respect to the potential basis function only involves the \((N - 2)\)-electron Fock matrix. And the gradient of the ppTDA excitation energies is formulated with eigenvectors of ppTDA and the exchange-correlation (XC) kernel of the chosen DFA, which was derived in previous works.\textsuperscript{33,45} We demonstrate that the optimization of the multireference DFT approach with conventional DFAs in the OEP method can produce physical potentials for most systems. In contrast, the GOEP method fails to converge for commonly used DFAs.\textsuperscript{33} Our approach thus opens up broad possibilities for the application of the multireference DFT approach.
In the multireference DFT approach, the total energy of the \( n \)-th eigenstate of the physical system \( E_v[\rho] \) is expressed as:

\[
E_{v,n}[\rho] = E_{v}^{\text{ref}}[\rho_{s}^{\text{ref}}] + \Delta E_{n}[\rho_{s}^{\text{ref}}],
\]  

(1)

where \( \rho \) is the density matrix of the physical system, \( \rho_{s}^{\text{ref}} \) is the density matrix of the noninteracting auxiliary reference system, \( E_{v}^{\text{ref}}[\rho_{s}^{\text{ref}}] \) is the energy of the auxiliary system determined by the chosen DFA, \( \Delta E_{n}[\rho_{s}^{\text{ref}}] \) is the excitation energy from a linear response theory that restores the symmetry of the physical system, and \( n \) is the energy level. Eq.1 indicates that the energy of excited states can also be obtained by selecting the target excitation energy from the linear response theory. The noninteracting auxiliary reference system can be an \((N-2)\)-electron system in conjunction with a ppRPA linear response for excitation or an \(N\)-electron high spin state system in conjunction with a SF-TDDFT calculation for excitation.\(^{33,45}\) The density of the physical system \( \rho \), not equal to \( \rho_{s}^{\text{ref}} \), is defined by the linear response of the total energy.

In present work, we chose the \((N-2)\)-electron system as the auxiliary system and the excitation energies are obtained by ppTDA for Eq.1. The working equation of ppTDA is obtained by keeping only the two-electron addition part in the ppRPA matrix:\(^{54,55,59}\)

\[
AX = \omega X,
\]  

(2)

where

\[
A_{ab,cd} = \delta_{ac}F_{bd} + \delta_{bd}F_{ac} + \langle ab||cd\rangle,
\]  

(3)

\( F \) is the one-electron KS or generalized KS Hamiltonian of the DFA used, \( X \) is the two-electron addition eigenvector, and \( \omega \) is the two-electron addition energy. In above equations,
the antisymmetrized two-electron integral $\langle pq||rs \rangle$ is defined as

$$\langle pq||rs \rangle = \langle pq|rs \rangle - \langle qp|rs \rangle = \int dx_1 dx_2 \frac{\phi_p^{*}(x_1)\phi_q^{*}(x_2)(1 - \hat{P}_{12})\phi_r(x_1)\phi_s(x_2)}{|r_1 - r_2|}$$

where $x$ stands for both spatial and spin coordinates. We use $i, j$ for occupied orbitals, $a, b$ for virtual orbitals and $p, q$ for general orbitals. Because we are only interested in the ground state and low-lying excited states, Eq.2 can be efficiently solved by the Davidson algorithm as implemented in Ref. 54.

Although Eq.1 provides a rigorous description for ground states and excited states, its accuracy strongly depends on the choice of the DFA. To reduce the dependence and improve the accuracy, we now introduce the RS method. The RS Hamiltonian is defined as

$$H^{RS} = PH^{HF}[\rho_s^{ref}]P + QH^{HF}[\rho_s^{ref}]Q,$$

where $P = \sum_{i}^{\text{occ}} |\phi_i \rangle \langle \phi_i|$ is the projection into the occupied orbital space and $Q = I - P$ is the projection into the virtual orbital space defined by the DFA used, $H^{HF}[\rho_s^{ref}]$ means the HF Hamiltonian is constructed with the KS density matrix. The RS Hamiltonian captures all contributions from single excitations of the $(N - 2)$-electron system. The RS Hamiltonian is inserted in Eq.2 as the generalized KS Hamiltonian of RS-DFA to get the excitation energy, which is expected to provide a better description for states with a multireference nature and with the static correlation. Because the working equation of ppTDA in Eq.2 only has the two-electron addition part, only the virtual-virtual block of the RS Hamiltonian is needed.

To achieve a SCF solution, we optimized the total energy in Eq.1 with the OEP method. In the OEP method, the potential is constructed as following

$$v_s(r) = v_{\text{ext}}(r) + v_0(r) + \sum_tb_tg_t(r),$$

9
where $v_{\text{ext}}(r)$ is the external potential due to the nuclei, $v_0(r)$ is a fixed potential and \{$b_i$\} are the coefficients for the potential basis sets \{$g_i$\}. The Fermi-Amaldi potential is chosen as the fixed potential $v_0(r)$\cite{63}, which is defined as

$$v_0(r) = \frac{N_0 - 1}{N_0} \int \frac{\rho_0(r)}{|r - r'|} dr',$$  \hspace{1cm} (7)

where $N_0$ is the number of electrons corresponding to a fixed density $\rho_0$. The optimization with respect to the coefficients \{$b_i$\} can be easily performed with gradient-based approaches. In principle, because of the flexibility from the last term in Eq.6, the fixed density $\rho_0$ in Eq.7 can be arbitrary, as long as the potential basis set \{$g_i$\} is sufficient. The fixed potential $v_0(r)$ using the density from the SCF calculation of the $(N - 2)$-electron system or the $N$-electron system give similar results as shown in the Section.S3 of the Supporting Information. In practice, we found that the density from the SCF calculation of the $(N - 2)$-electron system is a better choice to produce physical potentials and give better convergence behaviors. We thus use it in Eq.7 throughout this work.

Following Ref. 56, the gradient of the total energy in multireference DFT with respect to the coefficients \{$b_i$\} consists of two parts: the auxiliary system energy and the excitation energy

$$\frac{\partial E_{v,n}}{\partial b_i} = \sum_{i,a} \left( \frac{\delta E^\text{ref}_v}{\delta \phi_i} | \phi_a \rangle + \frac{\delta \Delta E_n}{\delta \phi_i} | \phi_a \rangle \right) \frac{\langle \phi_a | g_i | \phi_i \rangle}{\epsilon_i - \epsilon_a} + \text{c.c.} \hspace{1cm} (8)$$

where $\epsilon_i$ and $\epsilon_a$ are the occupied and the virtual orbital energy. The gradient of the $(N - 2)$-electron auxiliary system energy only involves the matrix elements of the (generalized) Kohn-Sham Hamiltonian $H^\text{ref}$\cite{33}

$$\frac{\partial E_{v,n}}{\partial b_i} = - \sum_{i,a} H_{ia}^\text{ref} \frac{\langle \phi_a | g_i | \phi_i \rangle}{\epsilon_i - \epsilon_a}. \hspace{1cm} (9)$$
Second, the gradient of the excitation energy from ppTDA is formulated as

\[
\frac{\partial \Delta E_{v,n}}{\partial b_t} = \sum_{i,a} \langle \phi_a | g_t | \phi_i \rangle \left\{ 2 \sum_{a' \neq b'} X_{aa'}^n H_{ib'} X_{b'a'}^n + \sum_{a' \neq b'} \sum_{c' \neq b'} X_{aa'}^n \langle ia' || b' c' \rangle X_{b'a'}^n - 2 \sum_{a' \neq b'} X_{aa'}^n K_{a'b',aa}^{Hxc} X_{b'a'}^n \right\}. 
\]

(10)

where \( X_{ab}^n \) is the eigenvector of the ppTDA equation defined in Eq.2, \( K_{Hxc} \) is the Hartree-exchange-correlation (Hxc) kernel that is the second derivative of the Hxc energy with respect to the electron density. In our ppTDA@RS-DFA approach, because the RS Hamiltonian defined in Eq.5 has the same form as the HF matrix, the evaluation of the kernel \( K_{Hxc} \) only involves two-electron integrals, which is

\[
K_{RS,Hxc}^{pq,rs} = \langle qp || rs \rangle 
\]

(11)

This leads to better efficiency in multireference DFT calculations for molecules.

In practical calculations, the frontier orbitals of the \((N - 2)\)-electron auxiliary system for a given trial potential \( v_s(r) \), can be degenerate or nearly degenerate, which gives incorrect gradient in Eq.8. Numerical techniques in the many-body perturbation theory such as using an energy level shift in the denominator in Eq.8 lead to the wrong gradient and failed optimization. To address the degeneracy in the optimization, we developed a hybrid algorithm. When the frontier orbitals are not nearly degenerate, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method is used. When the HOMO and LUMO orbitals, or more of the frontier orbitals of the \((N - 2)\)-electron auxiliary system are degenerate, its single determinant wavefunction is not uniquely defined. In addition, the gradient cannot be calculated from Eq.8 because of the singularity arising from the small HOMO-LUMO gap in the denominators. In case of degenerate frontier orbitals, we first selected the unique determinant wavefunction, \( \Psi_v \), or the unique set of \((N - 2)\) orbitals by the minimization of the total energy functional with respect to the selected frontier orbitals defined as unitary rotations of all frontier orbitals in the degenerate subspace. In the simple case of only degenerate HOMO and LUMO, the unitary rotation is only performed between two frontier orbitals,
this being the most frequent cases when our calculations encountered degeneracy. Thus the unique determinant wavefunction $\Psi_v$ is given as

$$\Psi_v = \arg \min_{\tilde{\Psi}} E_{v,n}[\tilde{\Psi}], \quad (12)$$

where $\tilde{\Psi}$ is the trial determinant for the $(N-2)$-electron auxiliary system with its frontier orbitals defined by the unitary rotation in the degenerate subspace and $E_{v,n}[\tilde{\Psi}]$ is the total energy functional of Eq. 1 but with the change of the variable from the density matrix to the determinant wavefunction to emphasize the determinant nature of the solution needed for the ppRPA or ppTDA linear response calculations. Thus only orbitals in the degenerate/nearly degenerate subspace are mixed. A single determinant $\Psi_v$ is thus uniquely defined for a trial potential $v_s(r)$ with degenerate frontier orbitals. This is a new development and a departure from the original formulation of potential functional theory (PFT)\textsuperscript{65} the theoretical foundation for the OEP approaches, where ensemble solutions have been used.

The optimization of energy with respect to the unitary transformation of degenerate or nearly degenerate frontier orbitals in the determinant wavefunction in Eq. 12

$$U = \prod_{p \in \text{deg}} \left[ \prod_{q \in \text{deg}, q < p} G_{pq}(\theta_{pq}) \right] \quad (13)$$

is carried out with the sequential rotations. Here deg means degenerate or nearly degenerate subspace, $G_{pq}$ is the $2 \times 2$ rotation matrix between orbital $p$ and $q$, $\theta_{pq}$ is the rotation angle. In the optimization of each orbital pair, the rotation angle is determined by a three-point parabolic interpolation. The sequential rotations are performed in a consistent ordering until the energy minimum is reached.

With the single determinant wavefunction uniquely defined for the trial potential with degenerate frontier orbitals, we next consider the optimization step for the trial potential.
In such a degenerate case, the functional derivative of the total energy with respect to the potential is not defined; only the energy variation for a given change of the potential is defined. Thus the energy gradient of the optimization defined in Eq.12 is not defined as shown in the Section S4 of Supporting Information. One way forward is to carry out optimization of potential without gradients. Instead, we use an approximate gradient with respect to the potential. The approximate gradient has a similar form as Eq.8 without contributions from degenerate or nearly degenerate orbitals

$$\frac{\partial E_{v,n}}{\partial b_t} = \sum_{i,a \notin \text{deg}} \left( \frac{\delta E_{v,n}^{\text{ref}}}{\delta \phi_i} | \phi_a \rangle + \frac{\delta \Delta E_{v,n}}{\delta \phi_i} | \phi_a \rangle \right) \frac{\langle \phi_a | g_t | \phi_i \rangle}{\epsilon_i - \epsilon_a} + c.c. \quad (14)$$

A line search along the approximate gradient defined in Eq.14 is then performed to obtain a new total energy and a new trial potential. This hybrid algorithm appropriately deals with the accidental degenerate cases in the optimization of the OEP method. In this work, we show that the ppTDA@RS-DFA approach provides the converged results in most \((N - 2)\)-electron systems, which are difficult to obtain in the conventional SCF calculation. For degeneracy originated from the symmetry of systems, the degeneracy persists during the optimization of the potential and the gradient can not be well approximated by Eq.14. Further study, such as optimization without gradient, is needed for such cases.

We implemented the ppTDA@DFA approach and the ppTDA@RS-DFA approach in the QM4D quantum chemistry package and applied the method to calculate single bond dissociations, double bond rotations and excitation energies of molecular systems. For the single bond dissociation, the cc-pVTZ basis set was used for LiH, BH and CH\(^+\), while the cc-pVDZ basis set was used for C\(_2\)H\(_6\) considering the computational cost. In the dissociation of C\(_2\)H\(_6\), the C-C bond was stretched. The equilibrium geometry of C\(_2\)H\(_6\) was taken from Ref. In ppTDA@DFA, ppTDA@RS-DFA, CCSD calculations, the total energies at the bond length 5.0\(\text{Å}\), 6.0\(\text{Å}\), 4.0\(\text{Å}\), 5.0\(\text{Å}\) were set as zero for LiH, BH, CH\(^+\), C\(_2\)H\(_4\)
respectively. In KS-DFT calculations, the total energies of the doublet Li atom and the
doublet H atom, the doublet B atom and the doublet H atom, the doublet C\(^+\) cation and
the doublet H atom, two double CH\(_3\) doublets were set as zero for LiH, BH, CH\(^+\), and C\(_2\)H\(_6\),
respectively. The reference for LiH was taken from Ref. 69 for BH was taken from Ref. 70
for CH\(^+\) was taken from Ref. 71 for C\(_2\)H\(_6\) was taken from Ref. 68. For the double bond
rotation of C\(_2\)H\(_4\), the cc-pVTZ basis set was used. Geometries of C\(_2\)H\(_4\) were taken from Ref.
33. The reference MR-ccCA values were taken from Ref. 72. For excitation energies, the
cc-pVTZ basis set was used for LiH and Ca, the aug-cc-pVDZ basis set was used for C\(_2\)H\(_4\),
and the aug-cc-pVTZ basis set was used for remaining systems. Geometries of BH, CH\(^+\),
CO and C\(_2\)H\(_4\) were taken from Ref. 33. The geometry of H\(_2\)O was taken from CORE65 set.\textsuperscript{52} The geometry of LiH was optimized at the CCSD level with cc-pVTZ basis set. The
reference value of LiH was obtained from EOM-CCSD with the cc-pVTZ basis set. The
reference value of H\(_2\)O was taken from Ref. 20. Reference values of remaining systems were
taken from Ref. 33. \textit{ppTDA@DFA}, \textit{ppTDA@RS-DFA}, \textit{post-SCF-ppTDA@DFA} and \textit{post-
SCF-ppTDA@RS-DFA} calculations were performed with QM4D, KS-DFT, CCSD, TDDFT
and EOM-CCSD calculations were performed with GAUSSIAN16 A.03 software.\textsuperscript{74} QM4D
uses Cartesian basis sets and the resolution of identity (RI) technique\textsuperscript{75–77} to compute two-
electron integrals in multireference DFT calculations. All basis sets were taken from the
Basis Set Exchange.\textsuperscript{64,78,79}

We first examined the performance of the \textit{ppTDA@RS-DFA} approach for describing sin-
gle bond breakings. The bond dissociation curves of LiH, BH, CH\(^+\) and C\(_2\)H\(_6\) molecules are
shown in Fig.1 with tabulated results of dissociation energies and equilibrium bond lengths
shown in Table.1 and Table.2. The results show that the \textit{ppTDA@RS-DFA} approach de-
scribes well the single bond dissociation process while preserving the proper spin density sym-
metry of the solution and significantly outperforms \textit{ppTDA@DFA} and restricted KS-DFT
for predicting both dissociation energies and equilibrium bond lengths. It is well known that
the single bond dissociation cannot be properly described by single-determinant KS-DFT
perform calculations with commonly used DFAs with proper spin density symmetry (in restricted calculations). Although restricted B3LYP and restricted HF give reasonable equilibrium bond lengths, they produce too high energies at dissociation limits, leading to large errors for dissociation energies. Compared with KS-DFT, the ppTDA@DFA approach provides correct dissociation limits for all systems because of proper multiconfigurational descriptions for broken bonds. However, the accuracy for predicting dissociation energies is not satisfactory. ppTDA@HF and ppTDA@B3LYP have a mean absolute error (MAE) for the dissociation energy of 0.45 eV and 1.99 eV, respectively. By including all one-body perturbations from the auxiliary system, our ppTDA@RS-B3LYP approach predicts accurate dissociation energies and equilibrium bond lengths for all systems. The ppTDA@RS-DFA approach even provides more accurate dissociation energies than the computationally expensive CCSD approach. The MAE of ppTDA@RS-B3LYP for predicting dissociation energies is only 0.30 eV and for predicting equilibrium bond lengths is only 0.01 Å.

We now show that the SCF solution of the multireference DFT approach is not affected by the choice of the optimization methods with OEP or GOEP, and the choice of methods for the two-electron addition energy from ppTDA or ppRPA. Dissociation curves of LiH and BH obtained from ppTDA@HF optimized with the OEP method, ppTDA@HF optimized with the GOEP method and ppRPA@HF optimized with the GEOP method are shown in Fig. 2. Comparing dissociation curves of ppTDA@HF optimized with OEP and GEOP, two optimization methods produce close results for both LiH and BH. We used the OEP method in the rest of this work because it produces physical potentials for most systems (with the exception of Be atom, which is discussed in the Section S2 of the Supporting Information), while the GOEP method can produce unphysical potentials with a negative HOMO-LUMO gap when combining with traditional DFAs. Comparing dissociation curves in Fig. 2 of ppTDA@HF and ppRPA@HF methods optimized with GOEP, we see that using ppRPA and ppTDA for excitation energies lead to very close results because they have sim-
Figure 1: Dissociation curves of LiH, BH, CH$^+$ and C$_2$H$_6$ obtained from ppTDA@HF, ppTDA@B3LYP, ppTDA@RS-B3LYP, restricted HF (RHF) and restricted B3LYP (RB3LYP) calculations. The cc-pVTZ basis set was used for LiH, BH and CH$^+$. The cc-pVDZ basis set was used for C$_2$H$_6$. Reference for LiH was taken from Ref. [69] for BH was taken from Ref. [70] for CH$^+$ was taken from Ref. [71] for C$_2$H$_6$ was taken from Ref. [68]
Table 1: Dissociation energies (eV) of LiH, BH, CH\(^+\) and C\(_2\)H\(_6\) obtained from restricted HF, restricted B3LYP, ppTDA@HF, ppTDA@B3LYP and ppTDA@RS-B3LYP.

|                 | LiH\(^1\) | BH  | CH\(^+\) | C\(_2\)H\(_6\) | MAE\(^2\) |
|-----------------|-----------|-----|----------|---------------|-----------|
| ref             | 2.50      | 3.64| 4.24     | 4.75          |           |
| CCSD            | 2.44      | 3.91| 4.45     | 5.69          | 0.37      |
|                 | **KS-DFT**|     |          |               |           |
| restricted HF   | 3.93      | 7.47| 7.20     | 9.39          | 1.25      |
| restricted B3LYP| 3.20      | 5.32| 6.86     | 3.59          | 0.25      |
|                 | **Multireference DFT**| | | | |
| ppTDA@HF        | 2.43      | 4.09| 4.69     | 3.93          | 0.45      |
| ppTDA@B3LYP     | 5.47      | 6.70| 3.59     | 1.99          |           |
| ppTDA@RS-B3LYP  | 2.44      | 3.84| 4.36     | 5.58          | 0.30      |

[1] ppTDA@B3LYP for LiH result is missing because the failure of the optimization.
[2] MAE stands for mean absolute error.
[3] The reference for LiH was taken from Ref. 69, for BH was taken from Ref. 70, for CH\(^+\) was taken from Ref. 71, for C\(_2\)H\(_6\) was taken from Ref. 68.
Table 2: Equilibrium bond lengths (Å) of LiH, BH, CH\(^+\) and C\(_2\)H\(_6\) obtained from restricted HF, restricted B3LYP, ppTDA@HF, ppTDA@B3LYP and ppTDA@RS-B3LYP.

|                  | LiH\(^1\) | BH   | CH\(^+\) | C\(_2\)H\(_6\) | MAE\(^2\) |
|------------------|-----------|------|----------|----------------|-----------|
| ref              | 1.60      | 1.20 | 1.12     | 1.52           |           |
| CCSD             | 1.61      | 1.24 | 1.11     | 1.53           | 0.02      |
| KS-DFT           |           |      |          |                |           |
| restricted HF    | 1.61      | 1.22 | 1.11     | 1.53           | 0.01      |
| restricted B3LYP | 1.59      | 1.23 |          | 1.53           | 0.02      |
| Multireference DFT |         |      |          |                |           |
| ppTDA@HF         | 1.61      | 1.22 | 1.11     | 1.48           | 0.02      |
| ppTDA@B3LYP      | 1.09      | 1.03 |          | 1.50           | 0.46      |
| ppTDA@RS-B3LYP   | 1.61      | 1.23 | 1.11     | 1.53           | 0.01      |

[1] ppTDA@B3LYP for LiH result is missing because the failure of the optimization.
[2] MAE stands for mean absolute error.
[3] The reference for LiH was taken from Ref. [69], for BH was taken from Ref. [70], for CH\(^+\) was taken from Ref. [71], for C\(_2\)H\(_6\) was taken from Ref. [68].
ilar physics for two-electron addition energies. We used ppTDA in the rest of this work for simplicity.

Figure 2: Dissociation curves of LiH and BH obtained from ppTDA@HF optimized with the OEP method, ppTDA@HF optimized with the GOEP method, and ppRPA@HF optimized with the GOEP method. The cc-pVTZ basis set was used.

Another example of the ppTDA@RS-DFA approach successfully describing the static correlation is the ethylene torsion. Relative energy curves along the ethylene torsional coordinate obtained from ppTDA@HF, ppTDA@B3LYP, ppTDA@RS-B3LYP, restricted HF and restricted B3LYP are shown in Fig. 3. The MR-ccCA results from Ref. 72 were used as the reference. Because of the diradical character, the static correlation is important in the twisted ethylene. Restricted HF and restricted B3LYP that have poor descriptions for the static correlation produce unphysical relative energy curves and large errors in the barrier heights. It has been shown that unrestricted KS-DFT can provide smooth curves for the ethylene rotation. However, finding an appropriate spin-symmetry broken solution is difficult in practical calculations. With the proper multiconfigurational description, ppTDA@HF, ppTDA@B3LYP and ppTDA@RS-B3LYP provide qualitatively correct relative energies at all angles. Although ppTDA@B3LYP gives an accurate barrier height, it shows increasing deviations at both ends. ppTDA@HF and ppTDA@RS-B3LYP provide accurate curves that
are in good agreement with the curve of MR-ccCA for all angles.

Figure 3: Relative energy curves of twisted ethylene obtained from ppTDA@HF, ppTDA@B3LYP, ppTDA@RS-B3LYP, restricted HF and restricted B3LYP at θ = 0°, 60°, 65°, 70°, 75°, 80°, 85° and 90°. The energy at θ = 0 is set as zero. The MR-ccCA results taken from Ref. [72] was used as the reference. All curves are shifted such that the energy at 0° is zero. Structures were taken from Ref. [33]. The cc-pVTZ basis set was used.

In addition to proper descriptions of ground state properties, our ppTDA@RS-DFA approach also predicts accurate excitation energies. Excitation energies were obtained by the energy difference between the target excited state and the ground state. To demonstrate the accuracy, excitation energies of molecular and atomic systems obtained from ppTDA@DFA, and ppTDA@RS-DFA, and post-SCF approaches post-SCF-ppTDA@DFA and post-SCF-ppTDA@RS-DFA as well as traditional TDDFT are listed in Table 3. It shows that the
conventional post-SCF approach post-SCF-ppTDA@DFA provides an adequate accuracy. B3LYP is the best starting point for post-SCF-ppTDA@DFA with a MAE of 0.48 eV. Only introducing the self-consistency or applying RS does not improve the accuracy. MAEs of post-SCF-ppTDA@RS-DFA are around 1.0 eV and MAEs of ppTDA@DFA can even exceed 2.0 eV. Combining the self-consistency and RS leads to considerable improvement. ppTDA@RS-B3LYP and ppTDA@RS-PBE provide the smallest MAEs of only 0.32 eV that are similar to ppTDA@HF. Besides the improved accuracy, the dependence on the choice of the DFA is also largely eliminated in the ppTDA@RS-DFA approach. ppTDA@RS-B3LYP and ppTDA@RS-PBE provide very similar results for all tested systems. ppTDA@RS-DFA also outperforms the traditional TDDFT approach. As shown in Table 3, TDDFT gives large errors for tested systems. TDDFT even provides negative excitation energies for triplet excitation BH, CH$^+$ and Ca, which are related to the triplet instability. Our ppTDA@RS-DFA approach describes excited states of tested small molecules and atoms well. The performance for larger systems needs to be further investigated.

The ppTDA@RS-DFA approach has a favorable computational scaling. For the energy, the scaling of evaluating the energy of the $(N - 2)$-electron system is $O(N^3)$ for a LDA or GGA functional or $O(N^4)$ for a hybrid functional, where $N$ is the size of the system. The scaling for evaluating the excitation energy from the ppTDA equation in Eq. 2 is $O(N^4)$ with the Davidson algorithm. For the gradient, the scaling of evaluating the gradient of the $(N - 2)$-electron system energy is $O(N^3)$. The evaluation of the gradient of the excitation energy is the bottleneck. For ppTDA@DFA where the DFA is not HF, the evaluation of the last term in Eq. 10 is the dominant step. Because the Hxc kernel used in Eq. 10 is a four-index quantity that cannot be decomposed into a summation with three-index matrices by the RI approximation, this leads the $O(N^5)$ scaling for evaluating Eq. 10. However, for ppTDA@RS-DFA, the Hxc kernel only involves two-electron integrals as shown in Eq. 11.
Table 3: Excitation energies of molecular and atomic systems obtained from ppTDA@DFA, ppTDA@RS-DFA, post-SCF-ppTDA@DFA, post-SCF-ppTDA@RS-DFA and TDDFT@DFA, all values in eV.

|          | ppTDA           | post-SCF-ppTDA | TD              |
|----------|-----------------|----------------|-----------------|
|          | ref\(^2\) a\(^3\) b\(^3\) c\(^3\) d\(^3\) e\(^3\) | a b c d e a b d |
| BH       |                 |                |                 |
| Triplet  | 1.27 1.54 1.72 1.46 1.89 1.46 1.63 1.33 1.66 1.19 1.67 -1.63 -0.44 |
| Singlet  | 2.85 3.45 3.53 3.25 3.63 3.21 3.15 3.11 3.14 3.01 3.13 2.66 2.69 |
| CH\(^+\) |                 |                |                 |
| Triplet  | 1.15 1.48 0.68 1.36 0.62 1.35 1.66 1.06 1.69 0.91 1.69 -1.86 -1.23 |
| Singlet  | 3.07 3.81 2.87 3.55 2.79 3.50 3.54 3.10 3.53 2.98 3.52 2.65 2.83 |
| LiH\(^1\)|                 |                |                 |
| Triplet  | 3.25 3.23 3.23 3.23 3.16 3.53 3.17 3.49 3.17 2.80 2.65 2.35 |
| Singlet  | 3.61 3.60 3.60 3.60 3.53 3.89 3.53 3.85 3.53 4.04 3.21 2.99 |
| CO       |                 |                |                 |
| Triplet  | 6.32 6.45 6.07 7.07 10.23 7.24 5.61 5.82 6.18 5.80 6.35 5.28 5.86 5.74 |
| Singlet  | 8.51 9.35 8.67 9.37 12.65 9.42 7.86 8.15 8.26 8.13 8.40 8.79 8.40 8.25 |
| C\(_2\)H\(_4\)\(^1\)|                 |                |                 |
| Triplet  | 4.50 4.50 3.83 4.50 3.64 4.49 3.95 3.64 3.92 3.49 3.91 1.05 4.12 4.31 |
| Singlet  | 7.80 6.93 10.15 6.78 10.39 6.77 4.54 7.82 4.45 8.63 4.45 7.16 6.65 6.51 |
| H\(_2\)O |                 |                |                 |
| Triplet  | 7.00 6.71 10.94 6.70 12.02 6.78 5.98 6.22 3.08 7.14 3.14 7.79 6.48 6.00 |
| Singlet  | 7.40 7.05 11.75 7.03 13.00 7.11 5055 6.63 3.31 7.62 3.36 8.57 6.86 6.35 |
| Mg       |                 |                |                 |
| Triplet  | 2.71 4.28 2.61 2.61 2.59 3.45 2.60 3.53 2.60 1.11 2.61 2.33 |
| Singlet  | 4.35 1.69 4.30 4.30 4.27 5.69 4.28 5.76 4.29 4.06 4.23 4.18 |
| Ca\(^1\)|                 |                |                 |
| Triplet  | 1.79 1.69 1.70 1.70 1.68 0.96 1.68 0.13 1.68 -0.48 1.52 1.16 |

MAE 0.32 1.21 0.32 2.06 0.32 0.60 0.48 0.96 0.54 0.94 1.26 0.61 0.64

[1] The cc-pVTZ basis set was used for LiH and Ca. The aug-cc-pVDZ basis set was used for C\(_2\)H\(_4\). The aug-cc-pVTZ was used for remaining systems.
[2] The reference value for LiH was obtained from the EOM-CCSD calculation. The reference value for H\(_2\)O was taken from Ref. [20]. Reference values for remaining systems were taken from Ref. [33].
[3] a=HF, b=B3LYP, c=RS-B3LYP, d=PBE, e=RS-PBE
Therefore, the last term in Eq.10 can be evaluated of $O(N^4)$ as

$$X_{a'b'}^n K_{a'a',ai'}^{RS,Hxc} X_{a'b'}^n = \sum_{P} \left[ X_{a'b'}^n \left( R_{P,a'a'} R_{P,ai} - R_{P,c'a'} R_{P,i'} \right) X_{a'b'}^n \right],$$

(15)

where the intermediate quantity $R_{P,pq} = \sum_{Q} (P|Q)^{-\frac{1}{2}} (Q|rs)$ is constructed in the RI approximation and \{ψ_Q\} is a set of auxiliary basis sets. By using Eq.15, the scaling of evaluating the gradient of excitation energy part is $O(N^4)$. Thus the formal scaling of the ppTDA@RS-DFA approach is $O(N^4)$, which is the same as the SCF HF/hybrid functional calculation.

The computational cost of ppTDA@RS-DFA can be further reduced significantly by using the active space method.\textsuperscript{37} In the active space method, the excitation energy is obtained by a direct diagonalization of the ppTDA equation in a small subspace. The scaling of solving the ppTDA equation with the active space method is $O(N^4)$, with a prefactor much smaller than a single SCF HF/hybrid functional calculation.\textsuperscript{37} Because of using the active space, the cost of evaluating the gradient is also greatly reduced because the two-electron addition eigenvector has a smaller dimension. Therefore, the ppTDA@RS-DFA approach is promising for application to larger systems.

In summary, we applied the RS approach in the multireference DFT approach to describe ground states and excited states of systems with static correlation. In ppTDA@RS-DFA, the RS Hamiltonian is used in the ppTDA equation to include all contributions from one-body perturbations. Then the SCF solution of the total energy is obtained from the optimization of the OEP method of Yang and Wu. We showed that the OEP method produces physical potential for most systems, which are not guaranteed in GOEP optimizations when using traditional DFAs. The ppTDA@RS-DFA approach was first examined on describing single bond breaking problems. We showed that ppTDA@RS-DFA provides accurate bond dissociation curves with proper spin density symmetry, dissociation energies and equilibrium bond lengths for all four systems, significantly outperforming ppTDA@DFA and conventional KS-DFT. Then we showed that the ppTDA@RS-DFA approach also successfully describes
the double bond rotation in ethylene. We also demonstrated that the ppTDA@RS-DFA approach is capable of describing excited states. ppTDA@RS-DFA provides accurate excitation energies for both molecular and atomic systems. And the dependence on the choice of the DFA in multireference DFT is largely eliminated. Beyond the ground state and excited state properties, for state-to-state properties such as the conical intersection search and couplings, further study is needed. Our ppTDA@RS-DFA approach scales as $O(N^4)$. The computational cost can be further reduced by using the active space method. The ppTDA@RS-DFA approach is expected to open up new possibilities for the application of the multireference DFT approach for large systems.

**Acknowledgement**

ACKNOWLEDGMENTS: J. L. and Z.C. acknowledge the support from the National Institute of General Medical Sciences of the National Institutes of Health under award number R01-GM061870. W.Y. acknowledges the support from the National Science Foundation (grant no. CHE-1900338).

**Supporting Information Available**

Supporting Information Available: orbital optimization for the total energy in multireference DFT, examples of unphysical energy in the optimization, comparison of choices of the fixed density, discussion of degeneracy in multireference DFT and potential functional theory.

**References**

(1) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* 1964, *136*, B864–B871.
(2) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 1965, 140, A1133–A1138.

(3) Parr, R. G.; Weitao, Y. Density-Functional Theory of Atoms and Molecules; Oxford University Press, 1989.

(4) von Barth, U.; Hedin, L. A Local Exchange-Correlation Potential for the Spin Polarized Case. i. J. Phys. C: Solid State Phys. 1972, 5, 1629–1642.

(5) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. Can. J. Phys. 1980, 58, 1200–1211.

(6) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A 1988, 38, 3098–3100.

(7) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. Phys. Rev. B 1988, 37, 785–789.

(8) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. Phys. Rev. B 1992, 45, 13244–13249.

(9) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

(10) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-functional Theories. J. Chem. Phys. 1993, 98, 1372–1377.

(11) Zhang, D.; Hermes, M. R.; Gagliardi, L.; Truhlar, D. G. Multiconfiguration Density-Coherence Functional Theory. J. Chem. Theory Comput. 2021, 17, 2775–2782.

(12) Li Manni, G.; Carlson, R. K.; Luo, S.; Ma, D.; Olsen, J.; Truhlar, D. G.; Gagliardi, L. Multiconfiguration Pair-Density Functional Theory. J. Chem. Theory Comput. 2014, 10, 3669–3680.
(13) Ren, X.; Rinke, P.; Scuseria, G. E.; Scheffler, M. Renormalized Second-Order Perturbation Theory for the Electron Correlation Energy: Concept, Implementation, and Benchmarks. *Phys. Rev. B* **2013**, *88*, 035120.

(14) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* **2008**, *321*, 792–794.

(15) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Fractional Spins and Static Correlation Error in Density Functional Theory. *J. Chem. Phys.* **2008**, *129*, 121104.

(16) Roos, B. O.; Taylor, P. R.; Sigbahn, P. E. M. A Complete Active Space SCF Method (CASSCF) Using a Density Matrix Formulated Super-CI Approach. *Chem. Phys.* **1980**, *48*, 157–173.

(17) Roos, B. O. In *Methods in Computational Molecular Physics*; Diercksen, G. H. F., Wilson, S., Eds.; NATO ASI Series; Springer Netherlands: Dordrecht, 1983; pp 161–187.

(18) Gagliardi, L.; Truhlar, D. G.; Li Manni, G.; Carlson, R. K.; Hoyer, C. E.; Bao, J. L. Multiconfiguration Pair-Density Functional Theory: A New Way To Treat Strongly Correlated Systems. *Acc. Chem. Res.* **2017**, *50*, 66–73.

(19) Ghosh, S.; Sonnenberger, A. L.; Hoyer, C. E.; Truhlar, D. G.; Gagliardi, L. Multiconfiguration Pair-Density Functional Theory Outperforms Kohn–Sham Density Functional Theory and Multireference Perturbation Theory for Ground-State and Excited-State Charge Transfer. *J. Chem. Theory Comput.* **2015**, *11*, 3643–3649.

(20) Hoyer, C. E.; Ghosh, S.; Truhlar, D. G.; Gagliardi, L. Multiconfiguration Pair-Density Functional Theory Is as Accurate as CASPT2 for Electronic Excitation. *J. Phys. Chem. Lett.* **2016**, *7*, 586–591.
(21) Grofe, A.; Chen, X.; Liu, W.; Gao, J. Spin-Multiplet Components and Energy Splittings by Multistate Density Functional Theory. *J. Phys. Chem. Lett.* 2017, 8, 4838–4845.

(22) Ren, H.; Provorse, M. R.; Bao, P.; Qu, Z.; Gao, J. Multistate Density Functional Theory for Effective Diabatic Electronic Coupling. *J. Phys. Chem. Lett.* 2016, 7, 2286–2293.

(23) Gao, J.; Grofe, A.; Ren, H.; Bao, P. Beyond Kohn–Sham Approximation: Hybrid Multistate Wave Function and Density Functional Theory. *J. Phys. Chem. Lett.* 2016, 7, 5143–5149.

(24) Su, N. Q.; Li, C.; Yang, W. Describing Strong Correlation with Fractional-Spin Correction in Density Functional Theory. *PNAS* 2018, 115, 9678–9683.

(25) Filatov, M. Spin-Restricted Ensemble-Referenced Kohn–Sham Method: Basic Principles and Application to Strongly Correlated Ground and Excited States of Molecules. *WIREs Comput. Mol. Sci.* 2015, 5, 146–167.

(26) Ullrich, C. A. *Time-Dependent Density-Functional Theory: Concepts and Applications*; OUP Oxford, 2011.

(27) Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* 1984, 52, 997–1000.

(28) Casida, M. E. *Recent Advances in Density Functional Methods*; Recent Advances in Computational Chemistry; WORLD SCIENTIFIC, 1995; Vol. Volume 1; pp 155–192.

(29) Casida, M.; Huix-Rotllant, M. Progress in Time-Dependent Density-Functional Theory. *Annu. Rev. Phys. Chem.* 2012, 63, 287–323.

(30) Peach, M. J.; Warner, N.; Tozer, D. J. On the Triplet Instability in TDDFT. *Mol. Phys.* 2013, 111, 1271–1274.

(31) Hait, D.; Head-Gordon, M. Orbital Optimized Density Functional Theory for Electronic Excited States. *J. Phys. Chem. Lett.* 2021, 12, 4517–4529.
(32) Horbatenko, Y.; Sadiq, S.; Lee, S.; Filatov, M.; Choi, C. H. Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT) as a Simple yet Accurate Method for Diradicals and Diradicaloids. *J. Chem. Theory Comput.* **2021**, *17*, 848–859.

(33) Chen, Z.; Zhang, D.; Jin, Y.; Yang, Y.; Su, N. Q.; Yang, W. Multireference Density Functional Theory with Generalized Auxiliary Systems for Ground and Excited States. *J. Phys. Chem. Lett.* **2017**, *8*, 4479–4485.

(34) van Aggelen, H.; Yang, Y.; Yang, W. Exchange-Correlation Energy from Pairing Matrix Fluctuation and the Particle-Particle Random-Phase Approximation. *Phys. Rev. A* **2013**, *88*, 030501.

(35) van Aggelen, H.; Yang, Y.; Yang, W. Exchange-Correlation Energy from Pairing Matrix Fluctuation and the Particle-Particle Random Phase Approximation. *J. Chem. Phys.* **2014**, *140*, 18A511.

(36) Yang, Y.; van Aggelen, H.; Steinmann, S. N.; Peng, D.; Yang, W. Benchmark Tests and Spin Adaptation for the Particle-Particle Random Phase Approximation. *J. Chem. Phys.* **2013**, *139*, 174110.

(37) Zhang, D.; Yang, W. Accurate and Efficient Calculation of Excitation Energies with the Active-Space Particle-Particle Random Phase Approximation. *J. Chem. Phys.* **2016**, *145*, 144105.

(38) Bannwarth, C.; Yu, J. K.; Hohenstein, E. G.; Martínez, T. J. Hole–Hole Tamm–Dancoff-approximated Density Functional Theory: A Highly Efficient Electronic Structure Method Incorporating Dynamic and Static Correlation. *J. Chem. Phys.* **2020**, *153*, 024110.

(39) Tahir, M. N.; Ren, X. Comparing Particle-Particle and Particle-Hole Channels of the Random Phase Approximation. *Phys. Rev. B* **2019**, *99*, 195149.
(40) Shao, Y.; Head-Gordon, M.; Krylov, A. I. The Spin–Flip Approach within Time-Dependent Density Functional Theory: Theory and Applications to Diradicals. *J. Chem. Phys.* **2003**, *118*, 4807–4818.

(41) Wang, F.; Ziegler, T. Time-Dependent Density Functional Theory Based on a Non-collinear Formulation of the Exchange-Correlation Potential. *J. Chem. Phys.* **2004**, *121*, 12191–12196.

(42) Bernard, Y. A.; Shao, Y.; Krylov, A. I. General Formulation of Spin-Flip Time-Dependent Density Functional Theory Using Non-Collinear Kernels: Theory, Implementation, and Benchmarks. *J. Chem. Phys.* **2012**, *136*, 204103.

(43) Li, Z.; Liu, W. Theoretical and Numerical Assessments of Spin-Flip Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2012**, *136*, 024107.

(44) Jin, Y.; Su, N. Q.; Chen, Z.; Yang, W. Introductory Lecture: When the Density of the Noninteracting Reference System Is Not the Density of the Physical System in Density Functional Theory. *Faraday Discuss.* **2020**, *224*, 9–26.

(45) Jin, Y.; Zhang, D.; Chen, Z.; Su, N. Q.; Yang, W. Generalized Optimized Effective Potential for Orbital Functionals and Self-Consistent Calculation of Random Phase Approximations. *J. Phys. Chem. Lett.* **2017**, *8*, 4746–4751.

(46) Head-Gordon, M.; Pople, J. A. Optimization of Wave Function and Geometry in the Finite Basis Hartree-Fock Method. *J. Phys. Chem.* **1988**, *92*, 3063–3069.

(47) Peverati, R.; Head-Gordon, M. Orbital Optimized Double-Hybrid Density Functionals. *J. Chem. Phys.* **2013**, *139*, 024110.

(48) Yaffe, L. G.; Goddard, W. A. Orbital Optimization in Electronic Wave Functions; Equations for Quadratic and Cubic Convergence of General Multiconfiguration Wave Functions. *Phys. Rev. A* **1976**, *13*, 1682–1691.
(49) Jin, Y.; Su, N. Q.; Yang, W. Renormalized Singles Green’s Function for Quasi-Particle Calculations beyond the G0W0 Approximation. J. Phys. Chem. Lett. 2019, 10, 447–452.

(50) Szabo, A.; Ostlund, N. S. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory; Courier Corporation, 2012.

(51) Slater, J. C. Note on Hartree’s Method. Phys. Rev. 1930, 35, 210–211.

(52) Li, J.; Chen, Z.; Yang, W. Renormalized Singles Green’s Function in the T-Matrix Approximation for Accurate Quasiparticle Energy Calculation. J. Phys. Chem. Lett. 2021, 12, 6203–6210.

(53) Ren, X.; Tkatchenko, A.; Rinke, P.; Scheffler, M. Beyond the Random-Phase Approximation for the Electron Correlation Energy: The Importance of Single Excitations. Phys. Rev. Lett. 2011, 106, 153003.

(54) Yang, Y.; Peng, D.; Lu, J.; Yang, W. Excitation Energies from Particle-Particle Random Phase Approximation: Davidson Algorithm and Benchmark Studies. J. Chem. Phys. 2014, 141, 124104.

(55) Yang, Y.; van Aggelen, H.; Yang, W. Double, Rydberg and Charge Transfer Excitations from Pairing Matrix Fluctuation and Particle-Particle Random Phase Approximation. J. Chem. Phys. 2013, 139, 224105.

(56) Yang, W.; Wu, Q. Direct Method for Optimized Effective Potentials in Density-Functional Theory. Phys. Rev. Lett. 2002, 89, 143002.

(57) Wu, Q.; Yang, W. A Direct Optimization Method for Calculating Density Functionals and Exchange–Correlation Potentials from Electron Densities. J. Chem. Phys. 2003, 118, 2498–2509.
(58) Wu, Q.; Cohen, A. J.; Yang, W. Analytic Energy Gradients of the Optimized Effective Potential Method. *J. Chem. Phys.* **2005**, *123*, 134111.

(59) Zhang, D.; Peng, D.; Zhang, P.; Yang, W. Analytic Gradients, Geometry Optimization and Excited State Potential Energy Surfaces from the Particle-Particle Random Phase Approximation. *Phys. Chem. Chem. Phys.* **2014**, *17*, 1025–1038.

(60) Martin, R. M.; Reining, L.; Ceperley, D. M. *Interacting Electrons*; Cambridge University Press, 2016.

(61) Davidson, E. R. The Iterative Calculation of a Few of the Lowest Eigenvalues and Corresponding Eigenvectors of Large Real-Symmetric Matrices. *J. Comput. Phys.* **1975**, *17*, 87–94.

(62) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An Efficient Implementation of Time-Dependent Density-Functional Theory for the Calculation of Excitation Energies of Large Molecules. *J. Chem. Phys.* **1998**, *109*, 8218–8224.

(63) Zhao, Q.; Morrison, R. C.; Parr, R. G. From Electron Densities to Kohn-Sham Kinetic Energies, Orbital Energies, Exchange-Correlation Potentials, and Exchange-Correlation Energies. *Phys. Rev. A* **1994**, *50*, 2138–2142.

(64) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C (2nd Ed.): The Art of Scientific Computing*; Cambridge University Press: USA, 1992.

(65) Yang, W.; Ayers, P. W.; Wu, Q. Potential Functionals: Dual to Density Functionals and Solution to the $v$-Representability Problem. *Phys. Rev. Lett.* **2004**, *92*, 146404.

(66) See http://www.qm4d.info for an in-house program for QM/MM simulations.

(67) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
(68) Li, C.; Evangelista, F. A. Driven Similarity Renormalization Group: Third-order Multireference Perturbation Theory. *J. Chem. Phys.* **2017**, *146*, 124132.

(69) Li, X.; Paldus, J. An Accurate Determination of Rovibrational Spectra Using the Externally Corrected Coupled-Cluster Approaches: LiH Ground State. *J. Chem. Phys.* **2003**, *118*, 2470–2481.

(70) Abrams, M. L.; Sherrill, C. D. An Assessment of the Accuracy of Multireference Configuration Interaction (MRCI) and Complete-Active-Space Second-Order Perturbation Theory (CASPT2) for Breaking Bonds to Hydrogen. *J. Phys. Chem. A* **2003**, *107*, 5611–5616.

(71) Biglari, Z.; Shayesteh, A.; Maghari, A. Ab Initio Potential Energy Curves and Transition Dipole Moments for the Low-Lying States of CH+. *Comput. Theor. Chem.* **2014**, *1047*, 22–29.

(72) Jiang, W.; Jeffrey, C. C.; Wilson, A. K. Empirical Correction of Nondynamical Correlation Energy for Density Functionals. *J. Phys. Chem. A* **2012**, *116*, 9969–9978.

(73) Golze, D.; Keller, L.; Rinke, P. Accurate Absolute and Relative Core-Level Binding Energies from GW. *J. Phys. Chem. Lett.* **2020**, *11*, 1840–1847.

(74) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H. et al. Gaussian16 Revision A.03. 2016; Gaussian Inc. Wallingford CT.

(75) Weigend, F. Accurate Coulomb-fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

(76) Ren, X.; Rinke, P.; Blum, V.; Wieferink, J.; Tkatchenko, A.; Sanfilippo, A.; Reuter, K.; Scheffler, M. Resolution-of-Identity Approach to Hartree–Fock, Hybrid Density Func-
tionals, RPA, MP2 and GW with Numeric Atom-Centered Orbital Basis Functions. 

*New J. Phys.* **2012**, *14*, 053020.

(77) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Auxiliary Basis Sets to Approximate Coulomb Potentials. *Chem. Phys. Lett.* **1995**, *240*, 283–290.

(78) Feller, D. The Role of Databases in Support of Computational Chemistry Calculations. *J. Comput. Chem.* **1996**, *17*, 1571–1586.

(79) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. Basis Set Exchange: A Community Database for Computational Sciences. *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.