Letter

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Zehua Chen, Du Zhang, Ye Jin, Yang Yang, Neil Qiang Su, and Weitao Yang

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Multireference Density Functional Theory with Generalized Auxiliary Systems for Ground and Excited States

Zehua Chen, Du Zhang, Ye Jin, Yang Yang, Neil Qiang Su, and Weitao Yang*

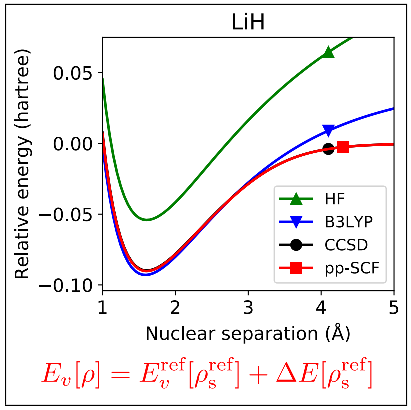
Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

E-mail: weitao.yang@duke.edu

Abstract

To describe static correlation, we develop a new approach to density functional theory (DFT), which uses a generalized auxiliary system that is of a different symmetry, such as particle number or spin, from that of the physical system. The total energy of the physical system consists of two parts: the energy of the auxiliary system, which is determined with a chosen density functional approximation (DFA), and the excitation energy from an approximate linear response theory that restores the symmetry to that of the physical system, thus rigorously leading to a multi-determinant description of the physical system. The electron density of the physical system is different from that of the auxiliary system and is uniquely determined from the functional derivative of the total energy with respect to the external potential. Our energy functional is thus an implicit functional of the physical system density, but an explicit functional of the auxiliary system density. We show that the total energy minimum and stationary states, describing the ground and excited states of the physical system, can be obtained by a self-consistent optimization with respect to the explicit variable, the generalized Kohn-Sham non-interacting density matrix. We have developed the generalized optimized effective potential method for the self-consistent optimization. Among options of the auxiliary system and the associated linear response theory, reformulated versions of the particle-particle random phase approximation (pp-RPA) and the spin-flip time-dependent density functional theory (SF-TDDFT) are selected for illustration of principle. Numerical results show that our multireference DFT successfully describes static correlation in bond dissociation and double bond rotation.

Graphical TOC Entry



The past half-century has seen increasingly rapid advances in the density functional theory (DFT).[1–4] While the Kohn-Sham DFT (KS DFT), is exact in principle, approximations to the exchange-correlation functional are necessary for practical calculations.[1–3] Many approximate exchange-correlation energy functionals have been proposed, such as local density approximations (LDAs),[5,6] generalized gradient approximations (GGAs)[7–10] and hybrid functionals.[11,12] These common density functional approximations (DFA), have been extensively applied in chemistry, solid state physics and biology.

However, there are still many cases in which conventional approximations fail. Bond breaking is an example where single determinantal methods such as restricted Hartree-Fock and KS DFT fail. It has been shown that errors in the dissociation energy can be decomposed into fractional charge errors and fractional spin errors.[13] Particularly, the fractional spin error occurs when the system is multiconfigurational. In this case, static correlation, which is included by multireference methods, has significant contributions to the total energy. In the wave function theory (WFT), multiconfiguration self-consistent field (MCSCF) methods, the complete active space self-consistent field (CASSCF) method[14] and other multireference methods, are used to properly describe near-degenerate states. Dynamic correlation is further taken into account by post-SCF methods. Multireference perturbation theories, such as the complete-active-space second-order perturbation theory (CASPT2),[15] or multireference configuration interactions (MRCI),[16] are typical post-SCF methods using the MCSCF wave function as the starting point. Attempts have also been made on the development of multireference DFT. For example, a range separated scheme, which treats the long range part by MRCI and the short range part by DFT, is available.[17] There are some other approaches that combine DFT calculations with multiconfiguration WFT. For example, in the multistate density functional theory (MSDFT), multiple KS DFT calculations are carried out, followed by a configuration interaction (CI)-like calculation to produce ground and excited state energies as a weighted sum.[18] The multiconfiguration pair density functional theory (MC-PDFT)[19] uses the MCSCF wave function to produce the on-top pair density, then evaluates the total energy by approximate functionals.

In this letter, we present a new approach to multireference DFT. This method uses a generalized auxiliary reference system. However, the auxiliary system is not designed to describe the interacting system density. The total energy of the physical system, $E_v[\rho]$, consists of two parts: $E_v^{\text{ref}}[\rho_{\text{s}}^{\text{ref}}]$, the energy of the auxiliary system, which is determined with a chosen density functional approximation (DFA), and $\Delta E[\rho_{\text{s}}^{\text{ref}}]$, the excitation energy from an approximate linear response theory that restores the symmetry to that of the physical system, which leads to multi-determinant description of the physical system naturally and rigorously. Thus,

$$E_v[\rho] = E_v^{\text{ref}}[\rho_{\text{s}}^{\text{ref}}] + \Delta E[\rho_{\text{s}}^{\text{ref}}], \tag{1}$$

where ρ is the density of the physical system to be studied and $\rho_{\text{s}}^{\text{ref}}$ is the density matrix of the non-interacting auxiliary reference system. The excited state energy functionals for the physical system are directly available by selecting different target states in the ΔE term:

$$E_{v,n}[\rho_n] = E_v^{\text{ref}}[\rho_{\text{s}}^{\text{ref}}] + \Delta E_n[\rho_{\text{s}}^{\text{ref}}], \tag{2}$$

where n indicates the energy level. In combination with the linear response theory, multireference effects are included. Specifically, N-electron physical systems can be recovered from an $(N-2)$-electron system with two-electron addition excitation energies provided by the particle-particle random phase approximation (pp-RPA).[20–22] Similarly, low-spin states can be generated by spin-flip excitations from the linear response theory as in the spin-flip time-dependent DFT (SF-TDDFT),[23–26] from a high-spin reference. These two methods are only examples to demonstrate our approach. There may exist other variants such as two-electron removal, one-electron addition/removal and multiple spin flips.

Note that without self-consistently optimizing the electron density of the physical system ρ, Eqs (1-2) revert to known approaches within the context of the pp-RPA and the SF-TDDFT for ground and excited energy calculations based on the self-consistent optimization of $E_v^{\rm ref}[\rho_{\rm s}^{\rm ref}]$ with respect to $\rho_{\rm s}^{\rm ref}$, which is just a regular ground state (G)KS calculation for the auxiliary system. This simplification recovers post-(G)KS calculations of the ground and excited states of the physical system.[23,25,27]

The key departure in our work is to recognize that Eqs (1-2) as total energy functionals of the physical system density ρ. This functional has major differences from the traditional (G)KS functional – it does not have the form of common (G)KS DFT and it naturally and rigorously has multiconfiguration description of the ground and excited states. Viewed as a density functional, the ground state energy is given by the minimum of Eq. (1):

$$E_v(N) = \min_{\rho \to N} E_v[\rho], \tag{3}$$

and the energies of excited states are given by the stationary solutions of $E_{v,n}[\rho_n]$. The electron density, $\rho(\mathbf{r})$, of the physical system is different from $\rho_{\rm s}^{\rm ref}$, that of the auxiliary system, and is uniquely determined from the functional derivative of the total energy with respect to the external potential ($v(\mathbf{r})$):

$$\rho(\mathbf{r}) = \left(\frac{\delta E_v(N)}{\delta v(\mathbf{r})}\right)_N. \tag{4}$$

In order to achieve self-consistency required in Eq. (3), optimization with respect to the physical density ρ is necessary, which would seem very challenging. However, since the total energy, Eq. (1), is given explicitly in terms of the auxiliary density matrix $\rho_{\rm s}^{\rm ref}$, and the physical density ρ is uniquely determined by $\rho_{\rm s}^{\rm ref}$ as in Eq. (4) (see the supporting information for a specific case), we can view the energy also as a functional of $\rho_{\rm s}^{\rm ref}$ explicitly:

$$E_v[\rho] = E_v[\rho_{\rm s}^{\rm ref}[\rho]]. \tag{5}$$

Consequently, the variation with respect to ρ is directly connected to the variation with respect to $\rho_{\mathrm{s}}^{\mathrm{ref}}$:

$$\delta E_v[\rho] = \int \frac{\delta E_v}{\delta \rho_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r},\mathbf{r}')} \frac{\delta \rho_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r},\mathbf{r}')}{\delta \rho(\mathbf{r}'')} \delta\rho(\mathbf{r}'')\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, \mathrm{d}\mathbf{r}'' \tag{6}$$

$$= \int H_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r}',\mathbf{r}) \delta\rho_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r},\mathbf{r}')\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}', \tag{7}$$

where the auxiliary Hamiltonian is defined as

$$H_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r}',\mathbf{r}) = \frac{\delta E_v[\rho_{\mathrm{s}}^{\mathrm{ref}}]}{\delta \rho_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r},\mathbf{r}')}. \tag{8}$$

Therefore, optimization with respect to $\rho_{\mathrm{s}}^{\mathrm{ref}}$ is necessary for the minimum required in Eq. (3), namely $\delta E_v[\rho] = 0$. The energy gradient, Eq. (8), allows the optimization in terms of $\rho_{\mathrm{s}}^{\mathrm{ref}}$. Another approach is to carry out the optimization in terms of orbitals $\{\phi_i(\mathbf{r})\}$, which constitutes the auxiliary non-interacting density matrix $\rho_{\mathrm{s}}^{\mathrm{ref}}$:

$$\rho_{\mathrm{s}}^{\mathrm{ref}} = \sum_i |\phi_i\rangle\langle\phi_i|, \tag{9}$$

using the energy gradient

$$\frac{\delta E_v[\rho]}{\delta \phi_i^*(\mathbf{r})} = \int \mathrm{d}\mathbf{r}' H_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r},\mathbf{r}') \phi_i(\mathbf{r}'). \tag{10}$$

Alternatively, we can also find the stationary condition for the SCF solution. Since the auxiliary system remains in a ground state (not of the same external potential) described by a single determinant, any $\delta\rho_{\mathrm{s}}^{\mathrm{ref}}(\mathbf{r},\mathbf{r}')$ near a stationary point $\rho_{\mathrm{s}}^{\star}$ can be expressed as

$$\delta\rho_{\mathrm{s}}^{\mathrm{ref}} = \rho_{\mathrm{s}}^{\star} \delta\rho_{\mathrm{s}}^{\mathrm{ref}} (1-\rho_{\mathrm{s}}^{\star}) + (1-\rho_{\mathrm{s}}^{\star}) \delta\rho_{\mathrm{s}}^{\mathrm{ref}} \rho_{\mathrm{s}}^{\star}, \tag{11}$$

The stationary solution satisfies $[H_{\mathrm{s}}^{\mathrm{ref}}, \rho_{\mathrm{s}}^{\star}] = 0$, which ensures

$$\delta E_v[\rho_{\mathrm{s}}^{\mathrm{ref}}[\rho]] = \mathrm{Tr}\left(H_{\mathrm{s}}^{\mathrm{ref}} \delta\rho_{\mathrm{s}}^{\mathrm{ref}}\right) = 0. \tag{12}$$

There are different ways to obtain the SCF solution. We here develop the generalized optimized effective potential (GOEP) method[28] (see the supporting information) to indirectly vary $\rho_{\mathrm{s}}^{\mathrm{ref}}$, by optimizing a non-local effective potential v^{GOEP} until

$$\frac{\delta E_v}{\delta (v^{\mathrm{GOEP}})_{ai}} = 0, \tag{13}$$

where $(v^{\mathrm{GOEP}})_{ai}$ stands for the occupied-virtual block of the non-local potential.

Within our approach, excited states are treated on the same footing as the ground state. To calculate the energy of the excited state, we minimize the excited-state energy functional, Eq. (2) with respect to $\rho_{\mathrm{s}}^{\mathrm{ref}}$. The excited-state information, namely the stationary nature, not the energy minimum, is built in $\Delta E_n[\rho_{\mathrm{s}}^{\mathrm{ref}}]$, the excitation energy part of the functional. The minimization with respect to $\rho_{\mathrm{s}}^{\mathrm{ref}}$ is justified, because even in the calculation of excitation energies, the auxiliary system remains in a ground state of the effective Hamiltonian $H_{\mathrm{s}}^{\mathrm{ref}}$. The minimization with respect to $\rho_{\mathrm{s}}^{\mathrm{ref}}$ is a part of the search for the optimal auxiliary system for the stationary state (the excited states), the other part being the construction of the excitation energy functional $\Delta E_n[\rho_{\mathrm{s}}^{\mathrm{ref}}]$.

We now consider two specific functionals. Both the pp-RPA and the SF-TDDFT have been carried out as post-DFT approaches. Here we need to reformulate them as a functional of the non-interacting auxiliary system density matrix $\rho_{\mathrm{s}}^{\mathrm{ref}}$. Consider an N-electron physical system, within the pp-RPA,[20] $E_v^{\mathrm{ref}}[\rho_{\mathrm{s}}^{\mathrm{ref}}]$ is the energy of the corresponding $(N-2)$-electron auxiliary system described with DFA. The two-electron addition excitation energy from the pp-RPA reads

$$\Delta E_n^{+2e} = \begin{bmatrix} (X^{+2e,n})^\dagger & (Y^{+2e,n})^\dagger \end{bmatrix} \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^{\mathrm{T}} & \mathbf{C} \end{bmatrix} \begin{bmatrix} X^{+2e,n} \\ Y^{+2e,n} \end{bmatrix}, \tag{14}$$

where $X^{+2e,n}$ and $Y^{+2e,n}$ are eigenvectors of the pp-RPA matrix, which correspond to the n-th two-electron addition state. The $\mathbf{A}$ and $\mathbf{C}$ matrices are rewritten into non-canonical forms:[27]

$$\mathbf{A}_{ab,cd} = \langle\phi_a|\hat{F}|\phi_c\rangle\langle\phi_b|\phi_d\rangle + \langle\phi_b|\hat{F}|\phi_d\rangle\langle\phi_a|\phi_c\rangle + \frac{1}{2}\langle ab\|cd\rangle, \tag{15}$$

$$\mathbf{C}_{ij,kl} = -\langle\phi_i|\hat{F}|\phi_k\rangle\langle\phi_j|\phi_l\rangle - \langle\phi_j|\hat{F}|\phi_l\rangle\langle\phi_i|\phi_k\rangle + \frac{1}{2}\langle ij\|kl\rangle, \tag{16}$$

where $\hat{F}$ is the non-interacting (G)KS Hamiltonian for the auxiliary system:

$$\hat{F} = \frac{\delta E_v^{\mathrm{ref}}[\rho_{\mathrm{s}}^{\mathrm{ref}}]}{\delta\rho_{\mathrm{s}}^{\mathrm{ref}}}. \tag{17}$$

The **B** matrix is

$$\mathbf{B}_{ab,ij} = \frac{1}{2}\langle ab\|ij\rangle. \tag{18}$$

Similarly, with the SF-TDDFT, $E_v^{\mathrm{ref}}[\rho_{\mathrm{s}}^{\mathrm{ref}}]$ is the energy of the corresponding high-spin auxiliary system described with DFA. The spin-flip excitation energy from the collinear SF-TDDFT with the Tamm-Dancoff approximation (TDA) is

$$\Delta E_n^{\mathrm{SF}} = (X^n)^\dagger \mathbf{A} X^n, \tag{19}$$

where X^n is the eigenvector corresponding to the n-th spin-flipped state. The non-canonical form of the **A** matrix here is (following what has been done in Refs 29–31 for the TDDFT/TDA.)

$$\mathbf{A}_{\bar{a}i,\bar{b}j} = \langle\phi_{\bar{a}}|\hat{F}|\phi_{\bar{b}}\rangle\langle\phi_i|\phi_j\rangle - \langle\phi_i|\hat{F}|\phi_j\rangle\langle\phi_{\bar{a}}|\phi_{\bar{b}}\rangle - c_{\mathrm{HF}}\langle i\bar{b}|j\bar{a}\rangle, \tag{20}$$

where c_{HF} is the percentage of the exact exchange in the functional used. The bars on top of the spatial orbital indices denotes β spins. It is easy to see that ΔE_n^{+2e} and ΔE_n^{SF} are rotational invariant, as long as the orbital rotation does not mix the occupied and virtual spaces. Thus given a density matrix $\rho_{\mathrm{s}}^{\mathrm{ref}}$, the total energy is uniquely determined. The multireference DFT functionals generated are denoted pp-SCF and SF-SCF, while the original methods are abbreviated as pp and SF. We add "@DFA" after the name to indicate which DFA is used as the reference functional. For example, "pp@HF" stands for the regular pp-RPA with the Hartree-Fock functional. For the sake of simplicity, we omit this suffix when using the Hartree-Fock reference functional. Analytic gradients used in the optimization are shown in the supporting information.

To illustrate the ability of this method to describe systems with multireference characters, we tested the methods with single bond dissociation and double bond rotation. Excitation energies in atoms and small molecules are computed as well. In this work, pp and pp-SCF calculations are performed with restricted singlet references with two electrons removed, followed by spin-adapted calculations. For the SF and SF-SCF, restricted open-shell high-spin triplet references are used. The target states are either singlet or $M_z = 0$ triplet. Since the SF-TDA is spin-incomplete, there will be spin contamination in the target states. The spin contamination observed in SF-SCF calculations is smaller than or comparable to that produced by the SF. Generally, the SCF density matrix for the reference DFA calculation is suitable to be used as the initial guess for $\rho_{\mathrm{s}}^{\mathrm{ref}}$. However, there are cases that this initial guess leads the optimization to be trapped in a local minimum. In these cases, density matrices from converged calculations of similar structures (bond stretch or shrink) may be utilized. The auxiliary system energy is computed with the Hartree-Fock functional unless the DFA functional is specified otherwise. Our methods have been implemented in the QM4D[32] package. Coupled-cluster singles and doubles (CCSD)[33] calculations for single bond molecules and ethylene are performed with Gaussian 09.[34]

The proper description of single bond breaking is challenging for single reference methods. It is well-known that restricted (G)KS DFT/Hartree-Fock produces a wrong dissociation limit. Although unrestricted (G)KS DFT/Hartree-Fock is reasonable in the energy of dissociated atoms, it has serious spin contamination problems and incorrect spin densities when the nuclear separation is large. Multireference methods are capable of predicting the correct dissociation limit. However, the conventional SF-TDA/SF-CIS usually underestimates the binding energy.[35–39] The pp-RPA could suffer from the problem that orbitals of the $(N-2)$-electron system are too contracted,[27] leading to underestimated equilibrium bond lengths for the ground state. We expect the optimization of density in our methods to improve the description. Dissociation curves of H_2, LiH, BH and HF molecules are shown in Figure 1, with pp, pp-SCF, SF and SF-SCF results. CCSD results are also shown for reference, except in H_2. In the case of H_2, the pp-RPA result is exact and the $N-2$ density is simply zero, thus making the self-consistent calculation unnecessary.[20] Binding energies and equilibrium bond lengths are presented in Tables 1 and 2. It can be seen that the description for single bond dissociation is significantly improved. Both the dissociation energy and the equilibrium bond length become more accurate after achieving self-consistency. The error in the equilibrium bond length is greatly reduced as the orbitals of the $(N-2)$-electron reference relax during the variation. For the LiH molecule, the pp-SCF curve coincides with the CCSD result. The pp-RPA predicts a state crossing around 1.2 Å for the HF molecule, which does not exist in the CCSD calculation. The pp-SCF corrects this behavior, making the curve relatively similar to the CCSD result.

The choice of the linear response theory affects the overall accuracy. Firstly, the linear response theory selected determines what configurations are considered in the target state. Secondly, even for conventional post-SCF excitation energy calculations, the SF-TDA and the pp-RPA certainly differ. The optimization is expected to improve the quality of the total energy over the parent linear response theory, thus the overall accuracy relies on the method chosen.

Table 1: Binding energies (eV) for H_2, LiH, BH and HF computed with the cc-pVTZ basis set.

Molecule	CCSD	pp	pp-SCF	SF	SF-SCF
H_2	—	4.70	—	3.73	4.13
LiH	2.44	2.39	2.46	1.22	1.91
BH	3.94	3.15	4.15	2.96	3.20
HF	6.71	0.18	5.36	2.45	4.69
MAD[a]	—	2.46	0.53	1.86	0.96

[a] Mean absolute deviations from CCSD values. For H_2, the standard value is chosen as the pp-RPA value. There is no error for pp and pp-SCF in this case, so MAD's for pp and pp-SCF are only computed for LiH, BH and HF.

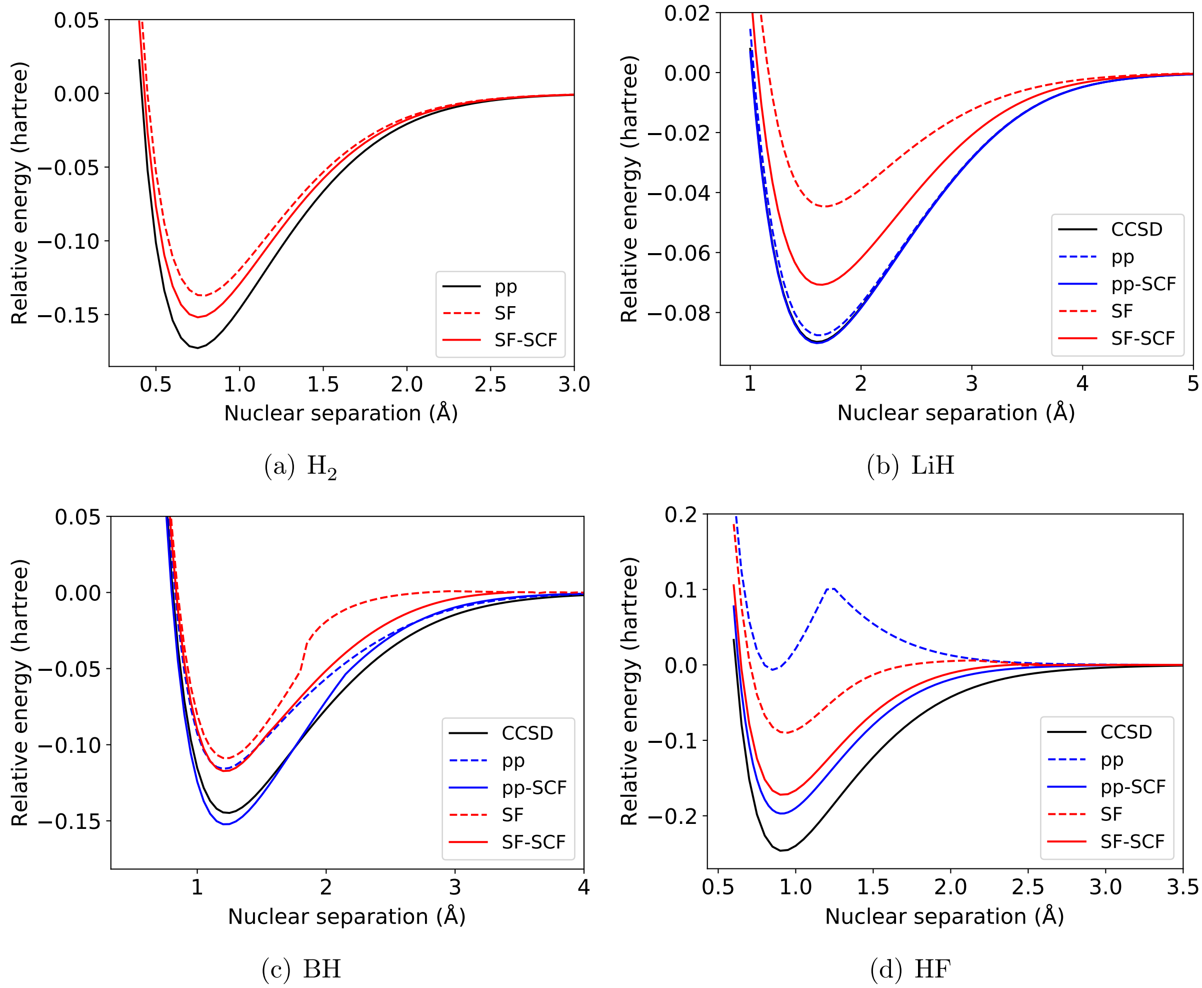


Figure 1: Relative energies of H_2, LiH, BH and HF molecules with respect to corresponding dissociated atoms. The cc-pVTZ basis set has been used.

Table 2: Equilibrium bond lengths (Å) for H_2, LiH, BH and HF computed with the cc-pVTZ basis set.

Molecule	CCSD	pp	pp-SCF	SF	SF-SCF
H_2	—	0.745	—	0.779	0.758
LiH	1.609	1.625	1.608	1.673	1.637
BH	1.236	1.209	1.223	1.225	1.219
HF	0.917	0.857	0.911	0.936	0.919
MAD[a]	—	0.034	0.007	0.032	0.015

[a] Mean absolute deviations from CCSD values. For H_2, the standard value is chosen as the pp-RPA value. There is no error for pp and pp-SCF in this case, so MAD's for pp and pp-SCF are only computed for LiH, BH and HF.

Although the Hartree-Fock functional is mostly used in this work as the reference DFA (the reason is given in the supporting information), subsequent works using functionals which have a good performance can follow straightforwardly. With the Hartree-Fock reference, the SF-TDA reduces to SF-CIS,[35,36] which makes SF-SCF@HF equivalent to MCSCF with spin-flipped configurations from the high-spin configuration. However, even with the Hartree-Fock reference, the pp-SCF@HF energy is not equal to an expectation value of a multiconfigurational wave function on the Hamiltonian. This makes pp-SCF different from MCSCF. Figure 2 shows an example where a DFT reference (the HFLYP functional, 100% Hartree-Fock exchange, 100% LYP correlation[8]) is used. Compared to SF-SCF@HF, SF-

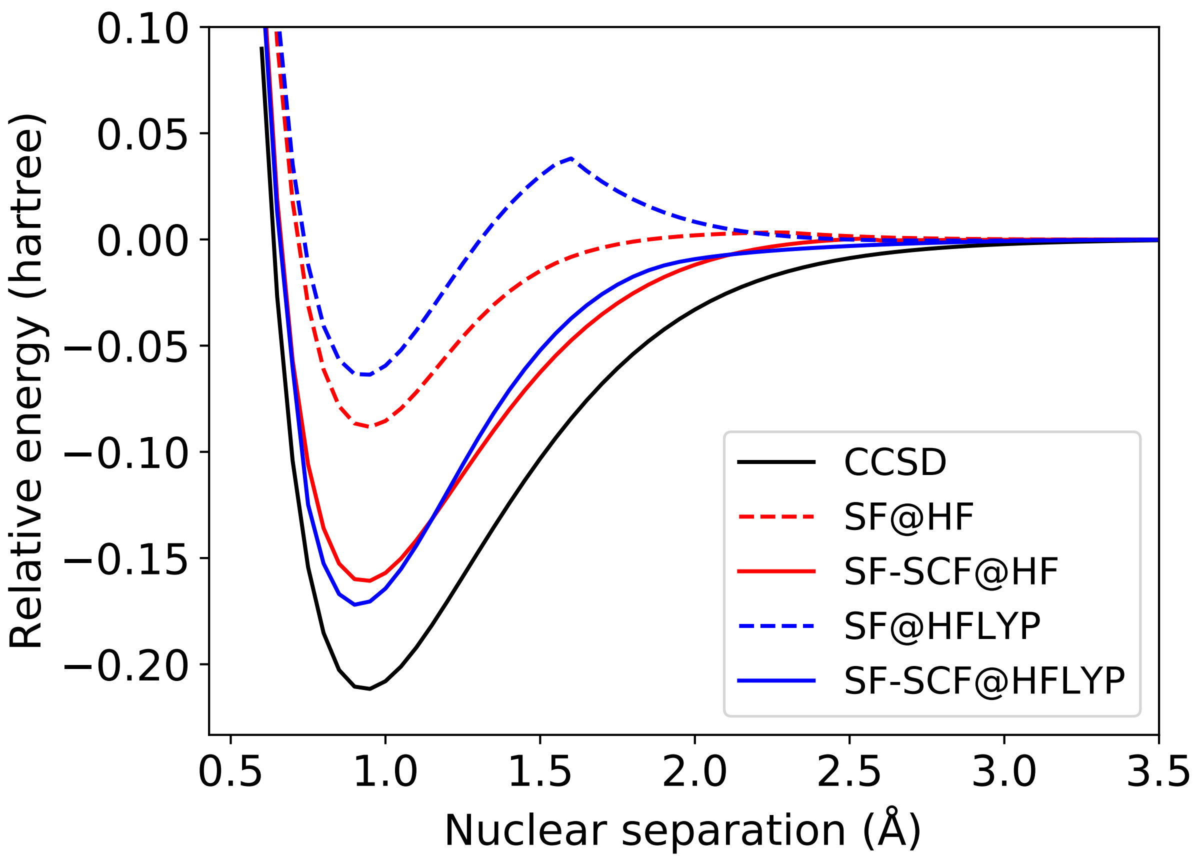


Figure 2: Relative energy of HF molecule with respect to dissociated atoms. The 6-31G* basis set has been used.

SCF@HFLYP gives slightly better binding energy, which may be attributed to the fact that DFT references provide dynamic correlation, in addition to the static correlation contribution which is already included by the multireference calculation.

The double bond rotation, for example, the ethylene torsion, is another example that static correlation contribution is significant. In this case, even the CCSD produces an unphysical cusp, because the Hartree-Fock calculation is already qualitatively incorrect. Unlike the N-electron singlet ethylene, the $(N-2)$-electron singlet for the pp-RPA and the high spin triplet for spin-flip methods are single determinantal. This fact makes the pp-RPA and the SF-TDDFT suitable for this problem. As shown in Figure 3, they will not give an unphysical cusp, but the barrier height is not optimal. Self-consistency corrects the barrier heights to be closer to the MR-ccCA value.[40]

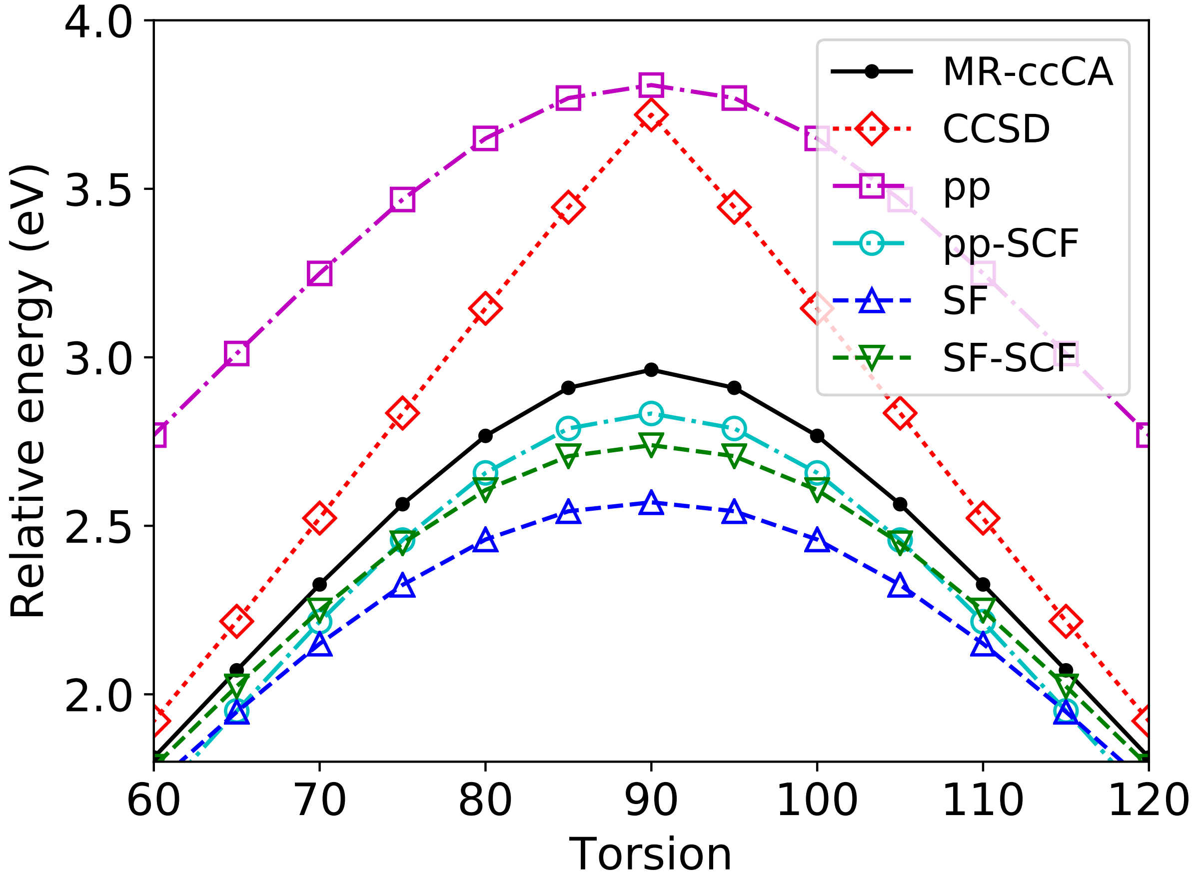


Figure 3: Relative energy of twisted ethylene with respect to flat ethylene. The cc-pVTZ basis set has been used. Structures are adapted from Ref. 40. The carbon-carbon distance varies when the torsion angle θ changes, $r_{\mathrm{CC}} = (1.339 + 0.12\theta/90)$ Å. Other parameters are fixed, $r_{\mathrm{CH}} = 1.0856$ Å, $\angle\mathrm{HCH} = 121.2°$.

These results demonstrate that the pp-SCF and SF-SCF are good ground state multireference energy functionals. Since their parent methods are mostly used to calculate excitation energies, it is also worthwhile to investigate their performance on excited states. Atomic excitation energies and molecular vertical excitation energies are presented in Tables 3 and 4. For atomic excitation energies, self-consistency seems not to change the results much, especially for the SF-SCF. Larger modifications occur when the pp-SCF calculates excitation energies for the oxygen atom. For molecular excitations, The pp-SCF outperforms the pp-RPA on singlet-triplet gaps, but singlet-singlet gaps seem to get overestimated. The SF-SCF generally performs better than the non-self-consistent SF.

Table 3: Atomic excitation energies (eV). The cc-pVTZ basis set has been used in the calculation for Ca, while the aug-cc-pVTZ basis set has been used for other calculations. Standard values are: Be: experimental values from Ref. 41. Mg: experimental values from Ref. 42. Ca: computed values from CR-EOM-CCSD(T).[43] O and S: experimental values from Ref. 44.

Term	Standard	pp	pp-SCF	SF	SF-SCF
Be					
^{3}P	2.73	2.74	2.74	2.06	2.11
^{1}P	5.28	5.34	5.34	5.60	5.25
Mg					
^{3}P	2.71	2.58	2.59	2.07	2.14
^{1}P	4.35	4.27	4.28	4.49	4.17
Ca					
^{3}P	1.79	1.66	1.68	1.26	1.32
O					
^{1}D	1.97	1.75	2.02	2.09	2.04
^{1}S	4.19	2.98	3.46	4.61	4.54
S					
^{1}D	1.15	1.20	1.30	1.21	1.15
^{1}S	2.75	1.95	2.09	3.07	3.02
MAD[a]	—	0.30	0.22	0.36	0.28

[a] Mean absolute deviations from standard values.

In conclusion, we present a new DFT approach. It uses the (G)KS description for the auxiliary systems, but for the physical system, the energy functional is a major departure from the (G)KS energy functional form. The utilization of generalized auxiliary systems, combined with the linear response theory, leads to natural and rigorous multireference en-

Table 4: Molecular vertical excitation energies (eV). The aug-cc-pVDZ basis set has been used for the calculations of ethylene excitation energies. For other molecules, the aug-cc-pVTZ basis set has been used. Standard values: BH and CH^+: computed values using CR-EOM-CCSD(T).[43] CO and N_2: experimental values from Ref. 45. Ethylene: computed values from Ref. 46.

Term	Standard	pp	pp-SCF	SF	SF-SCF
BH					
$^3\Pi$	1.27	1.66	1.61	0.77	1.03
$^1\Pi$	2.85	3.18	3.52	3.17	2.95
CH^+					
$^3\Pi$	1.15	1.72	1.59	0.54	0.87
$^1\Pi$	3.07	3.60	3.91	3.21	3.09
CO					
$^3\Pi$	6.32	5.63	6.47	5.42	6.17
$^1\Pi$	8.51	7.84	9.29	8.98	9.23
N_2					
$^3\Sigma_u^+$	7.75	8.32	9.03	7.96	7.51
$^1\Pi_g$	9.31	9.81	10.52	9.72	9.51
Ethylene					
$^3B_{1u}$	4.5	3.94	4.48	—	—
$^1B_{1u}$	7.8	6.28	8.69	—	—
MAD[a]	—	0.63	0.66	0.44	0.24

[a] Mean absolute deviations from standard values.

ergy functionals. Currently the GOEP method is used to obtain self-consistency, and the pp-RPA and the SF-TDDFT are shown as examples. Numerical results show the capability of our method for describing systems with multireference character such as single bond breaking and double bond rotation. Significant improvement in the energy profile, including relative energies and equilibrium geometries, is observed when comparing this method with corresponding parent methods. Excitation energies are also evaluated. As a method that describes the ground state and excited states on the same footing, it delivers better or comparable accuracy for excitation energies compared to the non-self-consistent pp-RPA and the SF-TDDFT. In order to explore more possibilities on reference functionals, a new and better DFT functional, such as the LOSC[47] may be applied. This work opens promising pathways to describe static/strong correlation within the density functional theory framework.

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