



Excitation Energies of Molecules from Ensemble Density Functional Theory: Multiconfiguration Approaches

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Abstract

Ensemble methods for excited states are based on the ensemble variation principle and in their simplest formulations can be either based on the wavefunction or the electron density. The latter group shares the favorable scaling of ground state density functional theory (DFT) and as such can be considered a computationally inexpensive alternative to time-dependent (TD)-DFT in cases where TD-DFT is not sufficiently accurate. The failures of TD-DFT most prominently include the poor description of conical intersections and excitations of multiple character, i.e., when multiconfigurational effects play a significant role. To deal with such issues, quite recently a number of multiconfiguration ensemble methods have been designed that combine a wavefunction-based formulation with ensemble density functional theory. This chapter discusses the merits and shortcomings of such approaches. It also attempts to elucidate some of the essential problems associated with the ensemble DFT methods and their variants to the computational chemistry community.



1. ENSEMBLE VARIATION PRINCIPLE AND ITS DESCENDANTS

In the 1970s, when the ensemble methods for describing the excited states of molecules first appeared, available methods for calculating the excitation energies for molecules were either very inaccurate or very expensive. The subspace density functional theory, introduced by Theophilou,¹ gave hope that it would be possible to describe the correlation in the excited states at modest cost. Then, many difficulties associated with using ensemble methods and the rapid development of time-dependent density functional theory (TD-DFT) impeded the progress of ensemble methods, as well as the other time-independent density functional methods for excited states. Currently, it seems that TD-DFT is reaching the limits of its capabilities and while it is of impressive accuracy in describing single valence excitations, it is still having problems with Rydberg² and charge-transfer states^{3,4} and excitations of multiple character.⁵ These observations prompted a renaissance of time-independent density functional methods for excited states^{6–12}. Among them, the ensemble methods are prominent.

The foundation of all the ensemble methods is the ensemble minimum principle^{1,13} which states that if $\psi_1, \psi_2, \dots, \psi_m$ are orthonormal trial functions, then for m lowest eigenfunctions of N -electron Hamiltonian \hat{H} with eigenvalues $E_1 \leq E_2 \leq \dots \leq E_m$ the weighted sum of expectation values of energy obtained with the trial functions is bounded from below by a weighted sum of pertinent eigenvalues, i.e.,

$$\sum_{I=1}^m \omega_I \langle \psi_I | \hat{H} | \psi_I \rangle \geq \sum_{I=1}^m \omega_I E_I \quad (1)$$

provided that weights ω_I fulfil the condition

$$\omega_1 \geq \omega_2 \geq \dots \geq \omega_m > 0. \quad (2)$$

Inequality (1) allows all excited states, or just a chosen number of the lowest states, of a system to be treated as one ensemble (mixed) state. The sum on the left side of the inequality (1) is called the ensemble energy, E_{ens} . The minimum of the ensemble energy uniquely determines the eigenstates of the system if all the weights $\omega_1, \dots, \omega_m$ are different. If the weights are equal, the minimum of the ensemble energy determines only the subspaces in

which the eigenstates lie, therefore the methods based on the simplified ensemble minimum principle are called subspace methods (i.e., subspace Hartree–Fock (HF),¹⁴ subspace DFT¹).

The simplest method based on inequality (1) is ensemble HF,^{14–16} which consists in minimization of the ensemble energy within a set of single Slater determinants. While conceptually straightforward, this single-determinant wavefunction method is able to capture very little dynamic and no static correlation.

A more promising method is ensemble DFT (originally introduced under the name subspace DFT by Theophilou¹). It is based on a Hohenberg–Kohn (HK) type theorem introduced by Theophilou and extended by Gross et al.¹⁷ for ensembles of unequal weights (see also Refs. 18,19), chosen for an m -state ensemble as follows

$$\omega_1 = \omega_2 = \dots = \omega_{m-g} \equiv \frac{1 - \omega g}{m - g} \quad (3)$$

and

$$\omega_{m-g+1} = \omega_{m-g+2} = \dots = \omega_m \equiv \omega \quad (4)$$

where g is an integer satisfying $1 \leq g \leq m - 1$ and ω is a real parameter in the range $0 \leq \omega \leq 1/m$. The ensemble density matrix expressed in the basis of eigenstates $\{|j\rangle\}$ of the Hamiltonian $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}$ (with \hat{T} denoting the kinetic energy, \hat{V}_{ee} the electron–electron interaction and \hat{V} the external potential) reads

$$\hat{\Gamma}^{m,g}(\omega) = (1 - \omega_m) \left[\frac{1}{m-g} \sum_{j=1}^{m-g} |j\rangle\langle j| \right] + \omega_m \left[\frac{1}{m} \sum_{j=1}^m |j\rangle\langle j| \right]. \quad (5)$$

The theorem states that if for m lowest eigenstates $\{|m'\rangle\}$ of a Hamiltonian $\hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{V}'$ another density matrix is constructed:

$$\hat{\Gamma}^{m,g}(\omega)' = (1 - \omega_m) \left[\frac{1}{m-g} \sum_{j'=1}^{m-g} |j'\rangle\langle j'| \right] + \omega_m \left[\frac{1}{m} \sum_{j'=1}^m |j'\rangle\langle j'| \right] \quad (6)$$

then for fixed numbers m, g, ω the ensemble electron densities

$$\rho_{\text{ens}} = \text{Tr} \{ \hat{\Gamma}^{m,g}(\omega) \hat{\rho}(r) \} \quad (7)$$

and

$$\rho'_{\text{ens}} = \text{Tr}\{\hat{\Gamma}^{m,g}(\omega)' \hat{\rho}(r)\} \quad (8)$$

are different, provided that potentials \hat{V} and \hat{V}' differ by more than a constant. The proof of the HK theorem for ensembles allowed¹⁷ a universal HK functional to be defined

$$F^m[\omega, \rho_{\text{ens}}] = \text{Tr}\{\hat{\Gamma}^{m,g}(\omega)(\hat{T} + \hat{V}_{\text{ee}})\}, \quad (9)$$

where $\hat{\Gamma}^{m,g}(\omega)$ is a density matrix corresponding to a given density ρ . Note that there may be more than one density matrix generated by a unique potential and yielding ρ but each gives the same ensemble energy.¹⁷ The functional (9) is defined for ensemble ν -representable densities. As with a ground state theory, the extension of the universal functional to ensemble N -representable densities is possible if the constrained-search formalism construction is used. Namely, the universal functional for an ensemble density can be defined as

$$F_{m,\omega}[\rho_{\text{ens}}] = \min_{\{\Psi_I\} \rightarrow \rho_{\text{ens}}} \sum_{I=1}^m \omega_I \langle \Psi_I | \hat{T} + \hat{V}_{\text{ee}} | \Psi_I \rangle, \quad (10)$$

where the notation $\{\Psi_I\} \rightarrow \rho_{\text{ens}}$ indicates a set of m orthonormal wavefunctions forming an ensemble, which pertains to a given ensemble density by the relation

$$\rho_{\text{ens}}(\mathbf{r}) = \sum_{I=1}^m \omega_I \langle \Psi_I | \hat{\rho}(\mathbf{r}) | \Psi_I \rangle. \quad (11)$$

It is convenient to define an exchange–correlation (XC) ensemble density functional by introducing a Kohn–Sham (KS) system which shares an ensemble density with the interacting system (assuming that both densities are constructed from the m lowest states and with the same ensemble weights). The XC ensemble functional is then written by analogy to its ground state counterpart as

$$E_{m,\omega}^{\text{XC}}(\rho_{\text{ens}}) = F_{m,\omega}[\rho_{\text{ens}}] - T_{m,\omega}^{\text{s}}[\rho_{\text{ens}}] - \frac{1}{2} \int \int \frac{\rho_{\text{ens}}(\mathbf{r}) \rho_{\text{ens}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (12)$$

where $T_{m,\omega}^{\text{s}}$ stands for the kinetic energy of the KS system and the Coulomb term depends explicitly on the ensemble density ρ_{ens} .

The ensemble density functional theory formulated by Gross et al.^{13,17} has become a standard formulation for ensemble DFT over many years

and was used by Gross et al.²⁰ to calculate the spectra of a helium atom and a helium ion. In place of the ensemble XC energy, they used the ground-state local density approximation (LDA, Ref. 21) and also Kohn's quasi-local approximation (QLDA) for ensembles.²² The spectra obtained were blurred, a result which the authors blamed on the self-interaction error. Subsequently, many approaches based on the approximate ground-state XC functionals were formulated and tested: the exact-exchange^{23–27} and the local density approximation²⁸ or other approximations developed for the ground state DFT, reoptimized for ensemble calculations.^{29,30}

Most of the aforementioned work on ensemble DFT used optimized effective potential approach, which employs an ensemble KS potential. There are two reasons why it is desirable to use a local, multiplicative ensemble exchange and correlation potential $\nu_{XC}^{ens} = \nu_{XC}^{ens}(\mathbf{r})$. The first reason is formal. In ensemble DFT, the ensemble density is in one-to-one correspondence with the external (local) potential of the system.^{1,17} Furthermore, for the ensemble KS system, i.e., the virtual noninteracting system of electrons with the same ensemble density as the interacting system under study, the ensemble density is in one-to-one correspondence with the ensemble KS potential. The latter is the local effective potential that binds the noninteracting electrons in such a way that its ensemble density is the same as the ensemble density of the interacting system of interest. Therefore, determination of the ensemble KS potential is at the heart of ensemble DFT. The second reason is increased computational efficiency. The ensemble spin orbitals can be obtained by optimizing the ensemble energy (1). Like the HF equations, the direct minimization of the ensemble energy leads to single-particle eigenvalue-like equations for the spinorbitals, where the exchange potential term is not local. However, unlike the HF case, because the ensemble energy is not invariant to rotations of the spinorbitals, the Hamiltonian operator in the single-particle equations is in general not common to all spinorbitals. As a result, the orbitals which solve the ensemble single-particle equations are not automatically orthogonal and it becomes necessary, in general, to enforce their orthogonality, e.g., by employing off-diagonal Lagrange multipliers. The optimized effective potential method provides an elegant solution to the problem of a common Hamiltonian operator in the ensemble single-particle equations, with the additional benefit of a local exchange and correlation potential, as required by ensemble KS DFT.

Over the years, a lot of effort has been put into formulating the theoretical framework of ensemble DFT.^{31–35} It has become clear that there is no easy way to obtain a good approximation for the ensemble XC functional

and using the ground-state approximations might be the best starting point. Two approaches do not use existing functionals; first is the aforementioned QLDA due to Walter Kohn which was derived for a thermal ensemble and as such is not very successful in describing ensembles of states that do not interact with one another. The other is the recent work of Yang et al.³⁶ where the exact KS and XC potentials for given ensemble densities are extracted and applied to the helium atom. The authors speculate that knowledge of the exact potential can be useful in constructing ensemble density functionals. While this is certainly true, this sort of task has been attempted previously for ground-state functionals without much success (see e.g., Ref. 37) and it is not expected to be easier in case of ensemble density.

The use of ground state expressions for the Hartree, exchange and correlation energy introduces a self-interaction error in the ensemble energy. This error has been called “ghost interaction” by Gidopoulos et al.²⁶ The error lies in the conventional definition of the ensemble Hartree energy that employs the ground state expression $E_H = \frac{1}{2} \int \int \frac{\rho_{\text{ens}}(\mathbf{r})\rho_{\text{ens}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$. Consider the excitation of an electron occupied in an orbital of the state Ψ_1 to an orbital unoccupied in Ψ_1 but occupied in the excited state Ψ_2 . The ensemble density is the weighted sum of the densities of the states Ψ_1, Ψ_2 . Hence, the Hartree energy will include the spurious Coulomb interaction of the density from the orbital occupied by the electron before excitation with the density of the orbital hosting it after the excitation. This kind of self-interaction is not encountered in ground state DFT, nor ground state HF theory and the ground state expressions for the exchange energy cannot correct it. The best way to correct for the ghost self-interaction is to write the ensemble Hartree energy as the sum of the Hartree energies of the member configurations of the ensemble.^{24,26,38,39}

The spin-symmetry of the ensemble members introduces a further challenge to the ensemble theory for excited states (DFT and HF). Consider the He atom. The ground state is a singlet and the lowest excitation is a triplet. The next lowest excitation is a singlet. So, for the physical He atom, the ensemble with configurations of lowest energy may have one member (the singlet ground state), four members (singlet ground state and triplet excited state) or five members (the above plus the singlet excited state). If we now consider the noninteracting system, the ground state is nondegenerate but if we want to consider the lowest excitation, this is quadruply degenerate. Therefore one may consider just the ground state, or an ensemble of five

members. This places restrictions on the choice of ensemble weights for the noninteracting system. For example, the freedom to choose unequal weights is restricted, because if we imagine an adiabatic connection path, where we switch on the electron repulsion, a noninteracting ensemble with randomly unequal weights for the four degenerate excited states cannot in general connect smoothly to an ensemble of the physical system, where the fourfold degeneracy is broken and where the ensemble weights will satisfy the inequalities (2). In Ref. 26, the problem was addressed by choosing the members of the noninteracting ensemble to be eigenstates of S^2 and not single Slater determinants. Such a choice has also led to improved accuracy of the results (see table in Ref. 26). This point is discussed in Ref. 39, where eigenstates of S^2 are also used. Another way of bypassing the problem is to use Boltzmann weights for the members of the ensemble, which guarantee at least the existence of a smooth adiabatic connection between the noninteracting and interacting systems.

Another challenge for ensemble DFT, seemingly of lesser importance but with major impact on the quality of results is the lack of a clear path to obtain the energies of specific states in the ensemble. In the wavefunction approaches, it is fairly reasonable to identify the resulting set of wavefunctions with the true eigenvectors of the Hamiltonian. In the ensemble DFT, however, extracting the energies is not straightforward. Various methods have been proposed^{1,20,35,40,41,42} but those which are theoretically justified are not feasible in practical calculations and vice versa (with the exception of Levy's method which involves calculation of the first excitation energy from orbital energies resulting from an ensemble calculation—this, however, limits the method to calculating only the first excitation energy). We will not present all these methods in detail, this problem will be briefly discussed in Section 4.3 in the context of multi-configuration methods.

A final question which the quantum chemistry community has tried to address concerns the actual capabilities of ensemble methods. It has been shown^{25,28,38} that ensemble DFT methods employing the ground-state approximations as the XC functionals can (at least for small molecules) match the accuracy of some less sophisticated TD-DFT methods. However, so far only the multiconfiguration ensemble methods have been able to surpass the limits of standard TD-DFT. In the next sections, we will present basic ideas associated with this group of methods and some of their results.



2. MULTICONFIGURATION WAVEFUNCTION-BASED METHODS FOR ENSEMBLES

Before moving on to multiconfiguration ensemble density methods, we will briefly discuss how multireference effects in excited states can be taken into account within ensemble wavefunction-based methods. As mentioned in Section 1, in the simplest ensemble wavefunction method, the ensemble may be constructed from m single-determinant states $\{\Phi_I\}$. Then, application of the ensemble variational principle leads to the ensemble HF (eHF) method.⁴² In this method, the ensemble energy given as a weighted sum of the state energies

$$E^{\text{eHF}} = \sum_{I=1}^m \omega_I \langle \Phi_I | \hat{H} | \Phi_I \rangle, \quad (13)$$

is optimized with respect to spinorbitals $\{\varphi_p\}$ building single determinants subject to their orthonormality. Note that since the ensemble energy is in general not invariant to orbital rotations, it is possible to determine optimal spinorbitals uniquely. An exception is the hyper Hartree–Fock (HHF) method, an equiensemble method,^{14,43} where the ensemble is composed of all the N -electron Slater determinants that can be constructed from a given basis set of R orthonormal spin orbitals, with $R \geq N$. The inclusion of all Slater determinants in the HHF ensemble restores the invariance of the HHF ensemble energy with respect to orbital rotations and simplifies the HHF equations.^{14,44}

Since excited states are described in the eHF by single-determinant functions, the excited state energies predicted by this method are expected to be in error especially for states of multiconfigurational nature. A step beyond ensemble HF method would involve first doing the eHF calculation to obtain a set of eHF spinorbitals and then constructing an ensemble of states formed as linear combination of determinants

$$\forall_{I=1}^m \psi_I = \sum_J C_{IJ} \Phi_J^{\text{eHF}}, \quad (14)$$

where the superscript eHF indicates that spinorbitals used to construct a given determinant have been obtained from the eHF method. The corresponding ensemble energy would read

$$E = \sum_{I=1}^m \omega_I \sum_{JK} C_{IJ} C_{IK} \langle \Phi_J^{\text{eHF}} | \hat{H} | \Phi_K^{\text{eHF}} \rangle. \quad (15)$$

Its minimization with respect to the configuration interaction (CI) expansion coefficients $\{C_{IJ}\}$ with the constraint that wavefunctions $\{\psi_I\}$ stay orthonormal leads to a system of equations

$$\omega_I \sum_K \langle \Phi_J^{\text{eHF}} | \hat{H} | \Phi_K^{\text{eHF}} \rangle C_{IK} = \sum_K \Lambda_{IK} C_{KJ}, \quad (16)$$

where Λ is a Lagrangian matrix. If all the weights are different, then the minimization problem (16) is equivalent to diagonalisation of Hamiltonian matrix in the space spanned by the states $\{\Phi_I^{\text{eHF}}\}$ and approximating the ground and excited state energies of the system as eigenvalues of the Hamiltonian. On the other hand, when the weights are equal, the ensemble energy (15) is the trace of the Hamiltonian matrix and as such remains invariant to orthogonal rotations among the determinants $\{\Phi_I^{\text{eHF}}\}$. Hence, diagonalisation of the Hamiltonian in this case conserves the energy of the ensemble.

The method based on the ensemble energy given in Eq. (15), introduced in Ref. 42 and called Ens-WF, is then a simple ensemble counterpart of the CI method. The accuracy of the state energies predicted by the Ens-WF method hinges on the choice of the configurations that enter the calculation and the choice of the ensemble weights. In Ref. 42, the configurations are selected based on chemical intuition. Using the fact that the ensemble variational principle is a special case of the Helmholtz free energy principle⁴², the weights have been established as Boltzmann factors:

$$\omega_I = \frac{\exp[-\beta E_I]}{\sum_K^m \exp[-\beta E_K]} \quad (17)$$

with approximate state energy values E_I and a tunable β parameter. Obviously, Boltzmann factors are only one possible choice but they have certain attractive properties, such as

- Weights corresponding to degenerate states are equal. This ensures the invariance of the ensemble energy to rotations among degenerate states;
- By choosing β parameter different from zero one can remove the high-lying states from the ensemble (see Fig. 1);

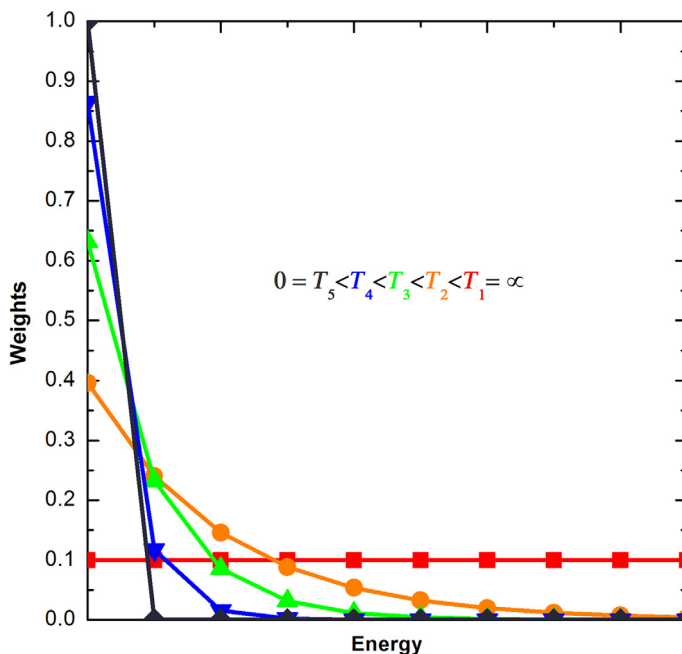


Figure 1 Distribution of Boltzmann weights in a 10-state ensemble for different temperatures. The horizontal axis represents the energies of states in the ensembles.

- It prevents the numerical phenomenon of “root flipping”, through keeping the right order of the expectation values of the trial functions throughout the optimization.

When $\beta \rightarrow \infty$ (or, equivalently, the temperature T is 0, see star-marked curve on Fig. 1), only the ground state has a nonzero weight. In such a case, the eHF and HF approaches are equivalent and consequently the Ens-WF method reduces to the CI method in the given space.

Since excited state energies result from a CI calculation anyway, does introducing an ensemble method of the same cost makes sense at all? These methods differ only in spinorbitals employed to built states (spinorbitals come from HF and eHF methods for CI and Ens-WF methods, respectively). In fact, it has been found that the Ens-WF method (with finite values of the β parameter) can produce more accurate energies than CI for systems with degenerate ground states (e.g., beryllium atom, see Fig. 2) and it can improve the shape of the dissociation curves of diatomic molecules, see Ref. 42.

One could go a step further and construct a fully self-consistent method, the ensemble analog of the multiconfiguration self-consistent field (MCSCF) method. In fact, such an approach would be equivalent to the

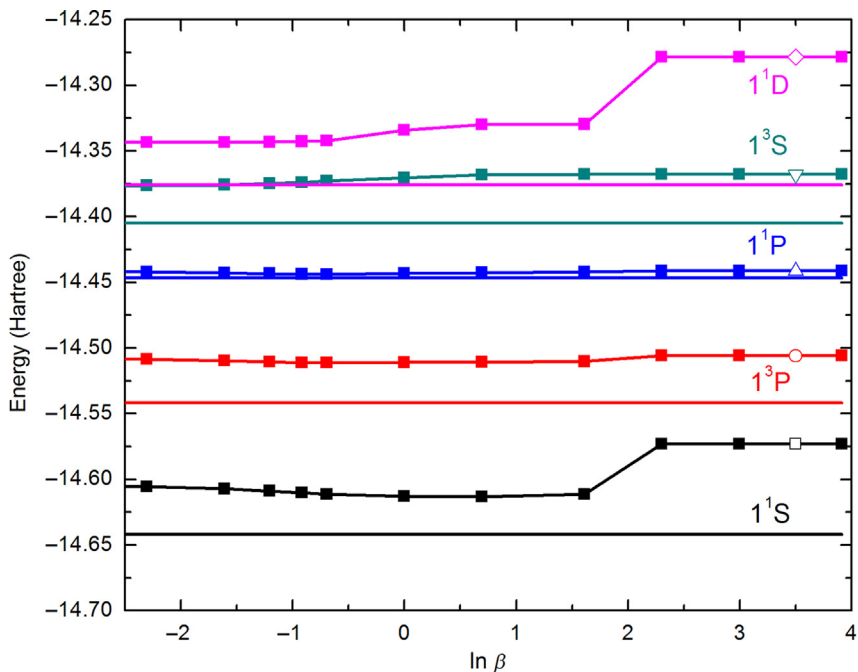


Figure 2 Energies of states of beryllium atom calculated for different values of β parameter. Unmarked solid lines, LR-CCSD reference; marked lines, Ens-WF; open markers, $\beta \rightarrow \infty$ (CI) limit.

state-average MCSCF (SA-MCSCF) method proposed by Werner and Meyer⁴⁵ without even referring to the ensemble theories. In SA-MCSCF, the orbitals and the expansion coefficients of the wavefunction are optimized in a self-consistent manner to minimize the mean average of energy for all states. The states in this average can be weighted equally but usually their weights reflect the significance of each state. SA-MCSCF was primarily introduced to avoid the problem of root flipping—a phenomenon in which the solution oscillates between two nearly degenerate states. It was also shown that the algorithms employing SA-MCSCF have better convergence properties than those for the standard MCSCF methods. SA-MCSCF is not entirely justified theoretically but it could be made rigorous if the weights were not chosen arbitrarily but rather according to the energy criterion. Interestingly, the SA-MCSCF method has been used to model chemical reaction mechanisms and it was shown that the choice of Boltzmann factors as weights improves in many cases the accuracy⁴⁶ of the method.

The accuracy of the Ens-WF method (with or without orbital minimization) is limited by the length of expansion of states in single-determinant function basis. Taking too large a space of determinants would lead to prohibitively expensive calculations. Shorter expansions, on the other hand, will still take into account multireference effects but the corresponding approximations to the state energies will be missing an important amount of the dynamic correlation energy. The remedy of this deficiency is offered by multiconfiguration ensemble density functional theory discussed in the next sections.



3. STATE-AVERAGED SPIN-RESTRICTED KS METHOD

One of the first density functional methods based on the ensemble representation of electron density is the spin-restricted ensemble-referenced Kohn-Sham method (REKS) developed by Filatov et al.^{47,48} Although originally formulated for predicting ground states of molecules the electronic structure of which is dominated by static correlation,⁴⁷ it has been later expanded to treat both a ground and a first singlet excited state.^{49,50}

The REKS method is particularly suited for molecules whose ground state wavefunction is well described using two configurations. In such a case, the ground state density of a physical (interacting) system of interest is represented by a two-state ensemble density of a noninteracting, KS, reference. The multiconfiguration character of the interacting wavefunction is manifested by non-integer occupation of some of the frontier KS orbitals. The underlying assumption in the REKS approach is that if a singlet ground state interacting wavefunction is well represented by a combination of two configurations $|\dots\varphi_a\bar{\varphi}_a\rangle$ and $|\dots\varphi_b\bar{\varphi}_b\rangle$, then a corresponding electron density can be obtained by taking an ensemble of two KS determinants. One of the determinants includes HOMO, $\{\varphi_a, \bar{\varphi}_a\}$, orbitals whereas the other one LUMO, $\{\varphi_b, \bar{\varphi}_b\}$. HOMO and LUMO orbitals form an active space. Thus, the REKS ensemble density takes the form

$$\rho^{\text{REKS}}(\mathbf{r}) = 2 \sum_i |\varphi_i(\mathbf{r})|^2 + n_a |\varphi_a(\mathbf{r})|^2 + n_b |\varphi_b(\mathbf{r})|^2, \quad (18)$$

where n_a and n_b are the occupation numbers constrained to a range $[0, 2]$ and summing up to 2, and the summation with respect to i runs through all orbitals, which are fully occupied in both determinants. Although the ensemble REKS density only approximately corresponds to the true

multiconfiguration wavefunction of the physical system, it is constrained to have the same spin and spatial symmetry as the interacting ground-state wavefunction. Such an approach, despite not being entirely rigorous, is very effective for systems where static correlation plays an important role. The REKS functional for the ensemble density given in Eq. (18) has been proposed to comprise a weighted sum of the KS density functional energies of the two configurations and a coupling term involving singly excited configurations generated out of the active space. It reads⁴⁷

$$E^0 = \frac{n_a}{2} E^{\text{KS}}[\Psi_1] + \frac{n_b}{2} E^{\text{KS}}[\Psi_2] - f(n_a, n_b) \left(E^{\text{KS}}[\Psi^T] - \frac{1}{2} E^{\text{KS}}[\Psi^{S1}] - \frac{1}{2} E^{\text{KS}}[\Psi^{S2}] \right), \quad (19)$$

where Ψ_1 , Ψ_2 are the two possibly nearly degenerate configurations, $|\dots\varphi_a\bar{\varphi}_a\rangle$ and $|\dots\varphi_b\bar{\varphi}_b\rangle$, and $\Psi^T = |\dots\varphi_a\varphi_b\rangle$, $\Psi^{S1} = |\dots\varphi_a\bar{\varphi}_b\rangle$ and $\Psi^{S2} = |\dots\bar{\varphi}_a\varphi_b\rangle$ are the remaining (respectively, triplet and two singlets) configurations constructed from the active orbitals. The function $f(n_a, n_b)$ has been found empirically and it interpolates between a single-configuration ($n_a \approx 2, n_b \approx 0$) case and a case when static correlation dominates ($n_a \approx n_b \approx 1$). A ground state energy follows by optimization of the functional (19) with respect to the orbitals and the occupation numbers $\{n_a, n_b\}$ under the orthonormality constraint for the former and the non-negativity and the normalization conditions for the latter.

Using orbitals and the occupation numbers obtained from the minimization of the REKS functional it is possible to find an approximation to the energy of the first open-shell singlet excited state and it is given by the following expression⁵¹

$$E^1 = E^{\text{KS}}[\Psi^{S1}] + E^{\text{KS}}[\Psi^{S2}] - E^{\text{KS}}[\Psi^T]. \quad (20)$$

Kazaryan et al.⁴⁹ proposed to obtain a better approximation to the excitation energy from the ground to the first open shell singlet state by considering a weighted sum of E^0 and E^1 , namely

$$E^{\text{SA-REKS}} = \omega_0 E^0 + \omega_1 E^1, \quad (21)$$

where $\omega_0 + \omega_1 = 1$; minimizing it with respect to the KS orbitals and the fractional occupation numbers and finally computing the energies of the ground and excited states from Eqs. (19) and (20), respectively. The state-averaged REKS (SA-REKS) functional given in Eq. (21) can be seen as

an orbital-dependent approximate realization of the Gross–Oliveira–Kohn (GOK) functional (Eq. (9)). Notice that functionals (19) and (20) are free from the ghost interaction and include spin polarization. Like the SA-MCSCF the choice of weights in the ensemble energy expression (21) is arbitrary. The application of the SA-REKS method is more justified for homosymmetric systems (e.g., molecules dissociating to equal fragments).⁴⁸ For heterosymmetric systems, it has been argued that more accurate values of the excitation energies will follow from diagonalization of the Hamiltonian in the two-dimensional space consisting of configuration state functions corresponding to a ground and an excited state⁵⁰ resulting in the state-interacting-state-averaged-REKS (SI-SA-REKS) method.

Because only a very small active space is used in the SI-SA-REKS methods, they are fairly computationally inexpensive and can be used for rather large systems.^{48,50} They offer a well-balanced treatment of the dynamic and static correlation and their multiconfiguration character allows conical intersections and some potential energy surfaces to be described. On the other hand, they are limited to only ground and open-shell first singlet excited states and the number of active orbitals is limited to 2. Moreover, their use demands some preliminary knowledge of the chemical system under study. Also, the theoretical foundations of SI-SA-REKS contain considerable empiricism—in the choice of the density functionals as well as in the construction of the function $f(n_a, n_b)$.



4. RANGE-SEPARATED APPROACHES

4.1 Generalized Adiabatic Connection for Ensembles

As hinted in Section 1, the XC component of the GOK universal functional (Eq. (12)) can be formulated in the adiabatic connection (AC) framework. Adiabatic connection⁵² allows one to find an XC ground state density functional by linking a physical system of interest with a KS (noninteracting) one. It is achieved by gradually turning on electron–electron interaction by increasing a coupling strength parameter and modifying the external potential so that a density of the partially interacting system equals that of the fully interacting one. The adiabatic connection approach has been brought to the realm of ensemble DFT by Nagy³⁴ who has shown that a Hartree–XC (HXC) ensemble density functional can be obtained by integrating ensemble electron interaction energy of the partially interacting system with respect to the coupling constant λ , namely

$$E_{m,\omega}^{\text{HXC}}[\rho_{\text{ens}}] = \sum_{I=1}^m \omega_I \int_0^1 d\lambda \langle \Psi_I^\lambda | \hat{V}_{\text{ee}} | \Psi_I^\lambda \rangle \quad (22)$$

where the wavefunctions are eigenfunctions of a partially interacting Hamiltonian

$$(\hat{T} + \lambda \hat{V}_{\text{ee}} + \hat{V}^\lambda) | \Psi_I^\lambda \rangle = \mathcal{E}_I^\lambda | \Psi_I^\lambda \rangle \quad (23)$$

with a local potential \hat{V}^λ assuring that the density constraint

$$\rho_{\text{ens}}(\mathbf{r}) = \sum_{I=1}^m \omega_I \langle \Psi_I^\lambda | \hat{\rho}(\mathbf{r}) | \Psi_I^\lambda \rangle \quad (24)$$

is fulfilled for any value of the coupling strength $\lambda \in [0, 1]$. Therefore, in the Nagy formulation, the density is fixed along the adiabatic connection and the ensemble weights are not varied.

Franck and Fromager³⁵ proposed a generalized adiabatic connection for ensembles (GACE) by demanding the density to be weight independent along the connection and varying coupling strength together with ensemble weights. This approach naturally leads to a weight-dependent ensemble density functional, in line with the early work of Gross, Oliveira, and Kohn.¹⁷ The greatest advantage of the generalized AC is that for a two-state ensemble the ω -dependent XC functional can be Taylor-expanded with respect to ω . This has led to deriving rigorous conditions satisfied by the exact ensemble functional.

In the GACE approach, an ensemble density $\rho_{\text{ens}}(\mathbf{r})$ is weight independent and one considers two-state ensembles formed from a ground and a first excited state of a partially interacting system (the electron–electron interaction is scaled with λ)

$$(\hat{T} + \lambda \hat{V}_{\text{ee}} + \hat{V}^{\lambda,\xi}) | \Psi_I^{\lambda,\xi} \rangle = \mathcal{E}_I^{\lambda,\xi} | \Psi_I^{\lambda,\xi} \rangle, \quad (25)$$

where a local potential $\hat{V}^{\lambda,\xi}$ fixes the ensemble density

$$\rho_{\text{ens}} = (1 - \xi) \rho_{\Psi_I^{\lambda,\xi}} + \xi \rho_{\Psi_2^{\lambda,\xi}}, \quad (26)$$

The density is constant both for varying coupling parameter $\lambda \in [0, 1]$ and weight parameter $\xi \in [0, \omega]$. For a two-state ensemble with $(1 - \omega)$ and ω being weights of the ground and the excited state, respectively, the generalized adiabatic connection expression for the XC ensemble density functional defined in Eq. (12) can be written as³⁵

$$E_{2,\omega}^{\text{XC}}[\rho_{\text{ens}}] = E^{\text{XC}}[\rho_{\text{ens}}] + \int_0^\omega d\xi \left[\left(\mathcal{E}_2^{\lambda=1,\xi} - \mathcal{E}_1^{\lambda=1,\xi} \right) - \left(\mathcal{E}_2^{\lambda=0,\xi} - \mathcal{E}_1^{\lambda=0,\xi} \right) \right] \quad (27)$$

where E^{XC} is the ground state functional. Interestingly, it is evident from (27) that a deviation of the ensemble XC energy from its ground state counterpart results from a difference of excitation energies of the fully interacting ($\lambda=1$) and noninteracting ($\lambda=0$) systems integrated with respect to an ensemble weight ξ . Franck and Fromager have shown that a GACE approach can be employed to rigorously define an ω -dependent short-range ensemble density functional, which is a component of the range-separated multideterminant ensemble DFT formalism presented in the next section.

Using the generalized adiabatic connection allows one to attempt to construct exact functionals for simple cases and use them together with the derived exact conditions to obtain approximations for ensemble density functionals in the future.

4.2 Range-Separated Ensemble DFT

While the pragmatic construction of a multiconfiguration method based on ensemble DFT proposed by Filatov et al. leads to encouraging results,⁴⁸ other approaches are feasible on firm theoretical ground. One of the possibilities to introduce multiconfiguration effects in ensemble DFT is based on using a range-separated ensemble density functional. Just like in ground-state theories,⁵³ in order to avoid double counting of the electron–electron interaction, one separates the electron–electron interaction operator $1/r$ into a short-range ($v_{\text{ee}}^{\text{SR}}$) and a long-range ($v_{\text{ee}}^{\text{LR}}$) part, namely

$$\frac{1}{r} = v_{\text{ee}}^{\text{SR}}(r) + v_{\text{ee}}^{\text{LR}}(r), \quad (28)$$

where

$$\lim_{r \rightarrow \infty} r v_{\text{ee}}^{\text{LR}}(r) = 1 \quad (29)$$

and

$$\lim_{r \rightarrow 0} r v_{\text{ee}}^{\text{SR}}(r) = 1. \quad (30)$$

The most commonly used range partitioning^{54,55} uses the error function and assumes the following expressions for the range components of the electron repulsion operator:

$$v_{ee}^{\text{SR},\mu}(r) = \frac{1 - \text{erf}(\mu r)}{r}, \quad (31)$$

$$v_{ee}^{\text{LR},\mu}(r) = \frac{\text{erf}(\mu r)}{r}. \quad (32)$$

The parameter μ governs the range separation and for $\mu=0$ the long-range function $v_{ee}^{\text{LR},\mu}(r)$ vanishes, while in the limit $\mu \rightarrow \infty$ it accounts for the full-range electron interaction, i.e., $\lim_{\mu \rightarrow \infty} v_{ee}^{\text{LR},\mu}(r) = 1/r$ and $\lim_{\mu \rightarrow \infty} v_{ee}^{\text{SR},\mu}(r) = 0$. The range-separated ensemble energy functional can be formally defined if the GOK universal functional (Eq. (10)) is decomposed into long- and short-range parts

$$F_{m,\omega}[\rho_{\text{ens}}] = F_{m,\omega}^{\text{LR},\mu}[\rho_{\text{ens}}] + E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}] \quad (33)$$

and the LR functional is defined by employing a Levy–Lieb constrained-search formulation, i.e.,

$$F_{m,\omega}^{\text{LR},\mu}[\rho_{\text{ens}}] = \min_{\{\Psi_I\} \rightarrow \rho_{\text{ens}}} \sum_{I=1}^m \omega_I \langle \Psi_I | \hat{T} + \hat{V}_{ee}^{\text{LR},\mu} | \Psi_I \rangle. \quad (34)$$

The functional $E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}]$ is therefore a short-range ensemble density complement, which can be further divided into a classical Hartree part being explicitly given in terms of an ensemble density and the remainder—the XC short-range ensemble density functional

$$E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}] = E_{m,\omega}^{\text{SR-H},\mu}[\rho_{\text{ens}}] + E_{m,\omega}^{\text{SR-XC},\mu}[\rho_{\text{ens}}]. \quad (35)$$

If the ensemble energy functional is defined as follows

$$E_{m,\omega}[\{\psi_I\}] = \sum_{I=1}^m \omega_I \langle \psi_I | \hat{T} + \hat{V}_{ee}^{\text{LR},\mu} + \hat{V}_{\text{ext}} | \psi_I \rangle + E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}], \quad (36)$$

with ρ_{ens} yielded by states $\{\psi_I\}_{I=1}^m$ by the relation (11) and weights $\{\omega_I\}_{I=1}^m$, the GOK variational principle implies in a straightforward manner that a full minimization of the functional (36) under the orthonormality constraint for states leads to obtaining the exact energy of the ensemble

$$\begin{aligned} \min_{\{\psi_I\}} \quad & E_{m,\omega}[\{\psi_I\}] = E_{m,\omega}[\{\Psi_I^{\text{LR}}\}] = \sum_{I=1}^m \omega_I E_I^{(0)} \\ \forall_{ij} \quad & \langle \psi_i | \psi_j \rangle = \delta_{ij} \end{aligned} \quad (37)$$

and the exact ensemble density of a fully interacting system

$$\rho_{\text{ens}}^{(0)}(\mathbf{r}) = \sum_{I=1}^m \omega_I \langle \Psi_I^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_I^{(0)} \rangle = \sum_{I=1}^m \omega_I \langle \Psi_I^{\text{LR}} | \hat{\rho}(\mathbf{r}) | \Psi_I^{\text{LR}} \rangle. \quad (38)$$

$\{\Psi_I^{\text{LR}}\}_{I=1}^m$ are the first m eigenfunctions of the equation with a partially interacting Hamiltonian, i.e.,

$$\left(\hat{T} + \hat{V}_{\text{ee}}^{\text{LR},\mu} + \hat{V}_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}] + \hat{V} \right) \Psi_I^{\text{LR}} = E_I^{\text{LR}} \Psi_I^{\text{LR}} \quad (39)$$

sharing an external potential \hat{V} with the fully interacting Hamiltonian $\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}$ the eigenfunctions and eigenvalues of which are $\{\Psi_I^{(0)}\}$ and $\{E_I^{(0)}\}$, respectively. The short-range local potential $V_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}]$ present in Eq. (39) follows from taking a functional derivative of $E_{m,\omega}^{\text{SR},\mu}$ with respect to the density. Clearly, while a density of a partially interacting system coincides with the fully interacting density, cf. Eq. (38), the ensemble energies of the two systems are different. Thus Eq. (37) implies $\sum_{I=1}^m \omega_I E_I^{\text{LR}} \neq E_{m,\omega}[\{\Psi_I^{\text{LR}}\}]$.

Note that a formal definition of the short-range ensemble functional provided by Eq. (33) does not provide much insight on how to construct approximations. Interestingly, Franck and Fromager³⁵ derived an expression for $E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}]$ within a generalized adiabatic connection formalism for ensembles (GACE) and it may serve as a better starting point for finding rigorous conditions satisfied by the short-range functional and developing approximations to it. As it has been mentioned in Section 4.1, in GACE both a coupling constant and weights are varied along the adiabatic connection. In a range-dependent GACE, a range-separation parameter ν takes the coupling constant role c.f. λ in Eqs. (25)–(27). By considering a partially interacting system described by the equation

$$\left(\hat{T} + \hat{V}_{\text{ee}}^{\text{LR},\nu} + \hat{V}^{\nu,\xi} \right) \Psi_I^{\nu,\xi} = \mathcal{E}_I^{\nu,\xi} \Psi_I^{\nu,\xi}, \quad (40)$$

with the external potential $\hat{V}^{\nu,\xi}$ being such that Eq. (26) is satisfied (if λ is replaced with ν) Franck and Fromager obtained the following expression for the short-range XC ensemble functional for a two-state ($m=2$) ensemble

$$E_{2,\omega}^{\text{SR-XC},\mu}[\rho_{\text{ens}}] = E^{\text{SR-XC},\mu}[\rho_{\text{ens}}] + \int_0^\omega d\xi \left[\left(\mathcal{E}_2^{\nu=\infty,\xi} - \mathcal{E}_1^{\nu=\infty,\xi} \right) - \left(\mathcal{E}_2^{\nu=\mu,\xi} - \mathcal{E}_1^{\nu=\mu,\xi} \right) \right], \quad (41)$$

where $E^{\text{SR-XC},\mu}[\rho_{\text{ens}}]$ is simply a ground state short-range XC functional. It is therefore evident from Eq. (41) that the error one introduces by neglecting the ω dependence of the ensemble functional and using a ground state functional instead amounts to neglecting differences between excitation energies of the fully interacting system ($\nu = \infty$) and the partially interacting one ($\nu = \mu$).

4.3 Multiconfiguration Methods Based on Range-Separated Ensemble DFT

The range-separated ensemble DFT has only been introduced as a means to construct a multiconfiguration method and is not generally expected—using the currently available XC approximations—to be able to capture bond-breaking and double excitations. If, however, one allows for the multiconfiguration wavefunctions in the ensemble, one can correctly reproduce whole dissociation curves of molecules.⁴² Explicitly, if the wavefunctions are expressed as linear combinations of the Slater determinants $\{\Phi_I^{\text{eHF}}\}$ built of optimal orbitals obtained from ensemble HF, then the ensemble energy functional takes the form

$$E_{m,\omega}[\mathbb{C}] = \sum_{I=1}^m \omega_I \sum_{JK} C_{IJ} C_{IK} \left\langle \Phi_J^{\text{eHF}} | \hat{T} + \hat{V}_{\text{ee}}^{\text{LR},\mu} + \hat{V} | \Phi_K^{\text{eHF}} \right\rangle + E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}]. \quad (42)$$

Minimization of the functional (42) with respect to C_{IJ} coefficients on condition that \mathbb{C} is unitary (in fact, \mathbb{C} is orthogonal, as we chose C_{IJ} to be real numbers) is equivalent to a diagonalization of the effective Hamiltonian, defined as

$$H'_{JK} = \left\langle \Phi_J^{\text{eHF}} | \hat{T} + \hat{V}_{\text{ee}}^{\text{LR},\mu} + \hat{V}_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}] + \hat{V} | \Phi_K^{\text{eHF}} \right\rangle, \quad (43)$$

where

$$\hat{V}_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}] = \sum_{i=1}^N \frac{\delta E_{m,\omega}^{\text{SR},\mu}[\rho_{\text{ens}}]}{\delta \rho_{\text{ens}}(\mathbf{r}_i)} \quad (44)$$

is the short-range potential. Hence, this gives a method very similar to the above Ens-WF method (cf. Section 2) and therefore we will denote it as Ens-lrWF+srDF.

Of course, one still needs to choose the short-range density functional describing the ensemble. Here, the chosen general form is

$$E_{m,\omega}^{SR,\mu}[\rho_{\text{ens}}] = \frac{1}{2} \iint \rho_{\text{ens}}(\mathbf{r}_1) \rho_{\text{ens}}(\mathbf{r}_2) \frac{\text{erfc}(\mu r_{12})}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E^{SR-XC,\mu}[\rho_{\text{ens}}], \quad (45)$$

where the functional is split into the short-range Hartree interaction and the XC part of the functional chosen to be a ground state functional. Since there are no XC functionals available designed specifically for ensembles, the short-range PBE functional^{56,57} was used in Ref. 42 and the following numerical examples. Although most states described have an open-shell character, a non-spin-polarized version of the functional was used. Hence, spin polarization is only introduced through the wavefunction part of the method.

Another problem in this method is that it is not clear how to calculate the energies of specific states. Identifying the states with the resulting wavefunctions is only justified in the $\mu \rightarrow \infty$ limit (which corresponds to the Ens-WF method). Nevertheless, calculating the energies as the expectation values of the (effective) Hamiltonian w.r.t. its eigenvectors seems to produce the best results. A result of such an approach is shown in Fig. 3 presenting the dissociation curves of the three lowest Σ states of BH molecule. When compared to Ens-WF and CI curves, definite improvement is visible—as expected, the method produces lower absolute energies than the purely wavefunction approaches but it does not significantly change the shapes of the curves. It still seems that a significant part of the correlation energy is missing.

Calculating the expectation value of the effective Hamiltonian w.r.t. to its eigenvectors is not the only possible way of calculating the energies. For example, Rebolini et al.⁹ suggested taking the differences of the eigenvalues of the effective Hamiltonian, Eq. (43),

$$\Delta E_I = E_I^{\text{LR},\mu} - E_0^{\text{LR},\mu} \quad (46)$$

as a rather crude approximations for excitation energies. In Ref. 9, this possibility has been explored for various systems along the adiabatic connection, with the exact (obtained from a full configuration interaction calculation) ground-state density used in $V^{\text{SR},\mu}$. We, on the other hand, did not perform a full CI calculation in the limit but used CI in the space built of the states included in the ensemble and compared ground-state (see Fig. 4) calculation with an equiensemble ($\beta=0$) one (Fig. 5) and an ensemble one, where the ground state is dominant—Fig. 6. The errors from the ground-state calculation are very large, up to 4.5 eV. If a full CI calculation was performed, the

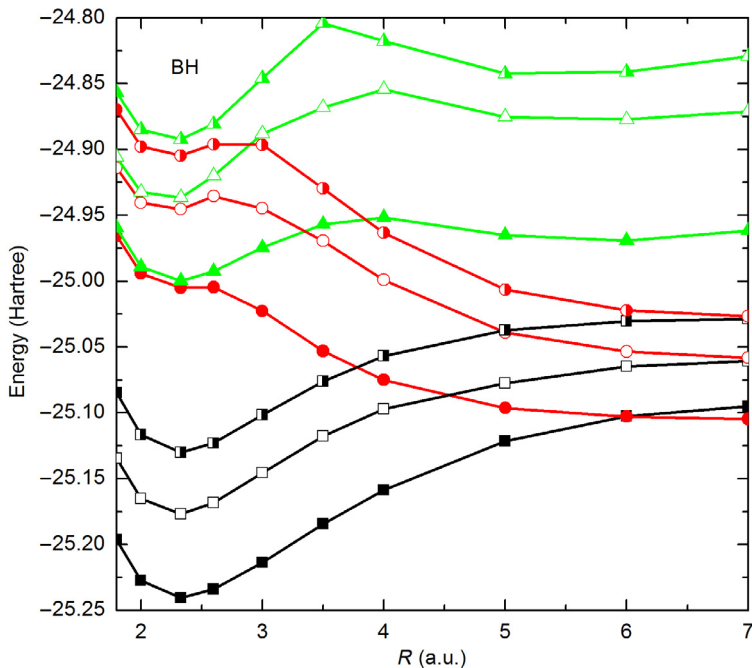


Figure 3 Dissociation curves of the first 3 Σ states of BH Ens-IrWF+srDF ($\beta=1$, $\mu=2$) versus Ens-WF ($\beta=1.0$) compared to CCSD results. Full markers, LR-CCSD; half-filled, Ens-WF; empty, Ens-IrWF+srDF. Squares, $1^1\Sigma^+$ state; circles, $1^3\Sigma^+$; triangles, $2^1\Sigma^+$.

excitation energies would be close to exact for large (10–15 a.u.) values of μ . Because of the small ensemble (i.e., also the configuration space), for large μ , e.g., the excitation energies of Π states are too high in the dissociation limit. Still, for the ground-state calculation for most excitations the CI limit of the method is optimal due to the fact that CI correctly separates the triplet and singlet states. On the other hand, both for the equiensemble case (see Fig. 5) and the $\beta=0.5$ (see Fig. 6) one, the errors for small and medium μ are much smaller than for the ground-state calculation. The optimal value of the range parameter μ both for $\beta=0.5$ and the equiensemble is $\mu=1$, while the optimum for the dissociation limit is shifted toward DFT— $\mu=0.2$ and $\mu=0.3$, respectively. While Rebolini’s approach (i.e., Eq. (46)) of obtaining the excitation energies does not seem suitable for Ens-IrWF+srDF method, it is encouraging that the quality of the excitation energies obtained from ensemble calculations is better than those arising from a ground-state one.

More examples of Ens-IrWF+srDF calculations can be found in Ref. 42 but it is clear that while the method includes the description of both static

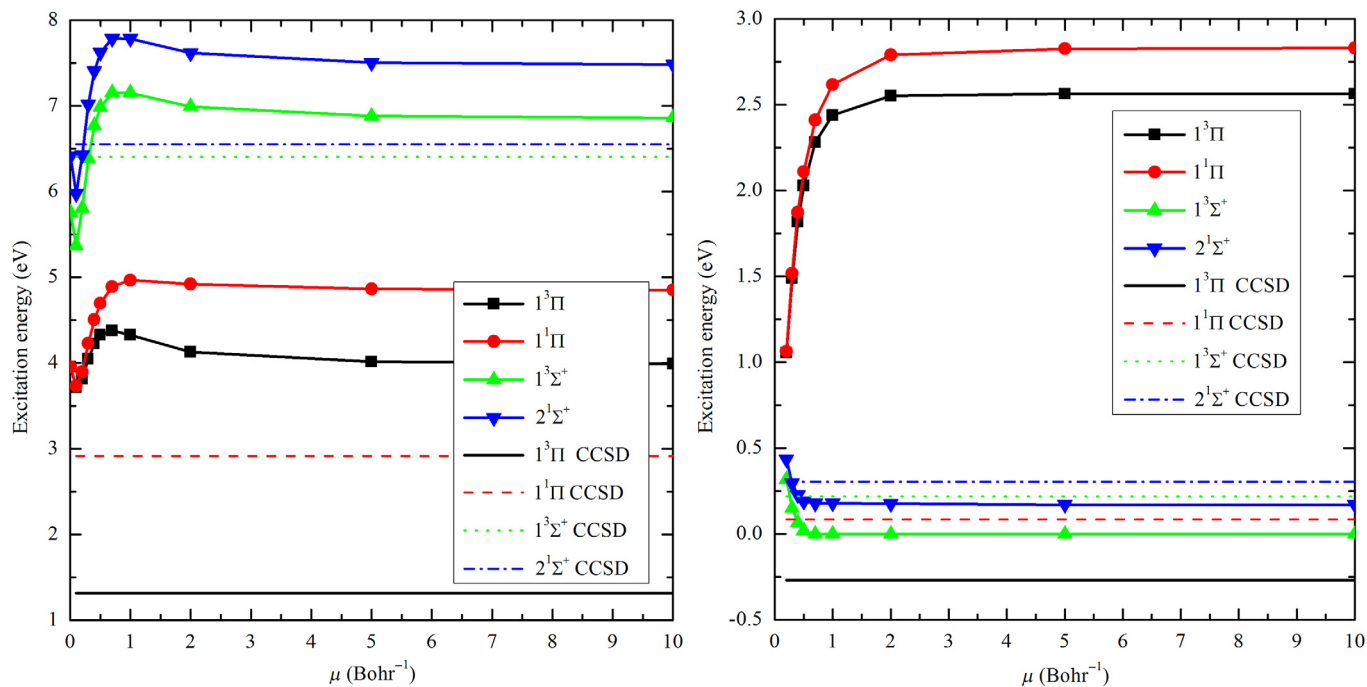


Figure 4 BH ($R_{BH}=2.329$ a.u.—left fig. $R_{BH}=7.0$ a.u.—right fig.) excitation energies along the μ parameter. Ground state (En-IrWF+srDF with $\beta \rightarrow \infty$) calculation versus LR-CCSD benchmark.

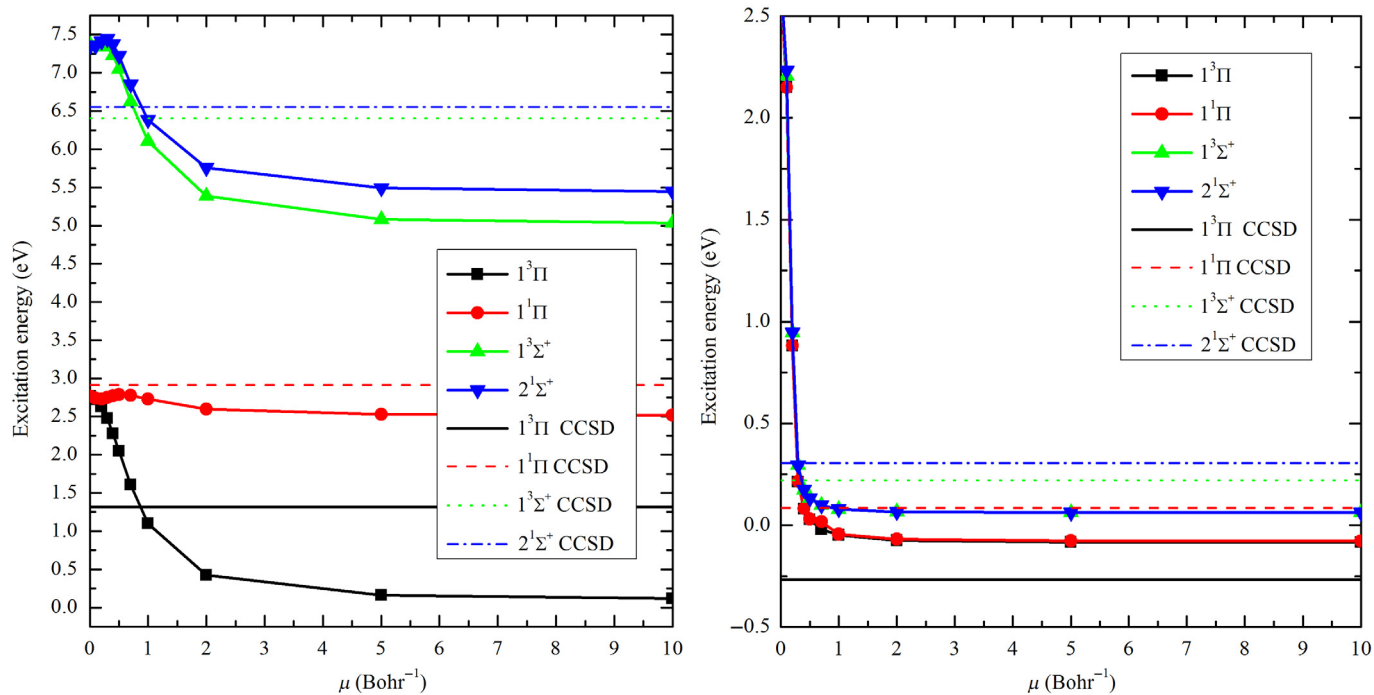


Figure 5 BH ($R_{BH}=2.329$ a.u.—left fig. $R_{BH}=7.0$ a.u.—right fig.) excitation energies along the μ parameter. Equiensemble ($\beta=0$) Ens-IrWF+sRDF calculation versus LR-CCSD benchmark.

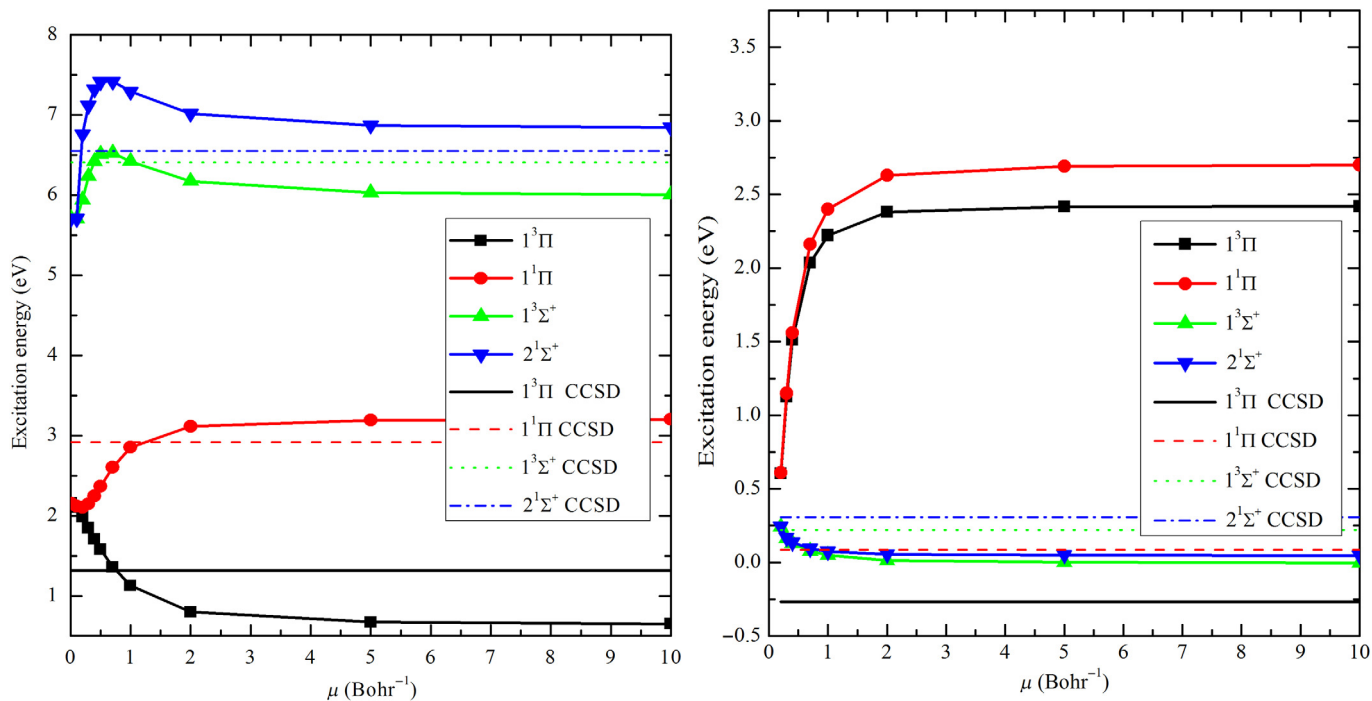


Figure 6 BH ($R_{BH} = 2.329$ a.u.—left fig. $R_{BH} = 7.0$ a.u.—right fig.) excitation energies along the μ parameter. Ens-IrWF+srDF ($\beta = 0.5$) calculation versus LR-CCSD benchmark.

and dynamic correlation at modest cost, it suffers from some serious problems. One of the sources of errors is the previously mentioned issue of describing open-shell states with a density functional without spin polarization. Another is the problem of “ghost interaction”, specific to ensemble DFT. To deal with those problems, a different density functional must be employed.

The solution of the first problem is fairly simple—one can just use a spin-polarized short-range functional. This would of course destroy the initial simplicity of the method—with the spin densities instead of the total ensemble density one cannot calculate a common short-range potential and it is impossible to construct an effective Hamiltonian which could then be diagonalized. To minimize the ensemble energy with respect to the expansion coefficients, one needs to use some direct minimization algorithm which is both more costly and more cumbersome.

The problem of the ghost interaction can be solved in a similar manner. As previously mentioned (see [Section 1](#)), best results seem to be obtained when the density functional is made ghost-interaction-free by construction.^{38,39,58} This leads to the following expression for the ensemble energy

$$E_{m,\omega}[\mathbb{C}] = \sum_{I=1}^m \omega_I \left\{ \sum_{JK} C_{IJ} C_{IK} \langle \Phi_J | \hat{H}^{\text{LR}} | \Phi_K \rangle + E_{m,\omega}^{\text{SR-HXC}} [\rho_I^\alpha, \rho_I^\beta] \right\}. \quad (47)$$

where \hat{H}^{LR} , the long-range Hamiltonian, consists of the one-electron operator and the long-range part of the two-electron interaction and $\rho_I^\alpha, \rho_I^\beta$ are the state spin densities. The possibility of building such a method will be explored in more detail in future work but the result of a test calculation for the hydrogen molecule, involving minimization of the expression (47) with respect to the expansion coefficients and the orbitals is presented in [Table 1](#) along with results calculated by other ensemble methods and a standard TD-DFT calculation. The new method, labeled here MCEdFT, produces more accurate excitation energies (ΔE) than TD-DFT, SA-REKS, and Ens-WF methods but slightly worse than Ens-lrWF+srDF, which can be explained by the introduction of some spin contamination during the optimization of the expansion coefficients. Results for the equilibrium geometry of the hydrogen molecule are not presented because of the lack of data for SA-REKS but also because all the methods are expected to perform well for that case. It has to be emphasized, however, that in MCEdFT a spin adaptation scheme is needed to improve quality of the results.

Table 1 Energies of the First Two Singlet States of H₂ Molecule and the Difference Between them (ΔE_{exc}) in Hartree, Obtained with Different Methods for Two Separations of Hydrogen Nuclei

	<i>R</i> (a.u.)	Ens-					Exact ^c
		WF ^a	IrWF+srDF ^a	SA-REKS ^b	MCeDFT ^a	TD-DFT ^b	
1 ¹ Σ _g ⁺	3	−1.0327	−1.0343	−1.0522	−1.0584	−1.0532	−1.0573
	7	−0.9798	−0.7212	−0.9994	−1.0188	−0.9197	−1.0002
1 ¹ Σ _u ⁺	3	−0.5631	−0.9686	−0.8329	−0.6841	−0.7891	−0.7525
	7	−0.5681	−0.6229	−0.8210	−0.5969	−0.8461	−0.6772
Δ <i>E</i>	3	0.4696	0.3131	0.2193	0.3743	0.2640	0.3048
	7	0.4018	0.3457	0.1784	0.4219	0.0736	0.3230

^aAug-cc-pVDZ basis set,

^bData from Ref. 49,

^cData from Refs. 59,60



5. SUMMARY AND OUTLOOK

Despite being somewhat older than the—currently most popular method for the excited states calculations—time-dependent density functional theory, the ensemble methods for the excited states are still in their infancy.

This group of methods is founded upon the ensemble variational (minimum) principle, which states that a weighted sum of m expectation values of the Hamiltonian of the system is greater or equal than the sum of m lowest eigenvalues of this Hamiltonian, provided that the expectation values are taken with respect to mutually orthogonal trial functions and weights in the sum form a nongrowing sequence with respect to the eigenvalues. This simple inequality is essential in the proof of a HK-type theorem for ensembles that maps the ensemble electron density to an external potential. The ensemble density functional theory established on the basis of the HK theorem is the most promising ensemble method, as it shares DFT's favorable scaling with the size of the system and is potentially able to describe electron correlation.

While ensemble DFT does not share some of TD-DFT's shortcomings caused by, e.g., the use of adiabatic approximations, it has a number of its own challenges and problems. Among them, lack of suitable HXC ensemble functional approximations is the gravest obstacle. Over the years, a number

of exact conditions and some clues pointing toward such approximations have been formulated but still most of the available expressions are only slightly modified versions of the ground-state functionals. In addition, imposing the orthogonality condition on the wavefunctions is a challenge in practical calculations and the task of extracting the state energies from the result of an ensemble calculation has no apparent solution.

All these problems inhibited the development and exploration of ensemble methods to theoretical considerations and calculations on small systems which made it difficult to evaluate their true potential. On the other hand, the experience of the ground-state DFT development suggests that even when good XC functional approximations are available, modeling multi-configuration effects—which is the key motivation to developing time-independent DFT for excited states—is not necessarily an easy task when using a single-reference wavefunction. One can expect similar problems when dealing with the excited states.

Through adapting the ground state DFT's solution to this problem, two types of multiconfiguration approaches to ensemble DFT have been developed. One, based on spin-restricted ensemble-referenced KS methods designed originally for strongly correlated systems, is indeed able to reproduce conical intersections of fairly large systems but is restricted to calculation of the first excited singlet state energy and contains a substantial portion of empiricism. The other path is a range-separated method combining an ensemble wavefunction configuration-interaction-like method and an ensemble density functional. It is able to reproduce dissociation curves of diatomic molecules but it also slightly overestimates the absolute energies (especially of the ground state) and requires some preliminary knowledge about the system. Currently, work is in progress to use ghost-interaction-free, spin-polarized density functionals in the multiconfiguration methods.

Summing up, ensemble DFT, in particular its multiconfiguration realizations have the potential to become an alternative to TD-DFT, especially for systems where multiconfiguration effects come into play. None of the existing approaches, however, has a “black-box” character, nor it is able to treat a wide class of systems with uniform accuracy, or is computationally efficient in its current implementation. These are obstacles that can be overcome in the future by formulating conditions regulating the size of the ensemble, the weights, using more suitable density functional approximations and formulating more efficient and fully self-consistent implementations. Until then, TD-DFT will most likely continue to dominate the density functional approach to the world of excited state calculations.

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