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Calculation of electronic excited states of molecules using the Helmholtz free-energy minimum principle

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We show that the Helmholtz free-energy variational principle is the physical principle underlying the ensemble variational theory formulated in seminal papers by Theophilou and by Gross, Oliveira, and Kohn. A method of calculating electronic excitations of atoms and molecules is then proposed, based on the constrained minimization of the free energy. It involves the search for the optimal set of Slater determinant states to describe low electronic excitations and, in a second step, the search for optimal rotations in the space spanned by these states. Boltzmann factors are used as weights of states in the ensemble since for these the free energy achieves a minimum. The proposed method is applied to the Be atom and LiH and BH molecules. The method captures static electron correlation but naturally lacks dynamic correlation. To account for the latter, we describe short-range electron-electron interaction with a density functional, while the long-range part is still expressed by a wave-function method. Using the example of the LiH molecule, we find that the resulting method is able to capture both static and dynamic electron correlations.

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I. INTRODUCTION

Predicting the electronic structure of the molecules is one of the most important contributions of quantum chemistry to other disciplines of science, e.g., spectroscopy, molecular physics, or biochemistry. The calculation of electronic excitations is of particular interest for scientists studying molecular systems, especially those designing new materials. While in recent years a significant progress has been made in this area, the existing methods of calculating excitation energies of molecules are often not sufficiently accurate or too expensive to apply to a system of interest.

Although *ab initio* methods such as complete-active-space second-order perturbation theory (CASPT2) or methods based on coupled cluster theory allow one to make accurate predictions for excitation energies of molecules, they are still prohibitively expensive computationally. Other routinely used methods are based on the time-dependent density functional theory (TDDFT). They have become the method of choice for predicting excitation energies of different systems mainly due to their relatively low computational cost and reasonable accuracy for some excitations. Most TDDFT methods rely on the adiabatic approximation and consequently they usually fail in describing states of multiconfigurational character. Also, the problematic behavior of charge-transfer and Rydberg states can be traced back to the wrong asymptotics of the approximate local potential underlying the method. A few remedies have been proposed to cure some of the problems of approximations to TDDFT but, in general, their accuracy still lags behind *ab initio* methods.

The above problems signal a need for different methods of calculation. This brings in the spotlight Theophilou's variational principle [1] and the more general Gross-Oliveira-Kohn (GOK) variational principle [2], which was in fact derived first by Theophilou [3]. Theophilou's variational principle states that if $\psi_1, \psi_2, \ldots, \psi_m$ are m orthonormal trial N-electron states and if $E_1^{(0)}, E_2^{(0)}, \ldots, E_m^{(0)}$ are in increasing order the m lowest eigenvalues of the N-electron Hamiltonian $\hat{H}$, then the following inequality holds:

$$\sum_{i=1}^{m} \langle \psi_i | \hat{H} | \psi_i \rangle \geqslant \sum_{i=1}^{m} E_i^{(0)}. \tag{1}$$

The GOK principle is more flexible and specifies that for the m real, positive weights $\omega_i \geqslant 0$ in decreasing order,

$$\omega_1 \geqslant \omega_2 \geqslant \cdots \geqslant \omega_m > 0,$$

it holds

$$\sum_{i=1}^{m} \omega_i \langle \psi_i | \hat{H} | \psi_i \rangle \geqslant \sum_{i=1}^{m} \omega_i E_i^{(0)}. \tag{2}$$

Both Theophilou's and the GOK variational principles have led to several formulations of the ensemble Hartree-Fock (HF) method.

In the case of equal weights (Theophilou's variational principle), the ensemble energy functional $\mathcal{E} = \sum_{i=1}^{m} \langle \psi_i | \hat{H} | \psi_i \rangle$ reduces to the trace of the Hamiltonian in the m-dimensional space spanned by the orthonormal basis $\{\psi_i\}$. Since the trace is invariant under rotation of the basis vectors and depends only on the m-dimensional space, Theophilou named the approach based on his theorem the subspace method, i.e., the subspace Hartree-Fock [4] as well as the subspace DFT [1,5,6]. The GOK variational principle with the flexibility of different weights (for nondegenerate states) affords not only the energies of the first m states, but also of the wave functions themselves. The GOK principle provided a basis

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for the ensemble DFT method [7,8] and its variants which employ the optimized effective potential (exchange only) [9–11]. Despite the substantial theoretical investigations of the ensemble variational theories, the practical implementations of the method have been rather scarce and limited to the calculation of excitation energies of atoms and small molecules at equilibrium geometries [12–16].

Although the results were quite promising, the implementation difficulties prevented those methods from being developed further. One of the problems is the enforcement of the orthogonality for the wave functions, but it is also clear that the ensemble HF or ensemble DFT methods inherit the disadvantages of the corresponding ground-state methods. These include the lack of correlation energy in Hartree-Fock and single-reference character of Kohn-Sham DFT that results in the wrong description of long-range electron-electron interactions. In addition, a serious problem is the absence of appropriate density functionals developed especially for ensembles. The existing density functionals, often heavily parametrized, were developed to accurately describe the ground states of systems and while they often do that successfully, they may behave erratically when dealing with a whole ensemble.

The GOK principle allows treating all (or a chosen number of lowest) excited states of a system as one supersystem containing molecules (or atoms) in all states included in the ensemble. The weights in such interpretation are the occupation numbers of each of those states. The description of such a system resembles the methods of describing electronic structure in finite temperature: the thermal Hartree-Fock [17], thermal single-determinant approximation [18], and finite-temperature DFT [19–21] that make use of the variational principle for the Helmholtz free energy known in statistical mechanics.

In this paper, we show the relation between the ensemble variational method and the variational principle for the free energy of canonical ensemble derived from statistical mechanics (Sec. II). This allows us to employ Boltzmann factors as weights in the ensemble variational method we propose (Sec. III). The method aims to describe efficiently both dynamic and static electronic correlations. The latter type of correlation is captured by going beyond a one-determinantal approximation and considering a space of configurations of highest importance for the description of the considered states. In order to include the missing part of the dynamic correlation, we exploit the idea of Savin *et al.* who proposed to describe the short-range electron-electron interaction by an appropriate density functional while having the long-range component of the interaction to enter the effective Hamiltonian [22–24]. Consequently, the ground-state energy emerges as the lowest eigenvalue of the effective Hamiltonian that includes the long-range electron interaction operator and the short-range local potential. Over the years, a number of methods exploiting the idea of range separation have been proposed that involve an effective wave function or a one-electron reduced density matrix description of the ground state [25–30]. Recently, the ground-state range-separated functionals have been employed in the time-dependent linear response framework to predict excitation energies of molecules [31,32]. We extend the idea of range separation to describe an energy of an ensemble and propose a practical algorithm that yields energies of states present in the ensemble. In Sec. IV, we show some illustrative results that confirm the usefulness of the approaches we introduce. The paper is summarized and concluded in Sec. V.

II. ENSEMBLE VARIATIONAL THEORY: FORMULATION FROM THE STATISTICAL MECHANICS PERSPECTIVE

In this section, we shall formulate the ensemble variational theory by minimizing the Helmholtz free energy for a canonical ensemble. For this purpose, let us first write the Helmholtz free energy for an N-electron system described with the Hamiltonian $\hat{H}$:

$$A[\hat{\Gamma}^N] = \mathrm{Tr}\hat{\Gamma}^N(\beta^{-1}\ln\hat{\Gamma}^N + \hat{H}). \tag{3}$$

As is well known [17], the free energy is minimized by the density matrix $\hat{\Gamma}^N_{eq} = \exp[-\beta\hat{H}]/\mathrm{Tr}\exp[-\beta\hat{H}]$ which can be written explicitly as a mixture of the eigenstates of the Hamiltonian weighted with Boltzmann weights, i.e.,

$$\hat{\Gamma}^N_{eq} = \sum_i \omega_i^{(0)}\big|\Psi_i^{(0)}\big\rangle\big\langle\Psi_i^{(0)}\big|, \tag{4}$$

where

$$\omega_i^{(0)} = \frac{\exp\left[-\beta E_i^{(0)}\right]}{\sum_k \exp\left[-\beta E_k^{(0)}\right]}. \tag{5}$$

In practice, we cannot deal numerically with a density matrix representing an ensemble of an infinite number of states. In the following, the minimization of the free energy will be restricted to cover N-electron density matrices representing ensembles of a finite number (m) of states, namely,

$$\hat{\Gamma}^N_m = \sum_{i=1}^m \omega_i|\psi_i\rangle\langle\psi_i|, \tag{6}$$

where

$$\sum_{i=1}^m \omega_i = 1. \tag{7}$$

When we restrict to the subset of such density matrices, the Helmholtz free-energy functional becomes a functional of the (orthonormal) states $\{\psi_i\}_{i=1,\ldots,m}$ and a function of m weights $\{\omega_i\}_{i=1,\ldots,m}$, normalized to 1. We find it convenient to denote this functional by A_m:

$$A_m[\hat{\Gamma}^N_m] = \sum_{i=1}^m \omega_i\left(\frac{1}{\beta}\ln\omega_i + \langle\psi_i|\hat{H}|\psi_i\rangle\right). \tag{8}$$

Since it is derived from the Helmholtz free energy, the two terms in the functional A_m afford a clear physical interpretation. The first one represents the negative entropy S,

$$S = -\sum_{i=1}^m \omega_i\ln\omega_i; \tag{9}$$

the other term is the average energy of an ensemble

$$E = \sum_{i=1}^m \omega_i\langle\psi_i|\hat{H}|\psi_i\rangle. \tag{10}$$

Minimization of the functional A_m is equivalent to the minimization of the free-energy functional (3) with respect to a subset of $\hat\Gamma^N$ comprising density matrices of m nonzero weights. In other words, only the set of density matrices $\hat\Gamma_m^N$ defined in Eq. (6) is searched. The variational equations for the functional A_m that take into account the normalization condition for the weights and the orthonormalization of the wave functions read as

$$\frac{\partial\{A_m[\{\omega_j\},\{\psi_j\}] - \alpha\sum_{j=1}^m \omega_j\}}{\partial\omega_j} = 0, \tag{11}$$

$$\frac{\delta\{A_m[\{\omega_j\},\{\psi_j\}] - \sum_{jk}^m \lambda_{jk}\langle\psi_j|\psi_k\rangle\}}{\delta\psi_j^*} = 0 \tag{12}$$

[and equations analogous to (12) with derivatives taken with respect to ψ_i], where α and $\{\lambda_{ij}\}$ are pertinent Lagrange multipliers. Solutions to Eqs. (11) are easily found and they read as

$$\bar\omega_i = \frac{\exp[-\beta\langle\psi_i|\hat H|\psi_i\rangle]}{\sum_{j=1}^m \exp[-\beta\langle\psi_j|\hat H|\psi_j\rangle]}. \tag{13}$$

For fixed wave functions, the functional A_m achieves a minimum for the optimal weights $\{\bar\omega_i\}$, i.e.,

$$A_m[\{\omega_i\},\{\psi_i\}] \geqslant A_m[\{\bar\omega_i\},\{\psi_i\}], \tag{14}$$

which is immediately seen upon employing Gibbs inequality that in the considered case takes the form $\sum_{i=1}^m \omega_i \ln[\omega_i/\bar\omega_i] \geqslant 0$.

After performing the functional differentiation, the variational equations shown in Eq. (12) yield

$$\omega_i \hat H\psi_i - \sum_{j=1}^m \lambda_{ij}\psi_j = 0. \tag{15}$$

Depending on the relations between the weights, solutions to Eq. (15) take the form of either eigenfunctions of the Hamiltonian $\{\Psi_i^0\}$ or their linear combinations. In particular, if all weights are equal, one obtains

$$\forall_{i=1,\dots,m}\quad \psi_i = \sum_{j=1}^m C_{ij}\Psi_j^{(0)}, \tag{16}$$

where the matrix $\mathbf{C}$ is unitary and the functions ψ_i are expanded in an m-dimensional space spanned by m arbitrary eigenfunctions. In the case of all weights being different, Eq. (15) is satisfied by the eigenfunctions $\Psi_i^{(0)}$ [notice that in this case linear combinations of $\Psi_i^{(0)}$ do not satisfy Eq. (15) since the matrix of Lagrange multipliers λ would not be Hermitian]. Finally, in the intermediate case, $\omega_1 = \cdots = \omega_n$ and $\forall_{\substack{i>n\\ j\neq i}}\ \omega_i \neq \omega_j$ (this may be generalized to more than one blocks of equal weights)

$$\forall_{i\leqslant n}\quad \psi_i = \sum_{j=1}^n C_{ij}\Psi_j^{(0)}, \tag{17}$$

$$\forall_{i>n}\quad \psi_i = \Psi_i^{(0)}, \tag{18}$$

where the sets $\{\Psi_i^{(0)}\}_{i=1,\dots,n}$ and $\{\Psi_i^{(0)}\}_{i=n+1,\dots,m}$ are disjoint and they include, respectively, n and $m-n$ arbitrarily chosen eigenfunctions. Clearly then for the fixed weights the considered functional A_m possesses in general infinitely many extremum points regardless of the weights. The minimum of A_m [and at the same time of the energy E given in Eq. (10)] is achieved for the extremum point determined by the m eigenfunctions corresponding to the m lowest eigenvalues of $\hat H$. This can be seen immediately since for an arbitrary extremum point given by Eqs. (17) and (18) after exploiting the unitarity of $\mathbf{C}$ the energy reads as

$$E = \sum_{i=1}^m \omega_i E_i^{(0)}, \tag{19}$$

and it takes the lowest value if the set $\{E_i^{(0)}\}_{i=1,\dots,m}$ includes m lowest eigenvalues and additionally the following condition is satisfied:

$$\forall_{i,j}\ \ \omega_i \geqslant \omega_j \quad\Rightarrow\quad E_i^{(0)} \leqslant E_j^{(0)}. \tag{20}$$

Consequently, reordering if necessary the weights in decreasing order $\omega_1 \geqslant \omega_2 \geqslant \cdots \geqslant \omega_m \geqslant 0$, one writes

$$A_m[\{\omega_i\},\{\psi_i\}] \geqslant A_m\big[\{\omega_i\},\{\Psi_i^{(0)}\}\big], \tag{21}$$

where the eigenstates correspond to the first m values of the energies and the ordering of $\Psi_i^{(0)}$ corresponds to the increasing ordering of $E_i^{(0)}$.

Taking into account relations (14) and (21), one writes

$$\begin{aligned} A_m[\{\omega_i\},\{\psi_i\}] &\geqslant A_m[\{\bar\omega_i\},\{\psi_i\}] \geqslant A_m\big[\{\bar\omega_i\},\{\Psi_i^{(0)}\}\big] \\ &\geqslant A_m\big[\{\omega_i^{(0)}\},\{\Psi_i^{(0)}\}\big], \end{aligned} \tag{22}$$

where the weights $\{\omega_i\}$ are normalized to 1 but otherwise they are arbitrary, $\bar\omega_i$ are obtained according to Eq. (13) using the orthonormal wave functions ψ_i, the set of states $\{\Psi_i^{(0)}\}_{i=1,\dots,m}$ is a set of eigenstates corresponding to the first m eigenvalues $E_i^{(0)}$, and the weights $\omega_i^{(0)}$ are given in Eq. (5). One should notice that the chain of relations shown in (22) is valid if the weights $\{\bar\omega_i\}$ are in a decreasing order. It follows that for $m\to\infty$ the functional $A_m[\{\omega_i\},\{\psi_i\}]$ achieves the minimum for the density matrix given in Eq. (4).

In (21) and in the second inequality in (22), the entropic parts of $A_m[\{\omega_i\},\{\psi_i\}]$ and $A_m[\{\omega_i\},\{\Psi_i^0\}]$ coincide and can be dropped. The inequalities then reduce to the GOK inequality [2] (with weights ω_i or $\bar\omega_i$)

$$\sum_{i=1}^m \omega_i\langle\psi_i|\hat H|\psi_i\rangle \geqslant \sum_{i=1}^m \omega_i E_i^{(0)}. \tag{23}$$

We conclude that the underlying variational principle is the statistical mechanics variational principle for the Helmholtz free energy. When we restrict the density matrix in the free-energy expression to belong to a subset of density matrices representing ensembles with fixed weights, we recover the GOK variational principle. In the limit of equal weights, we then recover Theophilou's variational principle. The opposite limit where all the weights vanish, except the first one, leads to the Rayleigh-Ritz variational principle for the ground state. For fixed weights $\bar\omega_i$ given by (13), Theophilou's result is obtained in the high-temperature limit $\beta\to 0$, while the ground-state Rayleigh-Ritz variational principle is obtained at low temperatures $\beta\to\infty$.

We have shown that minimization of the functional $A_m[\hat\Gamma_m^N]$ defined in Eq. (8) leads to obtaining m lowest energies of the system and the corresponding wave functions. Clearly, the same is achieved if one exploits the variational principle given in (23). Upon full minimization, the trial function ψ_1 corresponding to the lowest expectation value from the set $\{\langle\psi_i|\hat{H}|\psi_i\rangle\}_{i=1,\dots,m}$ and thus to the highest weight $\bar{\omega}_1$ will turn into the ground-state wave function. On the other hand, ψ_2 corresponding to the second highest weight will become the wave function of the first excited state, etc. One should notice that in the case of a degenerate Hamiltonian, the functional A_m is invariant to rotations among degenerate states. Intuitively, it would be desirable if the degeneracy was also reflected in the equality of the weights pertinent to the degenerate states. This requirement is satisfied naturally with the choice of Boltzmann weights (on condition, of course, that the pertinent trial wave functions are degenerate). Overall, the usage of Boltzmann weights for the ensemble should, in principle, ensure that the ordering of the expectation values of the trial functions will be preserved after the optimization (so the numerical phenomenon such as root flipping that plagues for example the multiconfiguration self consistent field (MC-SCF) will not occur). Additionally, by choosing the temperature parameter β different from zero (as already explained above, setting $\beta = 0$ leads to all weights being equal), the high-lying states are effectively removed from the ensemble.

III. COMPUTATIONAL ALGORITHMS BASED ON THE ENSEMBLE VARIATIONAL PRINCIPLE

Our aim is to exploit the variational principle (23) written with Boltzmann weights (13) and to propose a method capable of capturing dynamic and static electron correlation effects that yields a few low-lying excited-state energies. Being interested in the m low-lying states of a given system, we consider a set of m Slater determinants $\{\Phi_I\}$, which are built from M orthonormal spin orbitals $\{\varphi_i(\mathbf{x})\}$. The choice of the most relevant determinants to describe the sought states is not unique. It may be based on the energy criterion or on chemical intuition. As discussed later, we have followed the latter route. In case of degeneracies, all configurations from a multiplet should be included in the ensemble. In the first step, the ensemble energy is optimized with respect to the spin orbitals at fixed weights given by Eq. (13). This will already capture part of the dynamic correlation energy. Since

$$\langle\Phi_I|\hat{H}|\Phi_I\rangle = \sum_{i=1}^{M} n_i^I h_{ii} + \frac{1}{2}\sum_{ij}^{M} n_i^I n_j^I \langle ij||ij\rangle, \tag{24}$$

where $\{\langle ij||ij\rangle\}$ are the antisymmetrized two-electron integrals in the representation of the spin orbitals $\{\varphi_i\}$, n_i^I is an occupation number of the ith orbital in the Ith configuration, i.e.,

$$n_i^I = \begin{cases} 1, & i \in I \\ 0, & i \notin I \end{cases} \tag{25}$$

the expression (10) for the energy of an ensemble being a mixture of one-determinantal states can be conveniently written as

$$E[\{\varphi_i\}] = \sum_{i=1}^{M} n_i h_{ii} + \frac{1}{2}\sum_{ij}^{M} G_{ij}\langle ij||ij\rangle, \tag{26}$$

where

$$n_i = \sum_{I=1}^{m} \bar{\omega}_I n_i^I, \tag{27}$$

$$G_{ij} = \sum_{I=1}^{m} \bar{\omega}_I n_i^I n_j^I \tag{28}$$

and the Boltzmann weights $\bar{\omega}_I$ are computed according to Eq. (13) with the trial functions $\{\Phi_I\}$. The energy given in Eq. (26) is minimized with respect to the spin orbitals for fixed values of the occupation numbers n_i (the weights are normalized to 1 and, consequently, $0 \leqslant n_i \leqslant 1$ and $\sum_{i=1}^{M} n_i = N$, therefore, the numbers n_i can be interpreted as the occupation numbers). It is worth noticing that the form of the functional (26) is equivalent to the recently proposed natural spin-orbital functionals that include only the Coulomb and exchange integrals [33–35]. One can therefore employ one of the algorithms (and codes) proposed to find optimal orthonormal spin orbitals for such functionals [36–38].

The aim of the optimization is to bring in some portion of the dynamic correlation to states of interest. The static correlation is introduced by forming linear combinations of determinants built of the optimal orbitals. Namely, the m states are given as

$$\psi_I = \sum_{J}^{m} C_{IJ}\Phi_J^{\text{opt}}, \tag{29}$$

where the configurations $\{\Phi_I^{\text{opt}}\}$ are of the same type as initially assumed ($\{\Phi_I\}$) but they are formed from the optimal spin orbitals obtained in the first step. The ensemble energy written for the m wave functions ψ_I takes the form

$$E[\mathbf{C}] = \sum_{I=1}^{m} \bar{\omega}_I \sum_{JK}^{m} C_{IJ}^* C_{IK} \langle\Phi_J^{\text{opt}}|\hat{H}|\Phi_K^{\text{opt}}\rangle. \tag{30}$$

Its minimization under the constraint that the wave functions ψ_I stay orthonormal leads to the following variational equations:

$$\bar{\omega}_I \sum_{K}^{m} \langle\Phi_J^{\text{opt}}|\hat{H}|\Phi_K^{\text{opt}}\rangle C_{IK} = \sum_{K}^{m} \Lambda_{IK} C_{KJ}, \tag{31}$$

where $\mathbf{\Lambda}$ is a Lagrangian. If all weights are different, Eq. (31) is solved by the matrix $\mathbf{C}^{(0)}$ that diagonalizes the Hamiltonian $H_{IJ} = \langle\Phi_I^{\text{opt}}|\hat{H}|\Phi_J^{\text{opt}}\rangle$, namely,

$$\mathbf{C}^{(0)}\mathbf{H}\mathbf{C}^{(0)^T} = \mathbf{\Lambda}\bar{\boldsymbol{\omega}}^{-1}, \tag{32}$$

where the matrices $\mathbf{\Lambda}$ and $\bar{\boldsymbol{\omega}}$ are diagonal and the latter collects weights on its diagonal. Consequently, the optimized states read as

$$\psi^{(0)} = \mathbf{C}^{(0)}\Phi^{\text{opt}} \tag{33}$$

and the approximations to the energies of the system follow simply as eigenvalues of the Hamiltonian. On the other hand, in the case of all weights being equal (equiensemble), the variational equation (31) is satisfied by any unitary matrix $\mathbf{C}$, which is a direct consequence of the fact that the functional (30) is invariant to orthogonal rotations among the states $\{\Phi_I^{\text{opt}}\}$. In other words, for equiensembles the diagonalization of the Hamiltonian present in Eq. (30) does not lead to lowering the energy of the ensemble but it can be still used to obtain better approximations for the energy levels of the system by taking expectation values of $\hat{H}$ with $\psi^{(0)}$. In this sense, the actual values of the weights do not play a role in this step of the algorithm.

The aforedescribed algorithm, called from now on Ens-WF (WF refers to wave functions), based on employing Boltzmann weights given in (13) and consisting in minimization of (26) followed by optimization of the functional (30) constitutes a straightforward implementation of the ensemble variational principle (23). Despite its simplicity and including some portion of the dynamic correlation by relaxing the orbitals, a large portion of electron correlation is likely to be missed. A possible improvement could be achieved by significantly expanding the space of the considered configurations Φ_I and including all possible determinants built of the assumed active spin orbitals. Such an approach would be similar to the state-averaged MC-SCF calculations [39]. Unfortunately, expanding the space of configurations leads to a rapid increase in the computational cost. We propose to employ density functionals in the ensemble formulation to add a missing part of the dynamic correlation to our approach. In order to achieve this goal, we follow the idea of Savin *et al.* [23,24] who introduced separation of the electron-electron interaction operator into the short- and long-range parts υ_{ee}^{SR} and υ_{ee}^{LR}, respectively, i.e.,

$$\frac{1}{r} = \upsilon_{ee}^{SR}(r) + \upsilon_{ee}^{LR}(r), \tag{34}$$

where $\lim_{r\to\infty} r\ \upsilon_{ee}^{LR}(r) = 1$ and $\lim_{r\to 0} r\ \upsilon_{ee}^{SR}(r) = 1$ and formulated a density-functional-based formalism within which the short-range part of the electronic repulsion is effectively taken into account by a proper density functional. A number of methods that exploit short-range density functionals have been proposed for the prediction of ground-state energies. These methods employ either a wave function [25–28] or a reduced density matrix [29,30] description for the long-range regime of the electronic repulsion.

In analogy to these methods, the idea of range separation of the operator $1/r$ can be also applied for the prediction of the energy of an ensemble and, consequently, for the prediction of excited-state energies. With this idea in mind, we propose a universal ensemble energy functional of the density

$$F_{m,\boldsymbol{\omega}}[\rho_{ens}] = \min_{\substack{\{\psi_i\}\to\rho_{ens}\\ \forall_{ij}\ \langle\psi_i|\psi_j\rangle=\delta_{ij}}} \sum_{i=1}^{m} \omega_i \langle\psi_i|\hat{T}+\hat{V}_{ee}|\psi_i\rangle, \tag{35}$$

defined for m states in the ensemble and for fixed ensemble weights $\{\omega_i\}_{i=1,\ldots,m}$ normalized to 1. The notation $\{\psi_i\}\to\rho_{ens}$ means that the ensemble yields a given density ρ_{ens}. Notice that the functional is defined for any ensemble N representable ρ_{ens}, i.e., any density for which there exists a set of m wave functions $\{\psi_i\}_{i=1,\ldots,m}$ with the corresponding densities $\{\rho_i\}_{i=1,\ldots,m}$ such that $\rho_{ens} = \sum_{i=1}^{m}\omega_i\rho_i$. Therefore, the domain of the functional embraces a larger class of densities than that of the Gross-Oliveira-Kohn universal functional [2] defined for ensemble υ-representable densities. The values of both functionals coincide at the density given by $\rho_{ens}^{\min} = \sum_{i=1}^{m}\omega_i\langle\Psi_i^{(0)}|\hat{\rho}(\mathbf{x})|\Psi_i^{(0)}\rangle$, where $\hat{\rho}(\mathbf{x})$ stands for the density operator, $\{\Psi_i^{(0)}\}$ are eigenfunctions of the Hamiltonian $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$ ($\hat{T}$ and $\hat{V}_{ext}$ being, respectively, the kinetic and external potential operators), and it has been assumed that the weights are in a descending order. Exploiting the range separation of the electronic interaction (34), long- and short-range ensemble density functionals are introduced as

$$F_{m,\boldsymbol{\omega}}^{LR}[\rho_{ens}] = \min_{\substack{\{\psi_i\}\to\rho_{ens}\\ \forall_{ij}\ \langle\psi_i|\psi_j\rangle=\delta_{ij},}} \sum_{i=1}^{m} \omega_i \langle\psi_i|\hat{T}+\hat{V}_{ee}^{LR}|\psi_i\rangle \tag{36}$$

and

$$F_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}] = F_{m,\boldsymbol{\omega}}[\rho_{ens}] - F_{m,\boldsymbol{\omega}}^{LR}[\rho_{ens}], \tag{37}$$

respectively. The ensemble energy functional based on the range separation of the electron-electron interaction reads as

$$E_{m,\boldsymbol{\omega}}[\{\psi_i\}] = \sum_{i=1}^{m} \omega_i \langle\psi_i|\hat{T}+\hat{V}_{ee}^{LR}+\hat{V}_{ext}|\psi_i\rangle + F_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}], \tag{38}$$

where ρ_{ens} corresponds to the ensemble determined by $\{\omega_i\}$ and $\{\psi_i\}$. For given weights, minimization of such a defined functional under the constraint that the functions are orthonormal yields the exact energy of the ensemble and the exact ensemble density (19), namely,

$$\min_{\substack{\{\psi_i\}\\ \forall_{ij}\ \langle\psi_i|\psi_j\rangle=\delta_{ij}}} E_{m,\boldsymbol{\omega}}[\{\psi_i\}] = E_{m,\boldsymbol{\omega}}\left[\left\{\Psi_i^{LR}\right\}\right] = \sum_{i=1}^{m}\omega_i E_i^{(0)} \tag{39}$$

and

$$\rho_{ens}^{(0)}(\mathbf{x}) = \sum_{i=1}^{m}\omega_i\left\langle\Psi_i^{(0)}\middle|\hat{\rho}(\mathbf{x})\middle|\Psi_i^{(0)}\right\rangle = \sum_{i=1}^{m}\omega_i\left\langle\Psi_i^{LR}|\hat{\rho}(\mathbf{x})|\Psi_i^{LR}\right\rangle. \tag{40}$$

It should be noticed that the minimizing wave functions $\{\Psi_i^{LR}\}$ are different from the eigenfunctions $\{\Psi_i^{(0)}\}$ of the Hamiltonian $\hat{H}$ since Ψ_i^{LR} solves the eigenequation of the modified Hamiltonian involving the long-range electron-electron interaction and the local short-range potential, i.e.,

$$\left(\hat{T} + \hat{V}_{ee}^{LR} + \hat{V}_{ext} + \hat{V}_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}]\right)\Psi_i^{LR} = E_i^{LR}\Psi_i^{LR}. \tag{41}$$

The short-range potential $\hat{V}_{m,\boldsymbol{\omega}}^{SR}$ is given by a density derivative of the functional (37), namely,

$$\hat{V}_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}] = \sum_{i=1}^{N} \left.\frac{\delta F_{m,\boldsymbol{\omega}}^{SR}[\rho]}{\delta\rho(\mathbf{x}_i)}\right|_{\rho=\rho_{ens}}. \tag{42}$$

Interestingly, one can employ the range-separated functional (38) to define a functional $\tilde{A}_m$:

$$\tilde{A}_m[\{\omega_i\},\{\psi_i\}] = E_{m,\boldsymbol{\omega}}[\{\psi_i\}] + \frac{1}{\beta}\sum_{i=1}^{m}\omega_i \ln\omega_i. \tag{43}$$

Then, taking into account Eqs. (8), (22), and (39), one concludes that the minima of the Helmholtz energy A_m and the functional $\tilde{A}_m$ coincide and, what is more, one obtains

$$\min_{\substack{\{\omega_i\}\,,\,\{\psi_i\} \\ \sum_i^m \omega_i = 1 \;\wedge\; \forall_{ij}\; \langle\psi_i|\psi_j\rangle = \delta_{ij}}} \tilde{A}_m[\{\omega_i\}\,,\{\psi_i\}] \\ = A_m\big[\{\omega_i^{(0)}\},\{\Psi_i^{(0)}\}\big] = \tilde{A}_m\big[\{\omega_i^{(0)}\},\{\Psi_i^{LR}\}\big], \quad (44)$$

where the optimal weights take the form of the Boltzmann factors [Eq. (13)] computed with the exact energies of the first m states, i.e., $\omega_i^{(0)} = \exp[-\beta E_i^{(0)}]/\sum_{j=1}^m \exp[-\beta E_j^{(0)}]$. This means that full minimization of the functional $\tilde{A}_m$that is based on the range-separation electron-electron interaction would yield the ensemble density and the ensemble energy coinciding with those obtained at the minimum of the Helmholtz energy functional A_m. What is more interesting is that the optimal weights corresponding to the minimum of $\tilde{A}_m$ would give an access to the excitation energies of the exact, fully interacting system [that is due to the fact that the optimal weights are simply the same as $\{\omega_i^{(0)}\}$ that allows one to determine the exact energies up to a constant shift, cf. Eq. (5)].

We propose to proceed with the optimization of the range-separated functional defined in (38) by applying the approach already described in the first part of this section pertaining to the method called Ens-WF. Therefore, in the first step, one assumes a set of m configurations (Slater determinants) $\{\Phi_I\}$ that are supposed to be significant in approximating the first m states of the system under study. For one-determinantal wave functions, the functional (38) turns into the functional depending on spin orbitals [cf. Eq. (26)], namely,

$$E_{m,\boldsymbol{\omega}}[\{\varphi_i\}] = \sum_{i=1}^{M} n_i h_{ii} + \frac{1}{2}\sum_{ij}^{M} G_{ij}\,\langle ij||ij\rangle^{LR} + F_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}], \quad (45)$$

where the indices of the occupation numbers n_i and the parameters G_{ij} pertain to the indices of the spin orbitals and their definitions are given, respectively, in Eqs. (27) and (28). M, as before, stands for the number of spin orbitals in the basis set. The antisymmetrized two-electron integrals $\langle ij||ij\rangle^{LR}$ involve the long-range electron-electron interaction operator $\upsilon_{ee}^{LR}(r)$ [cf. Eq. (34)]. Finally, the ensemble density in the case of one-determinantal states ensemble takes a simple form $\rho_{ens}(\mathbf{x}) = \sum_{i=1}^{M} n_i\varphi_i(\mathbf{x})^2$. In order to include part of the dynamic correlation, the optimal spin orbitals are found by minimizing the functional (45). Notice that the form of the latter is similar to that of the recently introduced range-separated reduced density matrix functional [cf. Eq. (12) in Ref. [30]], thus the optimization algorithms developed for the latter can be employed. The long-range static correlation, crucial for a correct description of molecules at stretched-bond geometries, is included in the second step, consisting in taking linear combinations of the initially selected determinants built of the optimal spin orbitals obtained in the first step and minimizing the functional

$$E_{m,\boldsymbol{\omega}}[\mathbf{C}] = \sum_{I=1}^{m} \bar{\omega}_I \sum_{JK}^{m} C_{IJ}^{*}C_{IK}\big\langle\Phi_J^{\mathrm{opt}}\big|\hat{T} + \hat{V}_{ee}^{LR} + \hat{V}_{ext}\big|\Phi_K^{\mathrm{opt}}\big\rangle \\ + F_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}] \quad (46)$$

with respect to the elements of the $\mathbf{C}$ matrix under the constraint that it is unitary [cf. Eqs. (30)–(33)]. Note that the Boltzmann weights $\bar{\omega}_I$ entering Eq. (46) are computed with functions Φ_I^{opt}. Constrained optimization of the functional (46) leads to diagonalization of the effective Hamiltonian, the elements of which read as

$$H'_{IJ} = \big\langle\Phi_I^{\mathrm{opt}}\big|\hat{T} + \hat{V}_{ee}^{LR} + \hat{V}_{ext} + \hat{V}_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}]\big|\Phi_J^{\mathrm{opt}}\big\rangle, \quad (47)$$

where ρ_{ens} is fixed. The above-described two-step procedure allows one to efficiently take into account the long-range electron interaction. In principle, it can be improved by extending the set of the initial configurations, but since part of the interaction is covered by the short-range density functional, the size of the subspace of configurations required to achieve a given accuracy is supposed to be much smaller than in the case of the full-range Hamiltonian (that is also a known advantage of using range-separated wave-function methods for predicting ground states [25]).

In the first approximation for $F_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}]$, we use one of the short-range functionals proposed for predicting ground-state energies, i.e., we assume $F_{m,\boldsymbol{\omega}}^{SR}[\rho_{ens}] = E_H^{SR}[\rho_{ens}] + E_{xc}^{SR\text{-PBE}}[\rho_{ens}]$, where the first term is the Hartree functional defined with the operator $\upsilon_{ee}^{SR}(r)$ and $E_{xc}^{SR\text{-PBE}}$ represents a short-range exchange-correlation Perdew, Burke, Ernzerhof (PBE) functional proposed in Ref. [27]. Choosing the short-range PBE functional implies a need for using the error function in the long-range electronic repulsion, i.e., we employ the operator $\upsilon_{ee}^{LR}(r) = \mathrm{erf}(\mu r)/r$, where μ is a positive real number. Using a ground-state functional in the description of an ensemble energy might seem to be quite a crude approximation, nevertheless, as we show below, it leads to a substantial improvement over the Ens-WF method described in the first part of the section. In order to obtain approximate values of energies for the considered m states, one would first perform the calculation for $m = 1$, then for $m = 2$ and by taking a difference of ensemble energies furnished by such calculations an approximation to $E_2^{(0)}$ would be obtained. If the procedure is repeated for increasing m, consecutive values of the energy would be recovered. Such an approach is neither computationally efficient nor likely to work well with the assumed ground-state approximation for the short-range functional. Instead, the energy of the Ith state is computed by taking the expectation value of the Hamiltonian involving only the long-range electronic interaction with the Ith state $\psi_I^{(0)}$ obtained from diagonalization of $\mathbf{H}'$ given in (47) and adding the short-range functional value for the relevant density, namely,

$$E_I^{(0)} = \big\langle\psi_I^{(0)}\big|\hat{T} + \hat{V}_{ee}^{LR} + \hat{V}_{ext}\big|\psi_I^{(0)}\big\rangle + E_H^{SR}[\rho_I] \\ + E_{xc}^{SR\text{-PBE}}[\rho_I], \quad (48)$$

where $\rho_I = \langle\psi_I^{(0)}|\hat{\rho}(\mathbf{x})|\psi_I^{(0)}\rangle$.

IV. ILLUSTRATIVE RESULTS

To illustrate how the static and dynamic electron correlations are captured via optimization of orbitals, employing range separation of the electronic interaction, and diagonalization of the effective Hamiltonian, and to show the influence of weights on the energies of states under study, we analyze three example systems: beryllium atom, boron hydride, and lithium hydride. In all calculations discussed in the following, aug-cc-pVQZ and aug-cc-pVTZ basis sets [40,41] were employed for the Be atom and the molecules, respectively. As a benchmark, coupled clusters singles doubles (CCSD) values of energies obtained with DALTON quantum chemistry package [42] in the same basis sets are used. Following, we use the acronym Ens-WF for the method based on Eqs. (26)–(33). Ens-WF consists of three steps: (1) selecting configurations that are significant for states of interest of a given system, (2) constrained minimization of the functional (26) with respect to orbitals, and (3) diagonalization of the Hamiltonian in a space spanned by determinants built of the optimal orbitals. To elucidate the properties of variational ensemble methods, the Ens-WF approach will be compared with the method consisting in diagonalization of the Hamiltonian involving Hartree-Fock orbitals. Since the latter approach is simply a configuration interaction method for a limited space of determinants, we call it CI. In all calculations we employ Boltzmann weights (13). Consequently, if the ground state is not degenerate, CI emerges as a limiting case of the Ens-WF approach when $\beta \to \infty$ (all weights equal zero except for the one corresponding to the ground state). On the other hand, the equiensemble case (all weights equal) is equivalent to taking Boltzmann weights at $\beta = 0$ value. For each system, we choose configurations that are the most significant for considered states and for Be, LiH, and BH they are, respectively, $\{1s^2 2s^2, 1s^2 2s2p, 1s^2 2s3s, 1s^2 2p^2, 1s^2 2s3p, 1s^2 2s3d, 1s^2 2s4s, 1s^2 2s4p\}$, $\{1\sigma^2 2\sigma^2, 1\sigma^2 2\sigma 3\sigma, 1\sigma^2 2\sigma 1\pi, 1\sigma^2 2\sigma 4\sigma, 1\sigma^2 3\sigma^2\}$, and $\{1\sigma^2 2\sigma^2 3\sigma^2, 1\sigma^2 2\sigma^2 3\sigma 4\sigma, 1\sigma^2 2\sigma^2 3\sigma 1\pi, 1\sigma^2 2\sigma^2 3\sigma 5\sigma, 1\sigma^2 2\sigma^2 4\sigma^2\}$ with all pertinent spin combinations.

It is well known that in the beryllium atom the static correlation plays an important role, i.e., a single Slater determinant is not sufficient to describe its ground state accurately. Rather, the ground state is dominated by two configurations, namely, $1s^2 2s^2$ and $1s^2 2p^2$. For this reason, it is interesting to study the influence of weights (that can be varied by changing β) on the ground-state energy of this system. In Fig. 1, one can see that the energy of the ground state lowers with the β parameter in the small-value range of the parameter and then stabilizes for the intermediate values of β. However, in the $\beta \to \infty$ limit (marked with open symbols on the plot) when only the weight of the ground state is different from 0, the $2p$ orbital is not optimized and the energy increases with respect to the values obtained for small β. Similarly, there is a large difference in the accuracy of $1\,^1D$ energy (this state is of a double excitation character dominated by $1s^2 2p^2$ configuration) obtained at $\beta = 0$ (equiensemble Ens-WF) and $\beta \to \infty$ (the CI limit) of the method. The errors with respect to the CCSD values of energies at both limits amount to 0.89 and 1.65 eV for equiensemble and CI, respectively. It is understandable because the weight of the $1s^2 2p^2$ determinants achieves the value zero for large β, and the corresponding energy is higher than that obtained for small β. On the other hand, the energies of the two lowest P states vary only very little with β, which is due to the fact that the total contribution of the $1s^2 2s2p$ determinants to the ensemble energy is smaller than the contribution of the doubly excited determinants. Also, the singly excited $1\,^3P$ and $1\,^1P$ states are not as sensitive to changes in the $2p$ orbitals as the ground or $1\,^1D$ states. Analysis

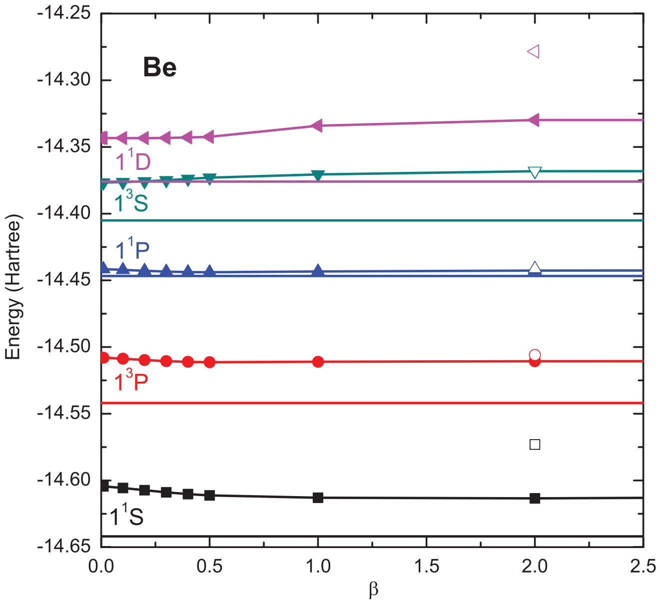

FIG. 1. (Color online) Energies of states of beryllium atom calculated for different values of β parameter. Unmarked solid lines: CCSD, marked lines: Ens-WF, open markers: $\beta \to \infty$ (CI) limit. Markers □, ○, △, ▽, and ◁ denote states $1\,^1S$, $1\,^3P$, $1\,^1P$, $1\,^3S$, and $1\,^1D$, respectively.

of the dependence on β of the errors of excitation energies with respect to the CCSD results reveals that for each state the minimum is achieved for a different value of β and the sum of errors is minimized at $\beta = 0.5$. For this value, the errors on excitations amount to 0.03, 0.78, 0.02, and 0.04 eV for excitations from the ground state to the $1\,^3P$, $1\,^1P$, $1\,^3S$, and $1\,^1D$ states, respectively. It is clear that while the energy of excitation to the $1\,^1P$ state suffers mainly from inaccuracy of the calculated ground-state energy, the others benefit from the cancellation of errors.

Looking at dissociation energy curves of the Σ^+ states presented in Fig. 2, one can see that while the equiensemble Ens-WF method raises the ground-state energy of LiH molecule around equilibrium by about 10 mHartree with respect to the CI value, it improves greatly its dissociation limit as well as the energies of $1^3\Sigma^+$ and $2^1\Sigma^+$ excited states along the whole curve. As in the case of beryllium, it is evident from Fig. 3 that also for LiH there is no common optimal value of β parameter for excitation energies to all considered states. It turns out, however, that the total error on excitation energies is smallest for the same value $\beta = 1$ for both the equilibrium distance ($R = 3.016$ a.u.) and the dissociation limit ($R = 8.0$ a.u.), the total errors being 0.84 and 0.57 eV, respectively.

The performance of the Ens-WF for the BH molecule is qualitatively similar to that of the above-discussed LiH. As one can see from Fig. 4, the ground-state energy obtained at $\beta = 0$ is slightly higher around the equilibrium geometry than its CI counterpart. In the dissociation limit, however, the energy from the equiensemble calculation is 40 mHartree lower than the CI one. The equiensemble triplet Σ^+ state is lower than the CI one by a few dozen mHartree for all distances between the atoms. The second Σ^+ singlet energy obtained from the equiensemble

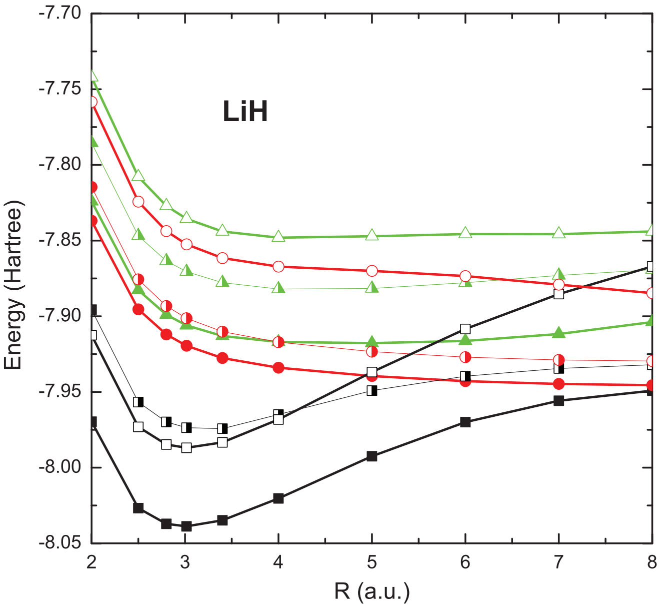

FIG. 2. (Color online) Dissociation curves of the first three Σ^+ states of LiH. Equiensemble Ens-WF, CI, and CCSD results are shown. Full markers denote CCSD, half-filled Ens-WF, and empty the CI data. Markers □, ○, and △ denote states $1^1\Sigma^+$, $1^3\Sigma^+$, and $2^1\Sigma^+$, respectively.

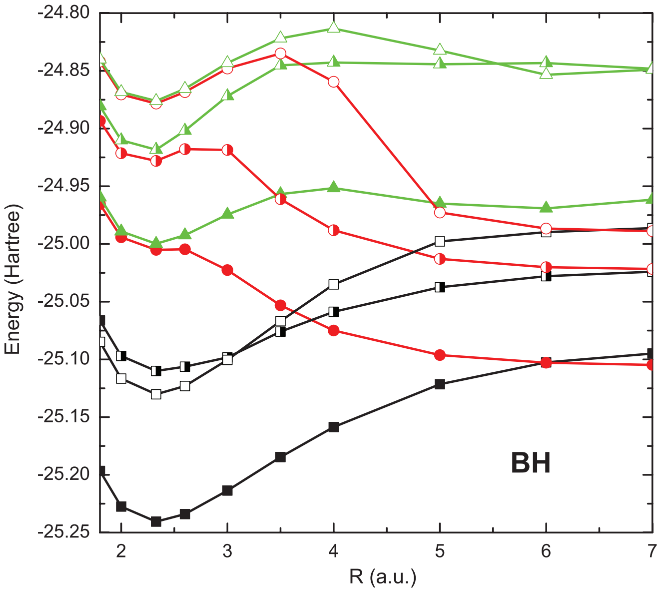

FIG. 4. (Color online) Dissociation curves of the first three Σ states of BH. Equiensemble Ens-WF, CI, and CCSD results are shown. Full markers denote CCSD, half-filled Ens-WF, and empty the CI data. Markers □, ○, and △, denote states $1^1\Sigma^+$, $1^3\Sigma^+$, and $2^1\Sigma^+$, respectively.

calculation is also lower than its CI counterpart, especially in proximity of equilibrium. Figure 5 shows that the errors on excitation energies for BH are larger than that of LiH. The minima of a total error as a function of β do not coincide for different distances between B and H atoms. The total error for the optimal $\beta = 1$ at $R = 2.329$ a.u. (equilibrium distance) equals 1.87 eV, whereas at $R = 7.0$ a.u., the smallest total error amounting to 2.21 eV is attained for $\beta = 0.2$. At the dissociation limit the main source of error can be attributed to the $2\,^1\Sigma^+$ state. The shape of the dissociation curve of this state is not correct and could be improved by adding more configurations of this symmetry to the ensemble. The errors at

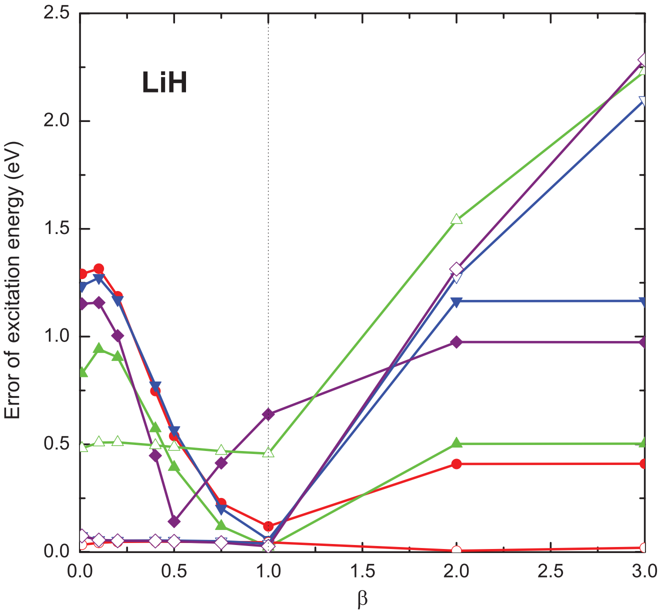

FIG. 3. (Color online) Errors of excitation energies of LiH for the equilibrium distance and the dissociation limit. Full markers denote data obtained at $R = 3.016$ a.u. distance, empty markers correspond to $R = 8.0$ a.u.. Markers □, ○, △, ▽, and ◊ denote states $1^1\Sigma^+$, $1^3\Sigma^+$, $2^1\Sigma^+$, $1^3\Pi$, and $1^1\Pi$, respectively.

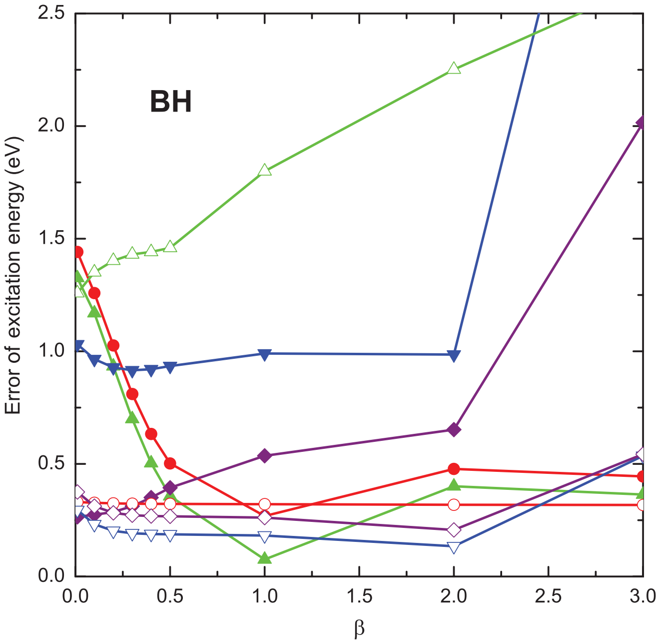

FIG. 5. (Color online) Errors of excitation energies of BH for the equilibrium distance and the dissociation limit. Full markers denote data obtained at $R = 2.329$ a.u. distance, empty markers correspond to $R = 7.0$ a.u.. Markers □, ○, △, ▽, and ◊ denote states $1^1\Sigma^+$, $1^3\Sigma^+$, $2^1\Sigma^+$, $1^3\Pi$, and $1^1\Pi$, respectively.

equilibrium geometry are in large part due to the fact that the minimum of the ground state is too shallow.

We conclude that the determination of the optimal value of β is a compromise between correct descriptions of the ground state (usually $\beta \to \infty$ limit is optimal for a ground state except for multideterminantal ground states, e.g., in beryllium) and excited states more accurately described with small values of β. Interestingly, at $\beta = 1$ (the value optimal for most presented cases), the weight of a ground state is usually close to 0.9 so the other states contribute very little to the energy of the ensemble.

Overall, as expected the Ens-WF method largely underestimates the energies due to a fact that only a small number of configurations are considered for each system. It is able to capture static correlation but misses a substantial part of the dynamic correlation. To recover a missing part of the dynamic correlation, we applied the range-separated scheme, Ens-lrWF + srDF, described in Sec. III. The short-range PBE functional together with the $\upsilon_{ee}^{LR}(r) = \mathrm{erf}(\mu r)/r$ long-range operator were utilized. Within the Ens-lrWF + srDF approach, first the ensemble energy calculated according to formula (45) is minimized with respect to the orbitals. Then, the functional (46) is minimized with respect to the expansion coefficients C_{ij}. Both functionals employ Boltzmann weights defined in Eq. (13). The energy of each state is subsequently calculated according to the approximate formula (48). In principle, the range-separation parameter μ can be chosen arbitrarily. After performing several tests on small systems, we have chosen $\mu = 1.0$ [a.u.] which seems to work best for the investigated cases. Here, we present the dissociation curves for the first three Σ^+ states of LiH. The ensemble was built in the same space of configurations as in case of the aforedescribed Ens-WF method, but we chose $\beta = 0.5$, optimal for this particular system and the separation parameter μ. A comparison of the performance of the Ens-WF and Ens-lrWF + srDF methods presented in Fig. 6 confirms that as expected the Ens-lrWF + srDF leads to lower energies of states than Ens-WF while keeping the shape of the curves correct. The absolute values of energies are greatly improved. The excitation energies, however, although improved as well do not gain as much in comparison to Ens-WF. At the dissociation limit, the total error of excitation energies (with optimal β for both methods) stays almost constant (0.56 eV for Ens-lrWF + srDF versus 0.57 eV for Ens-WF), while for equilibrium distance it changes from 0.84 to 0.77 eV. The reason why the excitation energies along the whole curve do not improve as much as the absolute energies did is that they do not benefit, as it was in the case of Ens-WF, from cancellation of errors.

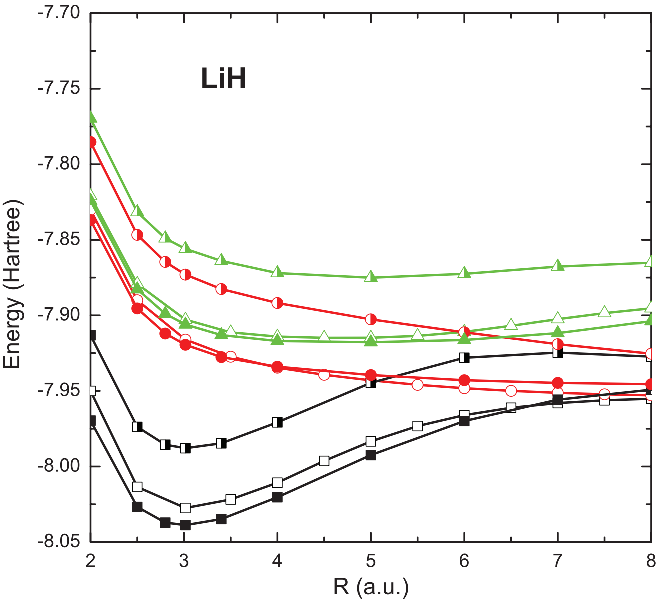

FIG. 6. (Color online) Dissociation curves of the first 3 Σ^+ states of LiH Ens-lrWF + srDF ($\beta = 0.5$) vs Ens-WF ($\beta = 1.0$) compared to CCSD results. Full markers denote CCSD, half-filled Ens-WF, empty Ens-lrWF + srDF. Markers □, ○, and △ denote states $1^1\Sigma^+$, $1^3\Sigma^+$, $2^1\Sigma^+$, respectively.

V. CONCLUSIONS

By considering the Helmholtz free energy [Eq. (3)], we have related its constrained minimization with the ensemble variational theorem. This has been achieved by considering minimization of the constrained free-energy functional A_m defined for N-electron density matrices that are mixtures of m pure states [cf. Eq. (8)]. A resulting chain of relations has been collected in Eq. (22). Based on them, one concludes that, clearly, a global minimum of A_m is achieved for m eigenstates of the Hamiltonian that correspond to the m lowest-energy levels, the pertinent weights given by the Boltzmann formula in Eq. (5). Inequality (21) and the second inequality in Eq. (22) imply that for fixed weights, the constrained minimization of the free-energy variational principle reduces to the ensemble variational principle [2] and in the special case when all weights are equal ($\beta = 0$) to the subspace variational principle [1] [cf. Eq. (23)]. We proposed a method (Ens-WF), which is based on inequality (23), that, upon minimization of the energy of an m component ensemble with fixed Boltzmann weights, Eq. (13), yields energies for the lowest m states. The Boltzmann weights, which include the common parameter β as the inverse of an effective temperature, are computed initially from the assumed trial functions and then remain fixed. The minimization of the ensemble energy functional [left-hand side of Eq. (23)] is carried out in two steps. First, the optimal space of states is searched for, which in the practical algorithm involves selecting configurations for the m states of a system under study and optimizing the energy with respect to orbitals [Eqs. (24)–(28)]. The second step consists in finding optimal rotations in the space spanned by the single Slater determinant states found in the first step. This amounts to minimizing the functional given in Eq. (30) with respect to orthogonal vectors of the expansion coefficients C_{IJ} introduced in Eq. (29). Such a procedure is reminiscent of the state-averaged, multiconfiguration, self-consistent field (SA-MCSCF) method [39]. It differs from SA-MCSCF in choosing Boltzmann weights, splitting the optimization into two steps, and by employing a much more limited space of states than it is done in SA-MCSCF, which is more expensive computationally than Ens-WF. Application of the Ens-WF approach to the Be atom and LiH and BH molecules leads to the conclusion that Ens-WF is able to capture static electron correlation but misses the dynamic correlation. This is expected since we employ relatively small configuration spaces. Investigation of the influence of the inverse effective temperature parameter β (in Boltzmann weights) on the obtained energy values has shown that a proper choice of β leads to the reduction of the average error, thus the $\beta = 0$ value (equiensemble limit) does not provide the most accurate results.

In order to cure the main deficiency of Ens-WF (missing of the dynamic correlation) and retain its low computational cost, we have proposed to exploit the idea of range separation of the electronic repulsion [Eq. (34)] and introduced a short-range ensemble energy functional of the density, defined in Eq. (37). Combining the short-range functional with the long-range wave-function functional has resulted in the ensemble, range-separated energy functional [Eq. (45)]. Similarly to the Ens-WF approach, the method, called Ens-lrWF + srDF, based on the optimization of the range-separated functional with respect to wave functions at fixed Boltzmann weights involves two steps: finding the optimal space of single-determinantal states and finding the optimal rotations of these states. A preliminary calculation of the potential energy curves of the LiH molecule confirms that adding the short-range density functional leads to including dynamic correlation that in turn results in deepening the potential curves in the neighborhood of the equilibrium geometry.

In summary, we have provided a theoretical framework for an approach based on the variational principle for the Helmholtz energy that in its constrained formulation is equivalent to the ensemble variational theory, with the ensemble weights taking the form of Boltzmann factors. The practical algorithm we have proposed is capable of capturing both static and dynamic correlation. The latter is reproduced by including the short-range PBE functional. Despite its simplicity, this functional performs well for small systems such as LiH but in the future, approximate density functionals more appropriate for describing ensemble energy should be developed. It is also of importance for the Ens-lrWF + srDF method to establish optimal values of the two parameters that the method involves: the inverse of the quasitemperature β and the range-separation parameter μ. Work along these lines is in progress.

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