

# Employing ensemble variational principle to calculate electron excitation energies of molecules: a range-separated approach

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We propose a method of calculating electronic excitation energies that is both computationally inexpensive and able to capture states of multiconfigurational character (single and double excitations are recovered). It exploits the ensemble variational principle [1, 2] (EVP) which states that if  $\psi_1, \dots, \psi_m$  are orthonormal trial functions and  $\omega_1 \geq \omega_2 \geq \dots \geq \omega_m \geq 0$  then for  $m$  lowest eigenstates of Hamiltonian  $H$  corresponding to eigenvalues  $E_1, E_2, \dots, E_m$  the following relation holds:  $\sum_{i=1}^m \omega_i E_i \leq \sum_{i=1}^m \omega_i \langle \psi_i | H | \psi_i \rangle$ . In principle, EVP allows for finding a desired number of lowest excited states of a system with a variational method of choice, e.g. ensemble Hartree-Fock [3] or DFT [4]. Unfortunately, the existing methods based upon EVP [1, 3, 4, 5] have difficulties with describing accurately both static and dynamic correlation.

We start with relating the ensemble variational theory with the minimization of the free energy of the canonical ensemble. This leads us to proposing to use Boltzmann factors as weights in the ensemble functional. Our method relies on minimization of the range separated ensemble functional with Boltzmann weights [6]. The dynamic correlation energy is recovered by orbital relaxation and the presence of the short-range density functional, whereas the long-range static effects are expected to be captured by going beyond the single-determinantal description of states.

Two approaches are considered. Either the density functional is dependent on the ensemble density or on the densities of the components of the ensemble. The latter approach removes the spurious "ghost" [4] terms from the interaction between electrons. Both versions of the method are applied to predicting potential energy curves of a few low-lying states of a number of small molecules. We show that the proposed method is indeed able to capture different types of excitations and produces the dissociation curves of correct shape.

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