Linearized Pair-Density Functional Theory

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Multiconfiguration pair-density functional theory (MC-PDFT) is a post-SCF multireference method that has been successful at computing excited states. However, MC-PDFT is a single-state method in which the final MC-PDFT energies do not come from diagonalization of a model-space Hamiltonian matrix. This can lead to inaccurate topologies of potential energy surfaces near locally avoided crossings and conical intersections, which are important for photochemistry and photodynamics. Therefore, in order to perform physically correct *ab initio* molecular dynamics with electronically excited states, it is necessary to develop a PDFT method that recovers the correct topology throughout the entire nuclear configuration space. Whereas MC-PDFT achieves useful accuracy by employing a functionalized energy expression, the goal here is to achieve that accuracy with a quantum mechanical operator whose eigenvalues also have the correct topology as functions of geometry.

Because the classical Coulomb and on-top functional terms in the MC-PDFT energy expression are nonlinear functionals of the wave function, we cannot construct a linear operator whose expectation values exactly equal the full set of single-state MC-PDFT energies. Instead, we seek a linear operator whose spectrum is an extension of MC-PDFT with the correct topology. Given a set of electron densities, $\{\rho_I\}$, and on-top densities, $\{\Pi_I\}$, we construct an effective Hamiltonian, $\hat{H}^{\mathrm{L-PDFT}}$, called the linearized PDFT Hamiltonian, that is a functional of the one-body and two-body reduced density matrices within a pre-defined model-space. One example of such a model space is the space spanned by the set of N lowest-energy SA-CASSCF eigenvectors, and this is the example used for the applications presented here. We construct $\hat{H}^{\mathrm{L-PDFT}}$ by expanding the MC-PDFT energy functional in a power series of ρ and Π variables about their state-averaged values within the model space and truncate this series at first order, such that for any state $|I\rangle$ within this model space, $\langle I|\hat{H}^{\mathrm{L-PDFT}}|I\rangle$ is a linear approximation to its MC-PDFT energy. By construction, $\hat{H}^{\mathrm{L-PDFT}}$ is a well-defined linear operator whose off-diagonal elements are generally nonzero, and diagonalization of $\hat{H}^{\mathrm{L-PDFT}}$ within a given subspace yields a set of potential energy surfaces with the correct topology near conical intersections and locally avoided crossings. Here we show that this linearized PDFT (L-PDFT) method yields good accuracy at a lower computational cost than MC-PDFT for a variety of challenging cases including phenol, methylamine, and the spiro cation.