THEORETICAL SPECTROSCOPY FOR MOLECULES WITH A DOWN-FOLDED EFFECTIVE HAMILTONIAN

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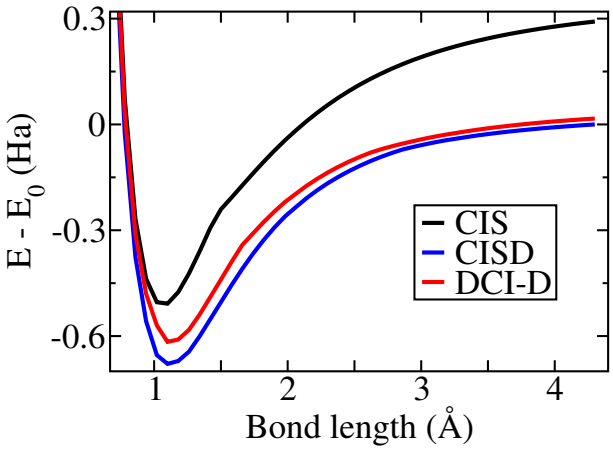
Strongly-correlated electrons coupled to a weakly-correlated bath are common in condensed matter physics, materials science, and chemistry. For example, metals with an isolated set of correlated d bands or molecules hosting a Kondo impurity fall under this classification. Quantum embedding, or down-folding, theories are designed exactly for such systems where two different subspaces with different levels of correlation are coupled to each other.

We present a new quantum embedding theory based on [1] to predict ground state, optical excitation, and ionization energies in correlated systems. We downfold the effect of the high-energy, less correlated space onto an energy dependent effective Hamiltonian in the low-energy space by combining many-body perturbation theory (MBPT) with configuration interaction (CI). Excitations in the high-energy space are described by a Green's function built up with MBPT. These high energy excitations are coupled to the correlated space by matrix elements of the exact Hamiltonian. The effective Hamiltonian in the correlated space is then diagonalized with a chosen level of CI. The effect of the downfolding procedure is to screen the low-energy Hamiltonian by high-energy electronic transitions. In this way, our dynamical configuration interaction method is a true *ab-initio* Hamiltonian with zero double-counting error, is systematically improvable, and is a single framework for ground and excited states.

Our initial work focuses on ground state energies using a simple approximation to the Green's function based only on mean-field theory. To test this approach (DCI-D), we compute the binding curve of the N_2 molecule. With the exact Green's function, the DCI-D result would perfectly match the CI singles-doubles (CISD) calculation. With our computationally efficient, mean-field Green's function, the agreement between DCI-D and CISD is still excellent.



[1] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, *Phys. Rev. A* **54**, 3948-3959 (1996).