Response theory methods for open-shell systems

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(Abstract)

Part I: Generalised perturbative orbital relaxation corrections based on random phase approximation.

We investigate our newly developed generalised perturbative orbital relaxation correction (F-RPASingles). 'F-RPASingles' is inspired from variationally minimised GKS-spRPA, and is based on random phase approximation (RPA) functional and includes relaxation-correlation effects via a screened RPA gradient and an approximate form of Hessian. It is computationally more efficient than GKS-spRPA, reducing its cost by a factor of number of orbital optimization steps.
Here, we test 'F-RPAsingles' for weak interactions in simple open-shell complexes and spin gaps. For weak interactions we report mean absolute error (MAE) of 1.07 kcal/mol as compared to MAE of 1.02 kcal/mol using GKS-spRPA, wrt CCSD(T). We test the behaviour of the method along the entire range of interaction for alkali metal-pi complexes. We then investigate the performance of the method along with exchange correction (AXK) for spin gaps of Fe(II) octahedral complexes and report its merit in predicting accurate spin gaps with MAE of 0.60 eV wrt benchmark DMC results.

Part II: Role of long-range correlation effects in resonance states of temporary anions.
Negative ion resonances find their importance from radiation damage to DNA to interstellar medium. These can be characterised by electron scattering experiments and have complex energies. Real energies are associated with energy of the resonance state whereas imaginary energies are associated with their lifetimes. Using our newly developed method, CAP-GKS-spRPA, we predict accurate estimates of both these energy properties. However, due to high scaling (O(N6)), it is limited to smaller systems. Analytic continuation based approximations to CAP-GKS-spRPA can reduce its scaling to (O(ngN4)). We test CAP-AC-GKS-spRPA for smaller systems and then use it to tackle challenging systems like DNA base pairs. Our method gives the resonance energy parameters within 0.2 eV as compared to the state-of-the-art method.