Benchmarking Starting-Points of the G_0W_0 for Open-Shell Molecules

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Hedin's GW approximation (GWA) has gained popularity in the material science community because of its high quality and relatively low computational cost. A prerequisite to describe magnetic materials is the capability to describe systems containing unpaired electrons. In this study, we benchmark the ionization energy calculated by G_0W_0 on top of different unrestricted starting-points for small open-shell molecules using Dunning's correlation-consistent basis sets expanded in terms of Gaussian functions. As an alternative route, electron affinity of the positively charged molecules are calculated as well. Results are carefully compared with a variety of correlated methods including CCSD(T).
It is revealed that G_0W_0 provides a systematic and accurate method to compute the quasi-particle energy levels of such molecules with convincing evidence of reliability similar to the case of closed-shell molecules.
Furthermore, GWA provides a correct ordering of the molecular orbitals based upon orbital energy eigenvalues in consistent agreement with the Dyson orbitals. The present implementation of GWA is based on the use of basis sets of atomic orbitals and provides a good compromise between accuracy and computational expense, suitable to be applied to study magnetic materials.

Figure

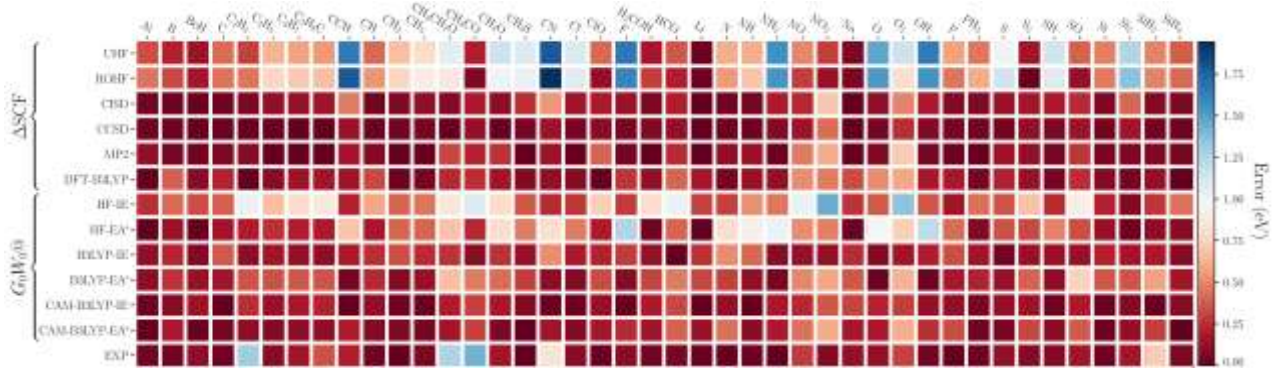

Figure 1. Heatmap presentation of errors in eV obtained from the various methods using a cc-pVQZ basis with respect to the ΔSCF-CCSD(T) total energy difference. G_0W_0 results were calculated by two ways: IE of neutral molecule and EA of the molecule's cation (EA^+).