Self-consistent *GW* calculations for molecules

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Quantum chemistry possesses a long list of methods which capture the effects of electron correlations. Unfortunately, these methods are based on a solution of Schrödinger equation which is known to be the harder the more electrons are present in the quantum system [1]. In fact, a "golden standard" of quantum chemistry, the coupled-cluster with single, double and perturbative triple excitations (CCSD(T)) exhibits $O(N^7)$ complexity scaling with the number of atoms N [2]. There is an alternative for the wave-function based methods originating from the solid state physics. It is Hedin's *GW* approximation for one-particle Green's function [3]. The computational complexity of Hedin's *GW* approximation can be as low as $O(N^3)$ in the limit of large number of atoms [4]. This favorable complexity scaling could allow for much larger systems to be treated quantum mechanically. Unfortunately, practical calculations with Hedin's *GW* approximation are rather computationally expensive. This fact has limited many studies to the so-called one-shot *GW* approach. One-shot *GW* (G_0W_0) calculations depend on the starting approximation for the Green's function, and, therefore, do not reveal the true merits of the *GW approximation* to capture *the effects of electron correlations*. Only recently self-consistent *GW* (SC*GW*) calculations have become affordable [5]. Apart from SC*GW* calculations, there is an interesting proposal of using *GW* approximation for computing a one-particle correlation operator [6]. This, the so-called quasi-particle self-consistent *GW* approach (QS*GW*) has been claimed to improve the results of G_0W_0 and gained much attention recently.

The goal of the present work is to compare the performance of SC*GW* and QS*GW* approaches, and of these two methods against well established quantum chemistry methods such as CCSD and CCSD(T) [7]. For the sake of such study we realized both *GW* algorithms using the same numerical implementation. Calculations has been done for the ionization potential of 16 atoms and molecules with the same basis sets of Gaussian functions in SC*GW*, QS*GW* and CCSD(T). We found that self-consistency in both *GW* approaches only marginally improves the G_0W_0 results with a Hartree-Fock starting point. Herewith, SC*GW* tends to underestimate the vertical ionization potential (IP)

with respect to CCSD(T) IPs, while QS*GW* tends to overestimate them. In the figure, we show IP-IP$_{CCSD(T)}$ differences for all considered species computed with the cc-pVTZ basis set. More work is necessary to fully understand and possibly improve SC*GW and* QS*GW* methods.

References

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Figures