GW and Bethe-Salpeter Approaches for Molecular Quantum Chemistry

A talk by Wim Klopper

Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Germany

DATE / TIME: Monday, Oct 9th 2017, 4:00 p.m.

LOCATION: TU Wien, Seminarraum 138C (Freihaus, Turm B/yellow, 9. OG)

We have implemented a computational approach based on the Bethe–Salpeter equation (BSE) for the theoretical description of electronically excited states of finite systems (atoms and molecules). The approach is much used in computational solid-state physics and materials science, but not so much in quantum chemistry. In recent years, however, interest in using the approach for molecular systems has increased [1, 2]. Within the framework of the TURBOMOLE program system, we have implemented the BSE approach using a resolution-of-the-identity (RI) approximation for all two-electron electron-repulsion integrals that are required for solving the equation [3]. Symmetry is utilized for the point group D2h and its subgroups, and the BSE approach can be applied in either a spin-restricted or a spin-unrestricted Kohn–Sham formalism. Triplet as well as singlet excited states of closed-shell atoms and molecules can be treated in the spin-restricted formalism. As a side product, our implementation also allows for the application of the RI approximation to the Hartree–Fock exchange contribution that occurs when a hybrid functional is used in time-dependent density-functional theory.

On input, BSE calculations need (Kohn–Sham) orbitals together with quasiparticle energies obtained from a GW calculation. In the present work, we have explored the use of quasiparticle energies obtained from linearized G0W0, eigenvalue self-consistent GW (evGW), and fully quasiparticle self-consistent GW (scGW) calculations. The performance of the GW/BSE approach is assessed by computing singlet and triplet excitation energies of 28 small organic molecules. CPU timings are reported as well.

With respect to total energies (of ground states), we will briefly discuss Ansätze in the framework of the random-phase approximation (RPA), in particular with respect to employing explicitly correlated variants [4].

[1]   D. Jacquemin, I. Duchemin, X. Blase, J. Phys. Chem. Lett. 8, 1524 (2017).
[2]   T. Rangel, S. M. Hamed, F. Bruneval, J. B. Neaton, J. Chem. Phys. 146, 194108 (2017).
[3]   K. Krause, W. Klopper, J. Comput. Chem. 38, 383 (2017).
[4]   A.-S Hehn, C. Holzer, W. Klopper, Chem. Phys. 479, 160 (2016).