An $O(N^3)$ implementation of Hedin's GW approximation for molecules

Peter Koval[1,2], Daniel Sanchez-Portal[1,2], Dietrich Foerster[3]

[1] Centro de Fisica de Materiales, Paseo Manuel Lardizabal, 5, Donostia-San Sebastian, Spain.
[2] Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, Donostia-San Sebastian, Spain.

[3] CPMOH/LOMA, Universite Bordeaux 1, Cours de la Liberation 351, Talence, France.

koval.peter@gmail.com

The knowledge of excitation properties of molecules is crucial in developing organic semiconductor devices. Many-body perturbation theory is one of the most promising theories for characterization of excitations in electronic systems. In particular, Hedin's GW approximation for one-electron Green's function is capable of calculating lumo and homo of molecules with $O(N^3)$ computational complexity like TDDFT.

In this work [1], we implement the Hedin's GW approximation on top of DFT calculations performed with SIESTA [2] code. We apply a dominant product technique [3] to span the space of orbital products and to reduce the dimensionality of dielectric matrix. Moreover, to describe the frequency/time dependence of necessary correlators, we use their spectral functions. The spectral function techniques avoids otherwise necessary analytical continuations and allow for Fast Fourier techniques to be applied in our method. As examples of application, we discuss several results for ionization potentials and electron affinities of large molecules, revealing strengths and limitations of our implementation.

References

[1] D. Foerster, P. Koval, D. Sánchez-Portal, J. Chem. Phys. **Submitted**. arxiv: http://arxiv.org/abs/1101.2065

[2] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, J. Phys. C **14**, 2745 (2002).

[3] P. Koval, D. Foerster, and O. Coulaud, J. Chem. Theory Comput. **6**, 2654 (2010).

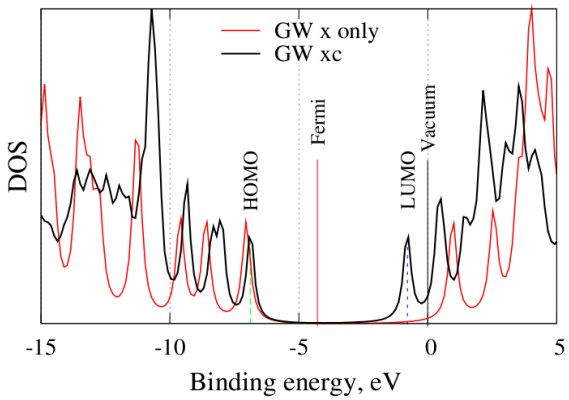

Figure1. The density of states of anthracene molecule computed in two approximations: “GW x-only” – only instantaneous part of self-energy is taken into account, while “GW xc” – the correlation effects due to dynamical screening are taken into account. Please, note that it is the correlation effects make our theoretical anthracene an aceptor, while exchange-only self-energy wrongly predicts our anthracene being donor.