

The linearized GW density matrix

Fabien Bruneval^a

^aService de Recherches de Métallurgie Physique, CEA Saclay, Université Paris-Saclay
fabien.bruneval@cea.fr

The electronic Green's function contains much information, much more than the mere quasiparticle energies. For instance, by contracting the time variables, one obtains the density matrix. Further contracting the space variables, one gets the electronic density. The density matrix gives a direct access to many physical observables: the kinetic energy, the exchange energy, the Hartree energy, the electric field, etc.

Using the GW approximation to the self-energy [1], we have obtained a compact expression for the density matrix that we have named linearized GW density matrix [2]. It allows one to obtain an improved density matrix (and density) directly from “one-shot” calculations. In other words, it is meant as a cheap approximation to the self-consistent GW without actually performing the self-consistency.

The approximation has been implemented in MOLGW [3], a Gaussian basis GW code. The performance of this approximation has been tested on a benchmark of 34 molecules. It gives excellent densities, Hartree, and exchange energies [4], better than quasiparticle self-consistent GW (QSGW) [5]. When used to evaluate the Fock operator, the linearized GW density matrix improves the ionization potential for some simple molecules, such as N₂, by as much as 0.5 eV!

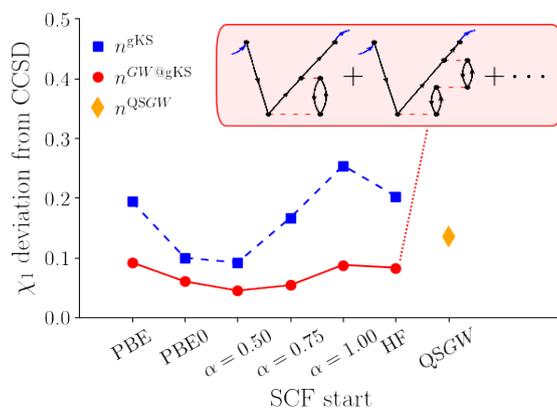


Figure 1: Error in the electronic density averaged over 34 small molecules for different density matrices as a function of the starting mean-field approximation.

References

- [1] L. Hedin, Phys. Rev. 139, A796 (1965).
- [2] F. Bruneval, Phys. Rev. B 99, 041118(R) (2019).
- [3] F. Bruneval, T. Rangel, S.M. Hamed, M. Shao, C. Yang, J.B. Neaton, Computer Phys. Commun. **208**, 149 (2016).
- [4] F. Bruneval, J. Chem. Theory Comput. *just accepted* (2019)
<https://pubs.acs.org/doi/abs/10.1021/acs.jctc.9b00333>
- [5] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).