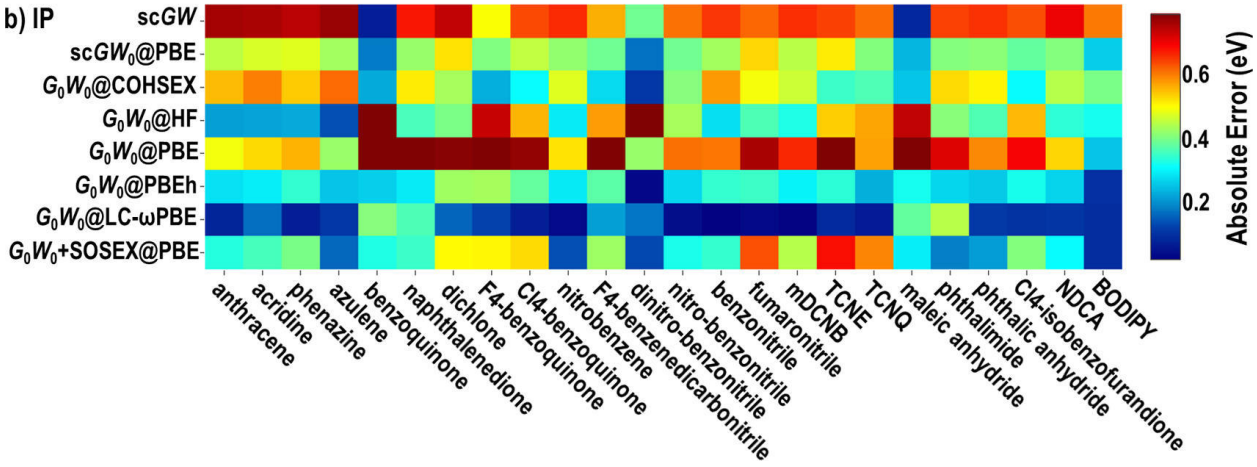
To GW and beyond – from weak to strong correlation

Patrick Rinke

Department of Applied Physics, Aalto University, Helsinki, Finland

Many-body theory in the *GW* approach has become the method of choice for calculating charged excitations in solids and is now also increasingly being applied to molecules. However, fundamental questions regarding its accuracy and applicability remain. In this talk, I will first address the numerical accuracy of perturbative G_0W_0 implementations. I will demonstrate for the GW100 benchmark set of atoms and molecules that different implementations now reach an unprecedented level of agreement [1]. Then I will address absolute as well as relative positions of ionisation energies and electron affinities (see Figure). For some aromatic molecules these are not well reproduced in perturbative G_0W_0 schemes with different starting points as well as in self-consistent *GW* [2]. Sometimes even the orbital order is incorrect [3].



Heat map representation of the absolute errors in eV with respect to CCSD(T) of different *GW* approximations for the ionization potentials of the benchmark molecules[2].

I will analyse these failures in terms of the many-body self-interaction error (also called deviation from the straight line error (DSLE)) [4]. Then I will present a second-order screened exchange correction (SOSEX) that goes beyond *GW* and ameliorates some of the aforementioned problems while keeping the DSLE to a minimum [5]. At the end, I will present latest developments that address strongly correlated systems.

1. M. J. van Setten, *et al.* J. Chem. Theory Comput. 11, 5665 (2015)
2. J. Knight, *et al.*, J. Chem. Theory Comput. 12, 615 (2016)
3. N. Marom, *et al.* Phys. Rev. B 86, 245127 (2012)
4. M. Dauth, F. Caruso, S. Kümmel, and P. Rinke, Phys. Rev. B 93, 121115(R) (2016)
5. X. Ren, N. Marom, F. Caruso, M. Scheffler, and P. Rinke, Phys. Rev. B 92, 081104(R) (2015)