Broken-symmetry fully self-consistent GW: analysis of spin contamination, extraction of effective magnetic Hamiltonians, and evaluation of Neel temperatures in solid antiferromagnets

Pavel Pokhilko[a], Dominika Zgid[a,b]
[a]*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA*
[b]*Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA*

Recently, we applied the thermodynamic Hellmann–Feynman theorem to fully self-consistent Green's function methods, derived two-particle density matrices for molecules, and analyzed electronic structure in terms of two-particle correlators. In this work, we extend this development to solids. Since the conventional measure of spin contamination based on $\langle S^2 \rangle$ is not thermodynamically extensive, we propose two new extensive quantities, $\langle SS_u \rangle$ and $\langle SS_u^{k=0} \rangle$, that are suitable for measuring spin contamination in solids, especially when a convergence to a thermodynamic limit is needed. We show that unlike previous DFT estimates, the unrestricted GW solutions in NiO and MnO are close to the ideal ferromagnetic and broken-symmetry solutions, making extraction of effective magnetic couplings J simple and unambiguous. The found Js agree well with very few available quantitative finite-cluster wave-function calculations for NiO (DDCI2, DDCI3, CASPT2). The constructed effective Hamiltonian can be extrapolated for the strongly correlated states and system sizes that cannot be easily captured by conventional calculations. However, for the description of macroscopic phenomena, such as phase transitions, a direct diagonalization of the extrapolated quantum effective Hamiltonian is not feasible. Instead, we apply a high-temperature expansion for the magnetic susceptibility and heat capacity to this extrapolated Hamiltonian. The radius of convergence of the obtained series determines the Neel temperature T_N. We show that the experimentally observed trend in Neel temperatures in transition metal compounds (NiO, CoO, FeO) is reproduced by broken-symmetry fully self-consistent GW.