Variational formulation of dynamical electronic response functions in Bethe-Salpeter, (screened) Hartree-Fock, Hybrid-DFT approaches

Giovanni Caldarelli[1], **Alberto Guandalini**[1], **Francesco Macheda**[1] **and Francesco Mauri**[1]

[1]*Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 5, I-00185 Rome, Italy*

For the large class of systems described via a time-dependent self-consistent mean field Hamiltonian including (screened) Hartree-Fock exchange, we demonstrate that any electronic linear response function allows for a formulation which is variational in the electronic density matrix. To achieve our goal, we consider the usual form of a response function, written in terms of a screened and a bare electronic vertices ('bare-screen'), and perform an exact rewriting in terms of purely screened electronic vertices ('screen-screen'). Within the 'screen-screen' formulation, the response function can be written as a stationary point of a functional of the exact density matrix. Further, we show that the imaginary part of any electronic response can be written in the form of a generalized Fermi Golden Rule, by introducing an exact complementary rewriting in terms of vertices related by complex conjugation ('screen*-screen'). The proposed approach encompasses different levels of linear response theory, such as time-dependent DFT with hybrid functionals, time-dipendent Hartree-Fock, and the Bethe-Salpeter Equation with the frequency independent approximation of the screened interaction. We demonstrate the effectiveness of our formalism by calculating the optical conductivity of graphene, which exhibits strong excitonic effects, using a tight-binding model including exchange effects in the response. Our findings show the advantages of the variationality of the screen-screen formulation over the others both in convergence properties and robustness with density-matrix approximations.