10 Approximate Functionals from Many-Body Perturbation Theory

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10.1 Motivations

As discussed in previous chapters, one of the main ingredients in TDDFT is the exchange-correlation (xc) kernel, \( f_{xc}(r, r', \omega) \), that includes all the many-body effects beyond the Hartree approximation.

In contrast with the original static derivation of density functional theory (DFT), that is not applicable to excited state properties, TDDFT has become a promising and appealing approach to the study of linear response properties. TDDFT is appealing because \( f_{xc} \) is a functional of the ground-state density only. Moreover, in TDDFT there exists an exact and simple relation between \( f_{xc} \) and the polarization function \( \chi \). TDDFT is promising because it gives excellent results in several cases even using simple approximations for \( f_{xc} \) [Onida 2002]. In particular, the photoabsorption cross section and polarizabilities of simple metal clusters and biomolecules is well reproduced by the standard time-dependent local-density approximation (TDLDA) [Onida 2002, Marques 2003a]. For these systems, like in the case of atoms and molecules, the Hartree term is dominant and the TDLDA only modifies slightly the result of a simpler calculation performed within the random-phase approximation (RPA). However, the scenario changes rapidly if we increase the size of the system towards a periodic structure in one, two, and three dimensions (i.e., polymers, slabs, surfaces, or solids). Difficulties arise, for example, in long conjugated molecular chains, where the strong non-locality of the exact functional is not well reproduced in the local and semi-local approximations. A related problem appears for semiconductors and insulators where these functionals fail to describe the optical absorption experiments. As we will discuss in the next section, the reason for this has been traced to the fact that the xc kernel \( f_{xc} \) should behave asymptotically, in momentum space, as \( 1/q^2 \) when \( |q| \to 0 \) [Onida 2002], which is not the case for the adiabatic LDA or GGA [Perdew 1996b].

An alternative, more traditional, approach to the study of correlation in many-body systems is given by many-body perturbation theory (MBPT) [Abrikosov 1975] where the response function \( \chi \) is expanded in powers of the screened electron-electron interaction \( W \). At variance with TDDFT, \( W \), in MBPT, is a well defined quantity, but there is not a simple relation between \( W \) and \( \chi \). In practical applications, the calculation of \( \chi \) within MBPT
can be cumbersome, but the results are often in very good agreement with experiment, both for finite and infinite systems [Onida 2002].

Thus the question is: can we benefit in some way of the good performance of MBPT to derive a more efficient approximation to $f_{xc}$? In what follows we will discuss different approaches to link TDDFT and MBPT: from the Bethe-Salpeter kernel (Sect. 10.3.1) or using the fully interacting response function (Sect. 10.3.2). Both approaches will be revisited in Sect. 10.4 in the spirit of a more general link between TDDFT and MBPT based on the many-body vertex function and Hedin’s equations. We also discuss some possible ideas for further developments and establish contact with other approaches based on the EXX or the Sham-Schlüter equation.

10.2 Hedin’s Equations and the Vertex Function

MBPT is a rigorous approach to describe the excited-state properties of condensed matter based on the Green’s function method [Abrikosov 1975], and provides a proper framework for accurately computing excited state properties. For example, knowledge of the one-particle and two-particle Green’s functions yields information, respectively, on the quasiparticle (QP) spectrum and optical response of a system.

For details of the Green’s function formalism and many-body techniques applied to condensed matter, we refer the reader to several comprehensive papers in the literature [Onida 2002, Abrikosov 1975, Hedin 1965, Hedin 1999, Hedin 1969, Aryasetiawan 1998, Aulbur 2000, Strinati 1988]. Here we shall just present some of the main equations used for the quasiparticle and optical spectra calculations. (To simplify the presentation, we use in the following atomic units, $e = \hbar = m = 1$.)

The basic brick in a perturbative expansion is the reference, non-interacting system whose Green’s functions $G_0$, that are known, enter in the terms of the perturbative expansion of $G$.

For the sake of simplicity, we consider here a non relativistic $N$-electrons system whose Hamiltonian $\hat{H}$ is decomposed into a non-interacting part plus a term containing the remaining electron-electron interaction. The system is assumed to interact with an external scalar potential through the operator

$$\hat{J}(t) = \int d^3r \, \hat{\psi}^\dagger(r) J(r, t) \hat{\psi}(r).$$

(10.1)

Following the equation of motion approach [Strinati 1988], or alternatively the standard diagrammatic technique [Abrikosov 1975] the exact Green’s function $G$ is found to satisfy the Dyson equation

$$G^{-1}(1, 2) = G_0^{-1}(1, 2) - J(1)\delta(1, 2) - \Sigma(1, 2),$$

(10.2)

that, connecting $G$ to $G_0$, defines the self-energy operator $\Sigma$ (numbers stands for space, time, and spin coordinates).