

# 10 Approximate Functionals from Many-Body Perturbation Theory

A. Marini, R.D. Sole, and A. Rubio

## 10.1 Motivations

As discussed in previous chapters, one of the main ingredients in TDDFT is the exchange-correlation (xc) kernel,  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ , 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  $|q| \rightarrow 0$  [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

$$\hat{J}(t) = \int d^3r \hat{\psi}^\dagger(\mathbf{r}) J(\mathbf{r}, t) \hat{\psi}(\mathbf{r}). \quad (10.1)$$

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

$$G^{-1}(1, 2) = G_0^{-1}(1, 2) - J(1)\delta(1, 2) - \Sigma(1, 2), \quad (10.2)$$

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

$$\Sigma(1, 2) = -i \int d3 \int d4 v_{ee}(1^+, 3) G_2(13, 43^+) G^{-1}(4, 2). \quad (10.3)$$

All operators are in the interaction representation [Abrikosov 1975] ( $\hat{\psi}(1) = \exp\{i\hat{H}t_1\}\hat{\psi}(\mathbf{r}_1)\exp\{-i\hat{H}t_1\}$ ,  $\hat{J}_1(t) = \exp\{i\hat{H}t\}\hat{J}(t)\exp\{-i\hat{H}t\}$ ) and  $G_2$  is the two-particle Green's function

$$G_2(12, 34) = (-i)^2 \langle \Psi | \hat{T} \{ \hat{U} \hat{\psi}(1) \hat{\psi}(2) \hat{\psi}^\dagger(4) \hat{\psi}^\dagger(3) \} | \Psi \rangle, \quad (10.4)$$

with  $\hat{U} = \exp\{-i \int_{-\infty}^{\infty} dt \hat{J}_1(t)\}$ . It is interesting to note that the self-energy  $\Sigma$ , even if directly connected to the single-particle Green's function (10.2) contains a reference to the two-particle Green's function. This is the source of the difficulties in developing simple approximations to  $\Sigma$ , as this corresponds to finding simple approximations to the complicate two-body operator  $G_2$ .

An important step forward in the derivation of simple and efficient approximations to  $\Sigma$  has been done in the Hedin's equations [Hedin 1965, Hedin 1969] where  $G_2$  is rewritten in terms of more "physical" quantities related to microscopic polarization effects. We derive shortly this set of equations using the identity

$$G_2(13, 23^+) = G(1, 2)G(3, 3^+) - \frac{\delta G(1, 2)}{\delta J(3)}, \quad (10.5)$$

and introducing the total potential  $V(1) = J(1) - i \int d3 v_{ee}(1, 3)G(3, 3^+)$ . After some mathematical manipulations of (10.3),  $\Sigma$  can be rewritten as

$$\Sigma(1, 2) \equiv \Sigma_H(1, 2) - i \int d3 \int d4 \int d5 v_{ee}(1^+, 3) G(1, 4) \frac{\delta G^{-1}(4, 2)}{\delta V(5)} \frac{\delta V(5)}{\delta J(3)}. \quad (10.6)$$

Here  $\Sigma_H(1, 2)$  is the Hartree self-energy

$$\Sigma_H(1, 2) = \delta(1, 2) \left[ -i \int d3 v_{ee}(1, 3) G(3, 3^+) \right]. \quad (10.7)$$

Equation (10.6) introduces two important quantities: (i) the scalar (irreducible) vertex function  $\tilde{F}(12, 3)$

$$\tilde{F}(12, 3) \equiv -\frac{\delta G^{-1}(1, 2)}{\delta V(3)}; \quad (10.8)$$

(ii) the inverse (longitudinal) dielectric function  $\epsilon^{-1}$

$$\epsilon^{-1}(1, 2) = \frac{\delta V(1)}{\delta J(2)}. \quad (10.9)$$

The self-energy can be rewritten in terms of  $\tilde{F}$  and  $\epsilon^{-1}$  as

$$\Sigma(1, 2) \equiv \Sigma_{\text{H}}(1, 2) + i \int d3 \int d4 W(1^+, 3) G(1, 4) \tilde{T}(42, 3), \quad (10.10)$$

with  $W(1, 2) = \int d3 \epsilon^{-1}(1, 3) v_{\text{ee}}(3, 2)$  the screened electron-electron interaction.  $\tilde{T}$  is a key quantity in Hedin's equations. The relation between  $\epsilon^{-1}$  and  $\tilde{T}$  follows from the introduction of the reducible polarization function  $\chi$

$$\epsilon^{-1}(1, 2) = \delta(1, 2) + \int d3 v_{\text{ee}}(1, 3) \chi(3, 2), \quad (10.11)$$

with  $\chi(1, 2) = \tilde{\chi}(1, 2) + \int d3 \int d4 \tilde{\chi}(1, 3) v_{\text{ee}}(3, 4) \chi(4, 2)$  and  $\tilde{\chi}$  the irreducible response function

$$\tilde{\chi}(1, 2) \equiv \frac{\delta \langle \hat{n}(1) \rangle}{\delta V(2)} = -i \int d3 \int d4 G(1, 3) G(4, 1) \tilde{T}(34, 2). \quad (10.12)$$

Within the linear response theory formalism, the inverse dielectric function  $\epsilon^{-1}(\omega)$  (10.9) relates the total effective potential to the external perturbation  $v_{\text{ext}}$  applied on an electronic system.  $\chi$  describes the dynamical properties of  $\epsilon^{-1}(\omega)$  relating the charge response ( $\delta n$ ) to the external potential:  $\delta n = \chi \delta v_{\text{ext}}$ .

Now the scheme is clear: once an approximated expression for  $\tilde{T}$  is given the response function  $\chi(1, 2)$  and the self-energy  $\Sigma$  are fully defined.

In practical implementations, the so-called *GW* approximation (GWA), the self-energy operator  $\Sigma$  is taken to be the first order term of a series expansion in terms of the screened Coulomb interaction  $W$  and the dressed Green function  $G$

$$\Sigma(1, 2) = \Sigma_{\text{H}}(1, 2) + iG(1, 2)W(1^+, 2). \quad (10.13)$$

Vertex corrections are not included in this approximation that corresponds to the simplest approximation for  $\tilde{T}$ : the vertex is assumed to be diagonal in space and time coordinates  $\tilde{T}(12, 3) \sim \delta(1, 2)\delta(1, 3)$ . Most ab-initio *GW* applications solve the Dyson equation at the *GW* level non self-consistently, finding the poles of  $G$  corresponding to the quasiparticle energies, while keeping fixed the wavefunctions at the DFT level. This corresponds to the  $G_0W_0$  scheme for the calculation of quasiparticle energies as a first-order perturbation to the Kohn-Sham energy [Aryasetiawan 1998].

### 10.2.1 The Bethe-Salpeter Equation

As we have already discussed, the GWA to the self-energy uses a rather rough approximation to the vertex function. More importantly the corresponding expression for  $\chi$ , the random-phase approximation (RPA), evaluated from (10.12) with  $\tilde{T}(12, 3) \sim \delta(1, 2)\delta(1, 3)$ , does not yield optical absorption spectra in good agreement with experiments for several insulating and

metallic systems [Onida 2002, Albrecht 1998, Benedict 1998a, Rohlfing 1998a, Rohlfing 2000a, Marini 2003a]. The reason is that the absorption intensity is given by the  $\Im[\epsilon(\omega)]$ , that is related to the response function via (10.11). The response function  $\chi$  measures the change in the electronic density induced by the external applied potential. In a non-interacting system the RPA for  $\chi$  is exact, but when self-energy corrections are included the electronic density  $n(1) \equiv -iG(1, 1^+)$  changes and, consequently, the RPA approximation is not valid anymore. This change is reflected in the vertex function, as can be devised from (10.8)

$$\tilde{T}(12, 3) = -\frac{\delta G^{-1}(1, 2)}{\delta V(3)} = \delta(1, 2)\delta(1, 3) + i\frac{\delta[G(1, 2)W(1^+, 2)]}{\delta V(3)} \quad (10.14)$$

Thus, the vertex function can be viewed as the linear response of the self-energy to a change in the total potential of the system. The vertex corrections account for xc effects between an electron and the other electrons in the screening density cloud. In particular this includes the electron-hole attraction (excitonic effects) in the dielectric response. Indeed, neglecting terms proportional to  $\delta W/\delta V$  in (10.14) and using the chain rule we obtain

$$\tilde{\Sigma}(12, 3) = \delta(1, 2)\delta(1, 3) + iW(1, 2)\frac{\delta G(1, 2)}{\delta V(3)}. \quad (10.15)$$

Then using the identity

$$\frac{\delta G(1, 2)}{\delta V(3)} = -\int d4 \int d5 G(1, 4)\frac{\delta G^{-1}(4, 5)}{\delta V(3)}G(5, 2), \quad (10.16)$$

to get the final closed equation for  $\tilde{T}$ :

$$\tilde{T}(12, 3) = \delta(1, 2)\delta(1, 3) + iW(1, 2) \int d6 \int d7 G(1, 6)G(7, 2)\tilde{T}(67, 3). \quad (10.17)$$

This is the Bethe-Salpeter equation (BSE) for the irreducible vertex function. The BSE defines a consistent method to go beyond the RPA. When the vertex  $\tilde{T}$ , solution of (10.2.1), is inserted in (10.12), the corresponding expression for  $\chi$  (and thus for  $\epsilon$ ) describes correctly the experimental spectra for a wide range of materials, including wide-gap insulators characterized by the presence of excitons (bound electron-hole states) [Onida 2002, Albrecht 1998, Marini 2003a]. The Bethe-Salpeter approach to the calculation of two-particle excited states is a natural extension of the GWA for the calculation of one-particle excited states, within the same theoretical framework and set of approximations (the *GW*-BSE scheme). The *GW*-BSE approach has successfully yielded the absorption spectra for a wide range of systems from molecules to nanostructures, from bulk semiconductors to surfaces and one-dimensional polymers and nanotubes [Onida 2002].

### 10.3 The xc Kernel: Different Schemes Based on MBPT

After the short review on MBPT, the aim of this section is to show how the knowledge gleaned in MBPT can be translated into a practical xc kernel, i.e, the challenge is now to construct  $f_{xc}$  using MBPT.

In TDDFT the exact, irreducible, response function is given by [Gross 1996, Petersilka 1996a, Petersilka 1996b]

$$\tilde{\chi}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \chi_{KS}(\mathbf{r}_1, \mathbf{r}_2, \omega) + \int d^3r_3 \int d^3r_4 \chi_{KS}(\mathbf{r}_1, \mathbf{r}_3, \omega) f_{xc}(\mathbf{r}_3, \mathbf{r}_4, \omega) \tilde{\chi}(\mathbf{r}_4, \mathbf{r}_2, \omega), \quad (10.18)$$

with  $f_{xc} \equiv \delta v_{xc} / \delta n$ , and  $\chi_{KS}$  the Kohn-Sham response function. The challenge is now how to link (10.18) with the BSE and construct  $f_{xc}$  using MBPT.

A first difficulty is  $\chi_{KS}$  and the xc potential  $v_{xc}$ . In MBPT there is a clear distinction between the self-energy and the electron-electron interaction effects. To obtain a final response function in agreement with experiment, the single-particle Green's functions entering the BSE *must* have poles corresponding to the physical quasiparticle states (10.2). This is not true in TDDFT, as the exact  $v_{xc}$  is not supposed to give the measurable quasiparticle energies. However, while  $\chi_{KS}$  differs from  $\chi_{QP}$  in MBPT, the final response function is exact in both frameworks. This means that looking at TDDFT from the MBPT point of view, any discrepancy between the KS and quasiparticle eigenvalues must be accounted for by  $f_{xc}$ .

This point had a strong impact on the development of many-body based  $f_{xc}$ 's. Two different classes of approaches can be identified: (i) methods based on approximated xc functionals [Städele 1997, Ullrich 1995a] or on the Sham-Schlüter equation (that impose the many-body density to be equal to the DFT one [Tokatly 2002, Stubner 2004]), (ii) methods that assume that the DFT Green's functions to be the same as the QP ones [Marini 2003b, Adragna 2003, Reining 2002, Sottile 2003, Del Sole 2003, Sottile 2005]. In the first class of methods, the xc potential and the kernel are derived consistently. As a consequence,  $f_{xc}$  contains terms that account for the difference between the bare and the KS states. In the second group of methods, the attention is concentrated on the effect of the electron-hole interaction in order to prove that  $f_{xc}$  can account for the excitonic effects provided by the BSE. To this end, the KS and the QP states are assumed to be the same.

In the next two sections we discuss two methods (contained in the second group of approaches) where the idea is to benefit from the good performance of MBPT response functions. We will analyze, in particular, the many-body properties of  $f_{xc}$  and the relation between its perturbative character and the inclusion of self-energy terms coming from  $v_{xc}$ .

### 10.3.1 Static Long-Range Kernels

A pioneering study of the link between MBPT and TDDFT was done by Reining et al. [Reining 2002], analyzing the structure of the BSE and of (10.18) when both are rewritten in the same electron-hole basis. The point is that the TDDFT equation for  $\tilde{\chi}$  can be expanded in the transition space, i.e., transformed using a basis of pairs of single-particle states. This allowed Reining et al. [Reining 2002] to compare directly (10.19) to the BSE scheme, for which this formulation is naturally adopted [Albrecht 1998, Benedict 1998a, Rohlfing 1998a, Rohlfing 2000a].

To start, we rewrite the Dyson-like matrix equation for  $\tilde{\chi}$  as

$$\hat{\tilde{\chi}}(\mathbf{q}, \omega) = \hat{\chi}_{\text{KS}}(\mathbf{q}, \omega) + \hat{\chi}_{\text{KS}}(\mathbf{q}, \omega) \hat{f}_{\text{xc}}(\mathbf{q}, \omega) \hat{\tilde{\chi}}(\mathbf{q}, \omega), \quad (10.19)$$

with  $\mathbf{q}$  the transferred momentum and  $\hat{\chi}_{\text{KS}}(\mathbf{q}, \omega)$  the matrix of the reciprocal space components of  $\chi_{\text{KS}}$ :

$$[\chi_{\text{KS}}(\mathbf{q}, \omega)]_{\mathbf{G}, \mathbf{G}'} = -\frac{2}{\Omega N_k} \sum_{c\mathbf{k}} \frac{\xi_{c\mathbf{k}}^*(\mathbf{q}, \mathbf{G}) \xi_{c\mathbf{k}}(\mathbf{q}, \mathbf{G}')}{\omega - \varepsilon_{c\mathbf{k}}^{\text{KS}} + \varepsilon_{v\mathbf{k}-\mathbf{q}}^{\text{KS}} + i0^+}. \quad (10.20)$$

Here we have considered only the resonant part (positive energy poles). The oscillators  $\xi$  are given by  $\xi_{c\mathbf{k}}(\mathbf{q}, \mathbf{G}) = \langle c\mathbf{k} | \exp\{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}\} | v\mathbf{k} - \mathbf{q} \rangle$ , in terms of the conduction and valence Kohn-Sham states with energies  $\varepsilon_{c\mathbf{k}}^{\text{KS}}$  and  $\varepsilon_{v\mathbf{k}-\mathbf{q}}^{\text{KS}}$ .

If we introduce the *interacting*, resonant, and irreducible electron-hole Green's function  $\tilde{L}$  as

$$[\tilde{\chi}(\mathbf{q}, \omega)]_{\mathbf{G}, \mathbf{G}'} = -\frac{2}{\Omega N_k} \sum_{\substack{c\mathbf{k} \\ c'\mathbf{v}'\mathbf{k}'}} \xi_{c\mathbf{k}}^*(\mathbf{q}, \mathbf{G}) \xi_{c'\mathbf{v}'\mathbf{k}'}(\mathbf{q}, \mathbf{G}') \tilde{L}_{c\mathbf{k}, c'\mathbf{v}'\mathbf{k}'}(\mathbf{q}, \omega) \quad (10.21)$$

the BSE can be rewritten as an equation for  $\tilde{L}$

$$\hat{\tilde{L}}(\mathbf{q}, \omega) = \hat{L}_{\text{QP}}(\mathbf{q}, \omega) + \hat{L}_{\text{QP}}(\mathbf{q}, \omega) \hat{W}(\mathbf{q}) \hat{\tilde{L}}(\mathbf{q}, \omega), \quad (10.22)$$

with  $[L_{\text{QP}}]_{c\mathbf{k}, c'\mathbf{v}'\mathbf{k}'}(\mathbf{q}, \omega) = i\delta_{cc'}\delta_{vv'}\delta_{\mathbf{k}, \mathbf{k}'}(\omega - \varepsilon_{c\mathbf{k}}^{\text{QP}} - \varepsilon_{v\mathbf{k}-\mathbf{q}}^{\text{QP}} + i0^+)^{-1}$ , in terms of the QP energies ( $\varepsilon^{\text{QP}}$ ). All quantities in (10.22) are matrices in the electron-hole basis.  $\hat{W}(\mathbf{q})$  is the Coulombic part of the Bethe-Salpeter kernel,

$$W_{c\mathbf{k}, c'\mathbf{v}'\mathbf{k}'}(\mathbf{q}) = i\langle c\mathbf{k}, v\mathbf{k} - \mathbf{q} | W(\mathbf{r}_1, \mathbf{r}_2) | c'\mathbf{k}', v'\mathbf{k}' - \mathbf{q} \rangle, \quad (10.23)$$

with  $W(\mathbf{r}_1, \mathbf{r}_2)$  the statically screened electron-hole interaction,  $W(\mathbf{r}_1, \mathbf{r}_2) = \int d^3r_3 \epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3, \omega = 0) v_{ee}(\mathbf{r}_3, \mathbf{r}_2)$ .

Following the same approach, (10.19) can be expanded in the  $|c\mathbf{k}\rangle$  basis using the expression for  $\tilde{\chi}$  given in (10.21)

$$\hat{\tilde{L}}(\mathbf{q}, \omega) = \hat{L}_{\text{KS}}(\mathbf{q}, \omega) + \hat{L}_{\text{KS}}(\mathbf{q}, \omega) \hat{F}(\mathbf{q}) \hat{\tilde{L}}(\mathbf{q}, \omega), \quad (10.24)$$

with

$$[\hat{F}(\mathbf{q}, \omega)]_{cv\mathbf{k}, c'v'\mathbf{k}'} \equiv \sum_{\mathbf{G}, \mathbf{G}'} \xi_{cv\mathbf{k}}(\mathbf{q}, \mathbf{G}) [f_{xc}(\mathbf{q}, \omega)]_{\mathbf{G}, \mathbf{G}'} \xi_{c'v'\mathbf{k}'}^*(\mathbf{q}, \mathbf{G}'). \quad (10.25)$$

A comparison of the TDDFT equation (10.24) and the BSE (10.22) tells us immediately that the BSE and TDDFT equations yield the same spectrum if

$$[F(\mathbf{q})]_{cv\mathbf{k}, c'v'\mathbf{k}'} = -I \delta_{cc'} \delta_{vv'} \delta_{\mathbf{k}\mathbf{k}'} \left[ \varepsilon_{c\mathbf{k}}^{\text{QP}} - \varepsilon_{v\mathbf{k}}^{\text{QP}} - \varepsilon_{c\mathbf{k}}^{\text{KS}} + \varepsilon_{v\mathbf{k}}^{\text{KS}} \right] + W_{cv\mathbf{k}, c'v'\mathbf{k}'}(\mathbf{q}). \quad (10.26)$$

It is important to note that a static  $f_{xc}$  in reciprocal (or real) space follows exactly from (10.26) only if the oscillators  $\xi$  can be inverted in (10.25) generating a one to one relation between  $[f_{xc}]_{\mathbf{G}\mathbf{G}'} \leftrightarrow [F]_{cv\mathbf{k}, c'v'\mathbf{k}'}$ . In practice this has been proved to hold only for a model case [Sottile 2003], while a more general approach presented in [Sottile 2003] has shown how to obtain a frequency-dependent  $f_{xc}$  imposing (10.26) at the level of the response function.

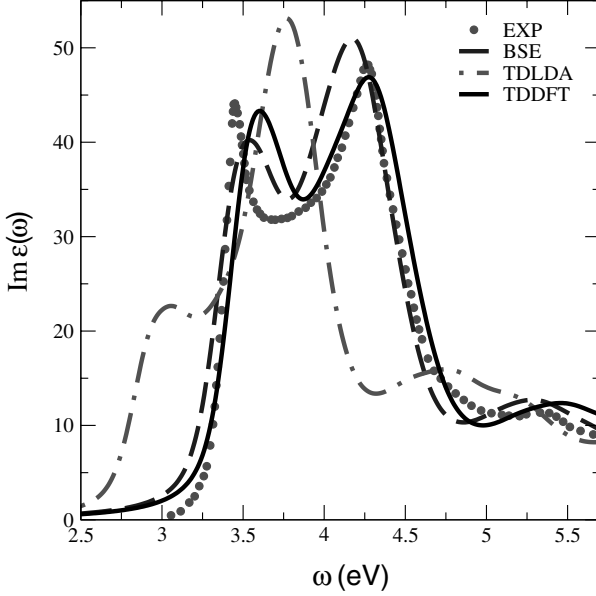
Nevertheless, the static kernel derived by Reining et al. [Reining 2002], given in (10.26) has been of great importance to discuss some of its features, and in particular its long-range behavior. In fact, for valence ( $v, \mathbf{k}$ ) and conduction ( $c, \mathbf{k} + \mathbf{q}$ ) states,  $\xi_{cv\mathbf{k}}(\mathbf{q}, \mathbf{G})$  goes to zero like  $q$  for small  $q$ . Since  $W_{cv\mathbf{k}, c'v'\mathbf{k}'}$  in this limit behaves as a constant, an  $f_{xc}(\mathbf{q}, \mathbf{G} = \mathbf{G}' = 0)$  obtained from (10.26) must behave as  $1/q^2$ . There is in fact a positive long-range contribution stemming from the QP shift of eigenvalues (as also predicted in [Gonze 1997a]), and a negative one resulting from the electron-hole interaction.

To show the crucial importance of the long-range tail of  $f_{xc}$ , a simple calculation using a model  $f_{xc}(\mathbf{r}, \mathbf{r}') \sim -\alpha/|\mathbf{r} - \mathbf{r}'|$ , with the empirical value  $\alpha = 0.2$  works pretty well in the case of silicon (see Fig. 10.1 and the extended discussion in Chap. 20 of this book).

### 10.3.2 A Perturbative Scheme

In the past section we have seen that it is possible to link  $f_{xc}$  with the BSE using the electron-hole basis and comparing directly the TDDFT and Bethe-Salpeter kernel [(10.26)]. An important property of the static kernel of (10.26) and of its dynamical extension [Sottile 2003] is that it is to first order in  $W$ . In this section, we introduce a more general approach for deriving a perturbative expansion of  $f_{xc}$ , without the assumption of linearity between  $f_{xc}$  and  $W$ .

The idea is to benefit from the good performance of MBPT *response functions* and build an  $f_{xc}$  that mimics those results. The kernel  $f_{xc}$  is derived by imposing TDDFT to reproduce the perturbative expansion of the BSE in terms of the screened Coulomb interaction at any order. In practice this



**Fig. 10.1.** Silicon, optical absorption spectra. *Dots*: experiment. *Dot-dashed curve*: TDLDA result. *Dashed curve*: result obtained through the Bethe-Salpeter method. *Continuous curve*: TDDFT result using the long-range model  $f_{xc}$  described in the text. (Adapted from [Reining 2002])

means that we assume  $\hat{\chi}^{\text{KS}}(\mathbf{q}, \omega) = \hat{\chi}^{\text{QP}}(\mathbf{q}, \omega)$ , i.e., the “exact” Kohn-Sham DFT response function is approximated by the independent-quasiparticle response. Second, we *assume* that there exists an  $\hat{f}_{xc}(\mathbf{q}, \omega)$  that reproduces the BSE spectra [Del Sole 2003], i.e., we impose

$$\hat{\chi}^{\text{BSE}}(\mathbf{q}, \omega) \equiv \hat{\chi}^{\text{TDDFT}}(\mathbf{q}, \omega). \quad (10.27)$$

From (10.19) we obtain an equation for the reciprocal-space matrix components of  $f_{xc}$  [Del Sole 2003]

$$\hat{f}_{xc}(\mathbf{q}, \omega) = \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega) \delta \hat{\chi}(\mathbf{q}, \omega) \hat{\chi}^{-1}(\mathbf{q}, \omega), \quad (10.28)$$

with  $\delta \hat{\chi}$  given by  $\hat{\chi} = \hat{\chi}_{\text{KS}} + \delta \hat{\chi}$ . More explicitly, from (10.21) and (10.22) we have

$$\begin{aligned} [\delta \hat{\chi}(\mathbf{q}, \omega)]_{\mathbf{G}, \mathbf{G}'} = & -\frac{2}{\Omega N_k} \sum_{\substack{c_1 v_1 \mathbf{k}_1, c_2 v_2 \mathbf{k}_2 \\ c_3 v_3 \mathbf{k}_3}} \xi_{c_1 v_1 \mathbf{k}_1}^*(\mathbf{q}, \mathbf{G}) \xi_{c_3 v_3 \mathbf{k}_3}(\mathbf{q}, \mathbf{G}') \quad (10.29) \\ & \times [L_{\text{KS}}(\mathbf{q}, \omega)]_{c_1 v_1 \mathbf{k}_1} W_{c_1 v_1 \mathbf{k}_1, c_2 v_2 \mathbf{k}_2} [\tilde{L}(\mathbf{q}, \omega)]_{c_2 v_2 \mathbf{k}_2, c_3 v_3 \mathbf{k}_3}, \end{aligned}$$

with  $L_{\text{KS}} = L_{\text{QP}}$ . From (10.28) it follows that  $f_{\text{xc}}$  is exactly first-order in  $W$  only if  $\delta\hat{\chi}/\hat{\chi} = \mathcal{O}(W)$ , but this is not true in general (as we will see shortly).

To inspect the analytic form of the perturbative series for  $f_{\text{xc}}$  obtained by (10.28) we note that

$$\begin{aligned}\hat{\chi}^{-1}(\mathbf{q}, \omega) &= [\hat{\chi}_{\text{KS}}(\mathbf{q}, \omega) + \delta\hat{\chi}(\mathbf{q}, \omega)]^{-1} \\ &= \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega) - \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega)\delta\hat{\chi}(\mathbf{q}, \omega)\hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega).\end{aligned}\quad (10.30)$$

Thus, (10.28) can be rewritten as an equation for  $f_{\text{xc}}(\mathbf{q}, \omega)$

$$\hat{f}_{\text{xc}}(\mathbf{q}, \omega) = \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega)\delta\hat{\chi}(\mathbf{q}, \omega)\hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega) - \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega)\delta\hat{\chi}(\mathbf{q}, \omega)\hat{f}_{\text{xc}}(\mathbf{q}, \omega).\quad (10.31)$$

The advantage of (10.31) is that, for any order of the perturbative expansion in  $W$ , it is possible to write an iterative form of the  $p$ -th order  $[\hat{f}_{\text{xc}}^{(p)}(\mathbf{q}, \omega)]$  contribution to  $f_{\text{xc}}$ , i.e.,  $\hat{f}_{\text{xc}}(\mathbf{q}, \omega) = \sum_p \hat{f}_{\text{xc}}^{(p)}(\mathbf{q}, \omega)$ , when all the lower order terms of the BSE are known:

$$\begin{aligned}\hat{f}_{\text{xc}}^{(p)}(\mathbf{q}, \omega) &= \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega)\delta\hat{\chi}^{(p)}(\mathbf{q}, \omega)\hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega) \\ &\quad - \sum_{m=1}^{p-1} \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega)\delta\hat{\chi}^{(m)}(\mathbf{q}, \omega)f_{\text{xc}}^{(p-m)}(\mathbf{q}, \omega),\end{aligned}\quad (10.32)$$

when  $p > 1$ , while the 1st order is simply given by

$$\hat{f}_{\text{xc}}^{(1)}(\mathbf{q}, \omega) = \hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega)\delta\hat{\chi}^{(1)}(\mathbf{q}, \omega)\hat{\chi}_{\text{KS}}^{-1}(\mathbf{q}, \omega).\quad (10.33)$$

The scheme proposed in [Reining 2002, Del Sole 2003, Sottile 2003] appears naturally as an approximate solution of (10.32). Moreover in the case of a fully invertible relation between  $f_{\text{xc}}$  and  $F$ , in (10.25), it can be easily shown that only the first order survives in (10.32). This shows the equivalence of the first-order version of (10.31) with the approach of Reining et al. [Reining 2002]. Such an equivalence was rather unexpected, in view of the different assumptions underlying the two methods.

At this stage, it is important to note the work done by Sottile et al. [Sottile 2005] in seeking alternative expressions for  $f_{\text{xc}}^{(1)}$ , based on the flexibility in the definition of  $\chi_{\text{KS}}$  in (10.33). The idea is to use, instead of  $\chi_{\text{KS}}$ , a less singular function that, yielding the same optical spectra, reduces the numerical instabilities and complexity in evaluating  $f_{\text{xc}}^{(1)}$ .

Another, correlated, many-body based approach to  $f_{\text{xc}}$  is through the Sham-Schlüter equation [Sham 1983] (SSE). We refer the reader to the original paper and subsequent extensions [van Leeuwen 1996] for mode details. Here we want to stress that this method links MBPT and TDDFT through the density operator (exact in both schemes). Thus, starting from an expression for the xc energy functional, a perturbative series for  $v_{\text{xc}}$  and  $f_{\text{xc}}$  is consistently derived. As showed by Stubner et al. [Tokatly 2002, Stubner 2004],

the expression for  $f_{xc}^{(p)}$  given in (10.32) is consistent with the SSE when only irreducible single-particle propagators are considered in the perturbative expansion. More importantly, Stubner et al. derive an integral equation for  $f_{xc}$  (derived from the vertex function) that is equivalent to the iterative procedure of (10.32).

As noted by in [Sottile 2003], the first order  $f_{xc}^{(1)}$  allows for a straightforward comparison with the EXX kernel of Kim and Görling [Kim 2002a, Kim 2002b]. Assuming that the EXX-KS states are equal to the Hartree-Fock states, the EXX kernel  $f_x$  corresponds to  $f_{xc}^{(1)}$  with, however,  $W$  replaced by the bare Coulomb interaction. The empirical cutoff in [Kim 2002a, Kim 2002b] can therefore be seen as a way to simulate the missing screening, which would be contained in further correlation terms of their expansion.

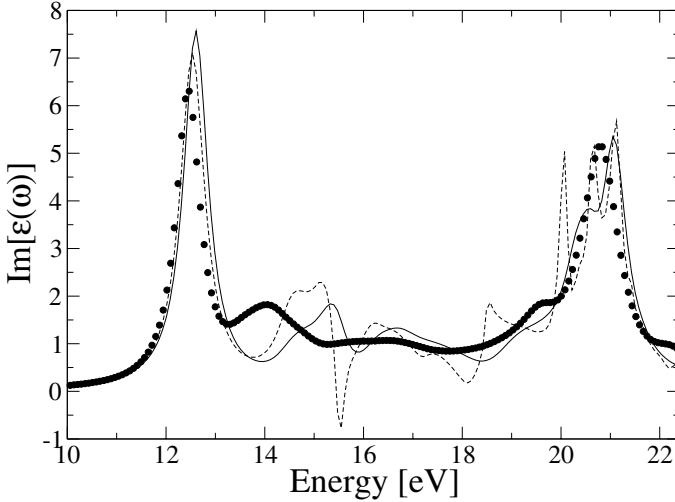
### 10.3.3 The $f_{xc}$ Perturbative Series: Convergence and Cancellations

The theoretical scheme presented in the last section allows to construct  $f_{xc}$  order by order. If the corresponding series converges, the polarization function calculated through the BSE is, by hypothesis, exactly reproduced by TDDFT, (10.19).

However,  $f_{xc}$ , to be useful, should be well described with only a few orders of the perturbative expansion, (10.32). Unfortunately, possible cancellations that can enhance the lower orders terms are difficult to prove from (10.32). We may note that, with the exception of the first order, all other contributions to  $f_{xc}$  [ $\hat{f}_{xc}^{(2)}(\omega)$ ,  $\hat{f}_{xc}^{(3)}(\omega)$ , ...] contain an even number of terms that, as we will see shortly, tend to cancel each other. But this is not enough, as the direct application of (10.32) leads to spurious oscillations in the calculated optical spectra. Those oscillations are moderate in the case of weakly interacting systems (like diamond) but they tend to destroy the spectra for the case of materials with strong electron-hole attraction, like LiF (showed in Fig. 10.2).

The intensity of the oscillations in  $\epsilon(\omega)$  increases with the order of  $\hat{f}_{xc}^{(p)}$  and eventually gives rise to non-physical regions of negative absorption. The reason for this numerical pathology stems from the way the Bethe-Salpeter kernel acts on the spectra: (i) redistributing the optical oscillator strength, (ii) shifting rigidly the spectra to account for the diagonal of the Bethe-Salpeter kernel,  $\Delta_{cv\mathbf{k}}(\mathbf{q}) = W_{cv\mathbf{k},cv\mathbf{k}}(\mathbf{q})$ , that should vanish in the limit of infinite  $\mathbf{k}$ -point sampling. However, with a finite  $\mathbf{k}$ -point grid corresponding to a fully converged BSE spectrum, we get  $\Delta_{\mathbf{q}\rightarrow\mathbf{0}} \sim -0.9$  eV in LiF. The diagonal of  $\hat{W}$  appears in  $f_{xc}$  through a series expansion in  $\Delta_{\mathbf{q}}$ ,  $\hat{f}_{xc}^{\Delta}$  that can be isolated from (10.32). If we note that  $\Delta_{cv\mathbf{k}}(\mathbf{q}) \sim \Delta_{\mathbf{q}}$  for all states ( $cv\mathbf{k}$ ) we obtain

$$\hat{f}_{xc}^{\Delta}(\mathbf{q}, \omega) = - \sum_p \Delta_{\mathbf{q}}^p \frac{\partial^p}{\partial \omega^p} [\hat{\chi}^{\text{KS}}(\mathbf{q}, \omega)]^{-1}. \quad (10.34)$$



**Fig. 10.2.** Optical absorption spectra of LiF. *Dots*: BSE. *Continuous curve*: TDDFT using  $f_{xc}^{(1)}$ . *Dashed curve*: TDDFT using  $f_{xc}^{(1)} + f_{xc}^{(2)}$ . While the first order  $f_{xc}$  reproduces quite well the main features of the BSE spectra, the second (and higher) order approximations to  $f_{xc}$  give unphysical negative absorption intensities

that is meaningful only when  $\Delta_{\mathbf{q}}$  is sufficiently small. This series, in general, oscillates and cannot be treated perturbatively. As this is not the case for  $\text{SiO}_2$  and LiF, natural oscillations are found in the naïve application of the perturbative expansion of (10.32). To circumvent this issue we included the diagonal part of  $\hat{W}(\mathbf{q})$  into the independent QP response function  $\hat{\chi}^{\text{KS}}(\mathbf{q}, \omega)$  and let  $f_{xc}^{(1)}$  account explicitly for the off-diagonal contributions to the Bethe-Salpeter kernel. Using this idea, the higher order corrections to  $f_{xc}^{(1)}$  are not only well defined, but numerically stable for all orders with the same  $\mathbf{k}$ -point sampling used in a standard BSE calculation.

The same holds for the description of the QP-shifts. Indeed, if we do not assume that the QP levels are equal to the KS ones, an additional contribution to  $\Delta(\mathbf{q})$  comes from the difference  $\chi_{\text{QP}} - \chi_{\text{KS}}$  in the form of a positive  $\Delta_{\mathbf{q}}^{\text{QP}}$ , that is small if and only if the QP and the KS energies are very similar. The interpretation of the above result is straightforward: An important gap correction due to a remarkable difference between the QP and the KS energy levels *cannot* be described with a perturbative (read finite order)  $f_{xc}$ .

The clear instability of the  $f_{xc}$  series when gap correction terms are included is extremely meaningful. Even if we consider approaches like the SSE or EXX, where  $v_{xc}$  and  $f_{xc}$  are consistently derived,  $f_{xc}$  will always contain terms that renormalize the electronic gap. In the EXX, for example, the  $f_x$  includes a  $\Delta(\mathbf{q})$  that is related to the difference between the Hartree-Fock self-energy and the EXX potential.

The last point we want to discuss in this paragraph is the numerical evaluation of  $\delta\hat{\chi}^{(1)}(\omega)$  that constitutes the most cumbersome part of  $f_{xc}^{(1)}$ :

$$[\delta\tilde{\chi}^{(1)}(\mathbf{q}, \omega)]_{\mathbf{G}, \mathbf{G}'} = -\frac{2}{\Omega N_k} \sum_{c_1 v_1 \mathbf{k}_1, c_2 v_2 \mathbf{k}_2} \xi_{c_1 v_1 \mathbf{k}_1}^*(\mathbf{q}, \mathbf{G}) \xi_{c_3 v_3 \mathbf{k}_3}(\mathbf{q}, \mathbf{G}') \quad (10.35)$$

$$\times [L_{KS}(\mathbf{q}, \omega)]_{c_1 v_1 \mathbf{k}_1} W_{c_1 v_1 \mathbf{k}_1, c_2 v_2 \mathbf{k}_2} [L_{KS}(\mathbf{q}, \omega)]_{c_2 v_2 \mathbf{k}_2},$$

So we have to perform two square matrix, and two rectangular matrix multiplications for every frequency. However, by looking at the analytic properties of  $\delta\hat{\chi}^{(1)}(\mathbf{q}, \omega)$  (for an explicit expression see [Del Sole 2003]) we can single out the contribution of degenerate non-interacting electron-hole states in (10.35) and write a general expression for  $f_{xc}^{(1)}$  [Marini 2003b]:

$$\hat{f}_{xc}^{(1)}(\mathbf{q}, \omega) = \frac{2}{\Omega} \hat{\chi}_{KS}^{-1}(\mathbf{q}, \omega') \sum_{cv\mathbf{k}} \left[ \frac{\hat{R}_{cv\mathbf{k}}^{(q)} + \hat{R}_{cv\mathbf{k}}^{(q)\dagger}}{\omega' - E_{cv\mathbf{k}}^{(q)} + i0^+} + \frac{\hat{Q}_{cv\mathbf{k}}^{(q)}}{(\omega' - E_{cv\mathbf{k}}^{(q)} + i0^+)^2} \right] \hat{\chi}_{KS}^{-1}(\mathbf{q}, \omega'). \quad (10.36)$$

Here,  $\omega' = \omega + \Delta_{\mathbf{q}}$ ,  $E_{cv\mathbf{k}}^{(q)} = \varepsilon_{c_1 \mathbf{k}_1}^{QP} - \varepsilon_{v_1 \mathbf{k}_1 - \mathbf{q}}^{QP}$ , and the sum runs through all independent electron-hole states with residual

$$[R_{cv\mathbf{k}}^{(q)}]_{\mathbf{G}_1, \mathbf{G}_2} = \sum_{\substack{c' v' \mathbf{k}' \\ E_{c' v' \mathbf{k}'}^{(q)} \neq E_{cv\mathbf{k}}^{(q)}}} \frac{\xi_{cv\mathbf{k}}^*(\mathbf{q}, \mathbf{G}_1) W_{cv\mathbf{k}, c' v' \mathbf{k}'}(\mathbf{q}) \xi_{c' v' \mathbf{k}'}(\mathbf{q}, \mathbf{G}_2)}{E_{cv\mathbf{k}}^{(q)} - E_{c' v' \mathbf{k}'}^{(q)}}, \quad (10.37)$$

for non-degenerate states, and

$$[Q_{cv\mathbf{k}}^{(q)}]_{\mathbf{G}_1, \mathbf{G}_2} = \sum_{\substack{c' v' \mathbf{k}' \\ E_{c' v' \mathbf{k}'}^{(q)} = E_{cv\mathbf{k}}^{(q)}}} \xi_{cv\mathbf{k}}^*(\mathbf{q}, \mathbf{G}_1) W_{cv\mathbf{k}, c' v' \mathbf{k}'}(\mathbf{q}) \xi_{c' v' \mathbf{k}'}(\mathbf{q}, \mathbf{G}_2), \quad (10.38)$$

for degenerate states. Equation (10.36) is very fast to compute as it has the form of a non-interacting polarization function with modified residuals ( $Q$ ,  $R$ ) that are evaluated only once as a result of two simple matrix-vector multiplications. Also, (10.36) can be made causal and be extended to higher orders of the perturbative expansion of  $f_{xc}$ .

## 10.4 The Vertex Function $\tilde{\Gamma}$ : a TDDFT-Based Approach

The validity of the GWA is based on the physical argument that the long-range collective excitations dominate the screening process. Consequently, the screened interaction is assumed to be at the RPA level and any effect due to the direct electron-hole interaction (short-range effects) is neglected.

However, we have seen how strong  $W$  can be, for example, in insulators, where  $\tilde{\chi}$  largely deviates from  $\tilde{\chi}_{\text{RPA}}$ . This corresponds to a non negligible kernel in the BSE, (10.17), that modifies both the polarization function, (10.12) and the self-energy operator, (10.10). The interplay between those two effects has been strongly debated in the last years, using different approximations for  $\tilde{T}$ , and different levels of self-consistency in the solution of the Dyson equation. Regarding the vertex function, two main classes of approximations can be identified: the first reduces the spatial non-locality of  $\tilde{T}$  (the vertex is a three-point function) using two-point DFT-based expressions [Mahan 1989, Hindgren 1997, Del Sole 1994], while the second takes only the first order terms in the vertex expansion [Bobbert 1994, Ummels 1994, Shirley 1996]. While those approximations can be justified in the case of the homogeneous electron gas or simple semiconductors, they are inadequate in the case of wide-gap insulators (e.g., LiF). To discuss more extensively this point, we will present recent approaches to  $\tilde{T}$  that, based on a “cooperation” of MBPT and TDDFT, respect the spatial and dynamical properties of the vertex function, without truncating its perturbative expansion.

We start the derivation recalling the definition of the irreducible response function in terms of  $\tilde{T}$ , (10.12)

$$\tilde{\chi}(1, 2) = -i \int d3 \int d4 G(1, 3) G(4, 1) \tilde{T}(34, 2). \quad (10.39)$$

Even if  $\tilde{T}$  is an highly non-local, three-point function, we have seen in Sect. 10.3.2 that, as long as we are interested in the two-point polarization function  $\tilde{\chi}$ , (10.39) can be cast in terms of  $f_{\text{xc}}$

$$\tilde{\chi}(1, 2) = \chi_{\text{KS}}(1, 2) + \int d3 \int d4 \chi_{\text{KS}}(1, 3) f_{\text{xc}}(3, 4) \tilde{\chi}(4, 2). \quad (10.40)$$

At this point if we take the xc potential corresponding to  $f_{\text{xc}}$  as a local approximation to the self-energy, then the vertex function can be easily contracted into a two-point function:  $\tilde{T}(67, 3) \equiv \tilde{T}_{\text{loc}}(6, 3) \delta(6, 7)$  [Mahan 1989, Hindgren 1997, Del Sole 1994], with

$$\tilde{T}_{\text{loc}}(1, 2) = \left[ \delta(1, 2) - \int d3 f_{\text{xc}}(1, 3) \chi_{\text{KS}}(3, 2) \right]^{-1}. \quad (10.41)$$

Thus (10.10) gives

$$\Sigma(1, 2) = iW_{\text{TDDFT}}(1^+, 2)G_{\text{KS}}(1, 2), \quad (10.42)$$

in terms of the TDDFT effective potential

$$W_{\text{TDDFT}}(1, 2) = \int d3 v_{\text{ee}}(1, 3) \times \left\{ \delta(3, 2) - \int d4 [v_{\text{ee}}(3, 4) + f_{\text{xc}}(3, 4)] \chi_{\text{KS}}(4, 2) \right\}^{-1} \quad (10.43)$$

This expression for the self-energy is extremely appealing and simple to implement in actual calculations [Del Sole 1994]. As an example we take the QP lifetimes, that, for a generic conduction state  $c$  with momentum  $\mathbf{k}$  is given by

$$\begin{aligned} \tau_{c\mathbf{k}}^{-1} = & -2\Omega^{-1} \sum_{\mathbf{G}_1, \mathbf{G}_2} \sum_{\mathbf{q}, c'} \xi_{cc'\mathbf{k}}(\mathbf{q}\mathbf{G}_1) \xi_{cc'\mathbf{k}}^*(\mathbf{q}\mathbf{G}_2) \\ & \times \Im[W_{\text{TDDFT}}(\mathbf{q}, \varepsilon_{c\mathbf{k}} - \varepsilon_{c'\mathbf{k}-\mathbf{q}})]_{\mathbf{G}_1\mathbf{G}_2}, \end{aligned} \quad (10.44)$$

Thus, using the  $f_{xc}$  given in (10.33), we would have a simple expression for  $\Sigma$  that also corresponds to an accurate response function. This is an important difference compared to previous expressions for  $\tilde{I}_{\text{loc}}$  [Hindgren 1997, Mahan 1989, Del Sole 1994] that produce optical spectra very similar to the RPA.

A crucial property of  $f_{xc}$  is its long-range behavior,

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \sim -\frac{\alpha(\omega)}{|\mathbf{r} - \mathbf{r}'|}. \quad (10.45)$$

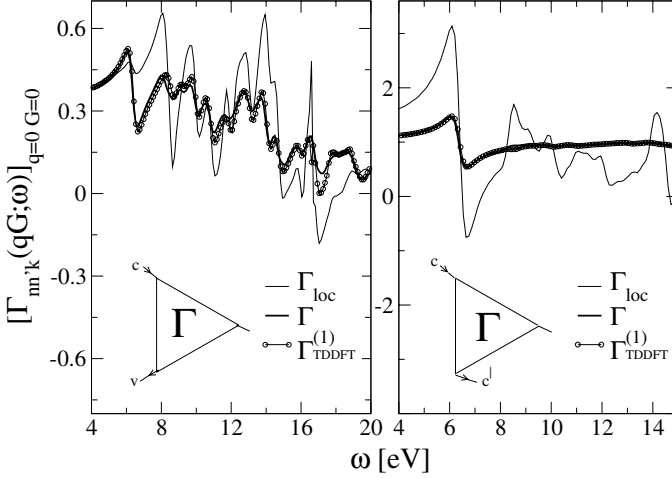
The stronger the electron-hole effects are, the larger is the correction embodied in  $\alpha$ . In the case of wide-gap insulators like LiF there is a large region of frequencies and transfer momenta  $\mathbf{q}$  where  $f_{xc}$  is stronger than the Hartree term (i.e.,  $\alpha > 1$ ). This leads to unphysical linewidths: for a large energy range,  $\Im\Sigma$ , and hence  $\tau^{-1}$ , has the wrong sign! This result is visualized by noticing that with respect to a  $GW$  calculation a change of sign of  $\tau^{-1}$  is controlled by  $\text{sign}(v_{ee} + f_{xc})$ , that is proportional to  $[1 - \alpha(\omega)]$ . A similar result was obtained in [Hindgren 1997] looking at the high  $\mathbf{q}$  limit of the TDLDA kernel that goes as  $f_{xc} \sim q^2$ . The reason for this important failure of the two-point vertex function is connected to the imposed reduction of the non-locality from the original, three-point vertex function. In physical terms,  $\tilde{I}_{\text{loc}}$  overestimates the intensity of the vertex correction because two incoming particles (entering in 1 and 2 in the exact vertex function  $\tilde{I}$ ) are supposed to coexist at the same space-time point.

To overcome this difficulty, we have to release the constraint on the spatial locality, and define a TDDFT vertex function  $\tilde{I}_{\text{TDDFT}}(12, 3)$  such that, for a given approximation of order  $n$  in  $W$ ,  $f_{xc}^{(p)}(1, 2)$ ,  $\tilde{I}_{\text{TDDFT}}$  is consistent with (10.40). By inspecting (10.39) and (10.40) we obtain

$$\tilde{I}_{\text{TDDFT}}^{(1)}(12, 3) \equiv \delta(1, 2)\delta(2, 3) + iW(1, 2) \int d4 G(1, 4)G(4, 2)\tilde{I}_{\text{loc}}(4, 3), \quad (10.46)$$

It is crucial to observe that  $\tilde{I}_{\text{TDDFT}}^{(1)}$  is *not* a first order vertex, as  $\tilde{I}_{\text{loc}}$ , but it sums an infinite number of diagrams. Equation (10.46) can be easily generalized to give higher order approximations for  $\tilde{I}$ , consistent with the high order corrections to  $f_{xc}$ ,  $f_{xc}^{(p)}$ .

As it is commonly done, we neglect dynamical effects in the BSE [Marini 2003a], i.e., we assume  $W(1, 2) \approx W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)$  in (10.46). This static



**Fig. 10.3.** LiF: the exact vertex function  $\tilde{\Gamma}$  is compared with the local approximation  $\tilde{\Gamma}_{\text{loc}}$  and the first-order TDDFT-based  $\tilde{\Gamma}_{\text{TDDFT}}^{(1)}$  in two of the possible scattering configurations. *Left panel:* the vertex describes an electron-hole scattering, involved in the BSE dynamics of an electron-hole pair (polarization function). *Right panel:* the vertex describes an electron-electron scattering, typical of the self-energy process. The dramatic failure of  $\tilde{\Gamma}_{\text{loc}}$  in the right panel, that overestimates the true vertex function, shows the crucial importance of the vertex spatial non-locality

approximation has been showed to be well-motivated when the BSE is used to calculate  $\chi$  [Marini 2003a], while there are no *a priori* reasons to confirm its validity in the vertex case, it remains a reasonable approximation in the present case as the dynamical part of  $W$  is not excited when we consider only low-energy excitations in  $\Sigma$ . This analysis is confirmed by an important property of  $\tilde{\Gamma}_{\text{TDDFT}}^{(p)}$  that can be devised from (10.46) when a dynamical  $W$  is used. From [Marini 2003a] we know that the BSE kernel embodies the correct *unscreening* effect that undresses the QP renormalization factors  $Z$  entering the response function. The very same property, extended to  $\tilde{\Gamma}$  gives the correct  $1/Z$  behavior expected on the basis of the Ward identities [Strinati 1988]. This property suggests and confirms the stringent relation between the dynamical properties of  $\tilde{\Gamma}$  and the self-consistent solution of the Dyson equation.

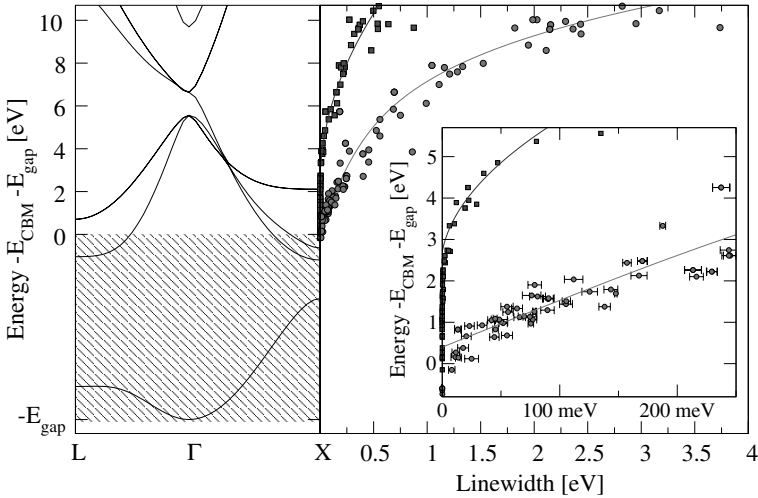
The performance of  $\tilde{\Gamma}_{\text{TDDFT}}^{(1)}$  is exemplified in Fig. 10.3, where the quantity

$$\tilde{\Gamma}_{nn'\mathbf{k}}(\mathbf{q}, \mathbf{G}, \omega) \equiv \int dt \int d^3 r_1 \int d^3 r_2 e^{i[\omega t + (\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}_3]} \varphi_{n\mathbf{k}}^*(\mathbf{r}_1) \varphi_{n'\mathbf{k}-\mathbf{q}}(\mathbf{r}_2) \tilde{\Gamma}(\mathbf{r}_1 \mathbf{r}_2, \mathbf{r}_3, t) \quad (10.47)$$

has been introduced.  $\tilde{\Gamma}_{nn'\mathbf{k}}$  describes the scattering amplitude of two states  $|n\mathbf{k}\rangle$ ,  $|n'\mathbf{k}-\mathbf{q}\rangle$  whose dynamics are governed by the BSE. In the case of

$(n, n') = (c, v)$  ([left panel of Fig. 10.3]) the process is an electron-hole attraction, relevant to the polarization function. From Fig. 10.3 it is clear the  $\tilde{\Gamma}_{\text{loc}}$  is an excellent approximation to the real vertex  $\tilde{\Gamma}$ . This confirms and provides a deeper explanation of the cancellations we have seen in Sect. 10.3.2 that appear in the  $f_{\text{xc}}$  perturbative expansion. However, in the case of  $(n, n') = (c, c')$  ([right panel of Fig. 10.3])  $\tilde{\Gamma}_{\text{loc}}$  dramatically overestimates the real vertex amplitude (as discussed above) while  $\tilde{\Gamma}_{\text{TDDFT}}^{(1)}$  is still a very good approximation to  $\tilde{\Gamma}$ . There is a clear message coming from Fig. 10.3: Even if the vertex function entering the BSE for the response function is analytically identical to the vertex entering the self-energy, the processes described in the two cases are completely different. Consequently, any approximation to  $\tilde{\Gamma}$  derived in a TDDFT context, even if corresponding to a correct response function, must be carefully compared with the real vertex, and the approximation involved (especially the imposed spatial nonlocality) must be attentively verified.

The expression for  $\Sigma$  corresponding to  $\tilde{\Gamma}_{\text{TDDFT}}^{(1)}$  can be calculated explicitly [Marini 2004]. The effect of the vertex corrections on the QP lifetimes of LiF is showed in Fig. 10.4. The overall effect is huge: the linewidths up to 3 eV above the forbidden region display a linear dependence with energy while in the RPA are almost zero because of the slow rise of the RPA loss function. A



**Fig. 10.4.** *Left panel:* calculated DFT band-structure of LiF (here  $E_{\text{CBM}}$  and  $E_{\text{gap}}$  stand for the DFT conduction band minimum energy and the energy gap). *Right panel:* Electron linewidths calculated “on mass-shell” as function of the single-particle energy. *Boxes:* RPA  $G_0W_0$ . *Circles:* TDDFT-based vertex correction to the self-energy, i.e. a  $G_0W\tilde{\Gamma}_{\text{TDDFT}}^{(1)}$  approach that turn out to be very close to a simpler  $G_0W$  calculation (see text). The *dashed* area denotes the forbidden energy region for quasiparticle decay into electron-hole pairs. Error bars represent the theoretical uncertainty. (Adapted from [Marini 2004])

similar energy dependence has been observed in highly correlated materials [Smith 2001]. Instead, the present linear dependence of the linewidths is due to the combination of an almost constant density of states close to the conduction band minimum and to a “step-like” energy dependence of the loss function.

#### 10.4.1 Including Density-Functional Concepts into MBPT

In this section we shortly review a very important step towards the rationalization of previous results, as well as to how to incorporate some concepts from density-functional theory into MBPT, in order to derive simplify expression for the electron self-energy and vertex corrections. The theory has been presented in [Bruneval 2005]. The fundamental idea is that the essential physics to describe excitations is captured in the density variations. Therefore, one can use an alternative chain rule in Hedin’s equations to express  $\delta\Sigma/\delta V$ , namely  $(\delta\Sigma/\delta n)(\delta n/\delta V)$ . By doing that, the equation for the vertex looks like

$$\tilde{\Gamma}(12, 3) = \delta(1, 3)\delta(2, 3) + \frac{\delta\Sigma(1, 2)}{\delta n(4)}\tilde{\chi}(4, 3), \quad (10.48)$$

where  $\tilde{\chi} = \delta n/\delta V$  is nothing but the irreducible polarizability that is usually calculated by solving the Bethe-Salpeter equations discussed above for the vertex function. Integrating with two Green’s functions  $G$ , one obtains

$$\tilde{\chi}(1, 2) = \chi_{\text{KS}}(1, 2) + \chi_{\text{KS}}(1, 3)f_{\text{xc}}^{\text{eff}}(3, 4)\tilde{\chi}(4, 2), \quad (10.49)$$

with  $\chi_{\text{KS}}(12) = -iG(12)G(21)$  and the two-point kernel that appears in the TDDFT-like response function formulation

$$f_{\text{xc}}^{\text{eff}}(3, 4) = -i\chi_{\text{KS}}^{-1}(3, 6)G(6, 5)G(5', 6)\frac{\delta\Sigma(5, 5')}{\delta n(4)}. \quad (10.50)$$

Finally, the self-energy becomes

$$\Sigma(1, 2) = iG(1, 2)W_{\text{TC-TC}}(2, 1) + iG(1, 4)\frac{\delta\Sigma(4, 2)}{\delta n(5)}\chi(5, 3)v_{\text{ee}}(3, 1^+). \quad (10.51)$$

where the reduced polarizability  $\chi$  is obtained by  $\chi = \tilde{\chi} + \tilde{\chi}v_{\text{ee}}\chi$ , and  $W_{\text{TC-TC}} = (1 + v_{\text{ee}}\chi)v_{\text{ee}}$  corresponds to the test-charge test-charge screening function [not to be confused with the test-charge test-electron screen function  $W^{\text{TDDFT}}$  discussed above in the context of a perturbative vertex function  $\tilde{\Gamma}$  in (10.46)]. Following [Bruneval 2005], it is convenient to reformulate the vertex equation as

$$\tilde{\Gamma}(12, 3) = \delta(1, 3)\delta(2, 3) + \delta(1, 2)f_{\text{xc}}(1, 4)\tilde{\chi}(4, 3) + \Delta\tilde{\Gamma}(12, 3), \quad (10.52)$$

where

$$\Delta\tilde{F}(12,3) = \left\{ \frac{\delta\Sigma(1,2)}{\delta n(4)} - \delta(1,2)f_{xc}(1,4) \right\} \tilde{\chi}(4,3). \quad (10.53)$$

The dominant terms in the polarization function dynamics are in fact contained in the first two (one- and two-point) contributions to  $\tilde{F}$ . On the contrary, as discussed in Sect. 10.4, the highly non-local character of  $\tilde{F}$  cannot be neglected in the self-energy operator. Nevertheless, (10.51) is a promising path to go beyond *GW* for many interesting applications as it represents a consistent approach to derive efficient approximations to the vertex function.

From the previous section, it is now clear that the TDDFT  $f_{xc}$  kernel consists of two terms, namely  $f_{xc}^{(1)}$  and  $f_{xc}^{(2)}$ :  $f_{xc}^{(1)}$  changes the Kohn-Sham response function into the independent QP one (band gap problem);  $f_{xc}^{(2)}$  accounts for the electron-hole interaction [Tokatly 2002, Stubner 2004]. By using the *GW* approximation for the self-energy, as it is customary done in the MBPT calculations, we can reproduce an approximate xc kernel [Bruneval 2005] that accounts for the electron-hole part, and looks like

$$\begin{aligned} f_{xc}^{(2)}(3,4) &= f_{xc}^{\text{eff}}(3,4) \\ &= \chi_{\text{KS}}^{-1}(3,6)G(6,5)G(5',6)W(5,5')G(5,7)G(7,5')\chi_{\text{KS}}^{-1}(7,4). \end{aligned} \quad (10.54)$$

This kernel coincides with the approximated kernels presented in previous works [Marini 2003b, Adragna 2003, Reining 2002, Sottile 2003], derived here in a more elegant, DFT-based approach.

## 10.5 Conclusions and Perspectives

In this chapter we have reviewed several promising attempts to include Many-Body effects in the TDDFT xc kernel. As it will be shown in 20 already a first order, simplified kernel provides a very good description of excitonic effects in both extended as well as low dimensional systems. As the present theory stands, the main drawback is the use of the quasiparticle wavefunctions and eigenstates for building the kernel. A major step forward would be to devise an  $f_{xc}$  that describes both effects simultaneously and that can be derived from the functional derivative of a given action functional. Work along those lines is in progress in different groups and we expect some important results to come up in the near future.

In addition to the “standard” use of the TDDFT kernel within the linear response regime we have also discussed how MBPT can benefit of the simple two-points structure of  $f_{xc}$  to derive efficient expressions for the self-energy vertex function. These expressions are promising, as they constitute non perturbative schemes to go beyond the usual *GW* approximation.

In conclusion, the main goal of this chapter is to illustrate that TDDFT and MBPT can be fruitfully combined to provide a better description of correlation effects both in single and in the two-particles dynamics with important application in the predicting power of the *ab-initio* techniques.

# 11 Exact Conditions

K. Burke

## 11.1 Introduction

In this chapter, we collect and discuss several of the exact conditions known about time-dependent density functional theory. The subject of TDDFT is still much less developed than its ground-state counterpart, and this is reflected in the number and usefulness of exact conditions known.

## 11.2 Review of the Ground State

In ground-state DFT, the unknown exchange-correlation energy functional,  $E_{xc}[n]$ , plays a crucial role. In fact, it is really this energy that we typically wish to approximate with some given level of accuracy and reliability, and *not* the density itself. Using such an approximation in a modern Kohn-Sham ground-state DFT calculation, we can calculate the total energy of any configuration of the nuclei of the system, and so extract the bond lengths and angles of molecules, and deduce the lowest energy lattice structure of solids. We can also extract forces in simulations, vibrational frequencies, phonons, and bulk moduli. We can also discover response properties to both external electric fields and magnetic fields (using spin DFT). The accuracy of the self-consistent density is irrelevant to most of these uses.

Given the central role of the energy, it makes sense to devote much effort to its study as a density functional. Knowledge of its behavior in various limits can be crucial to restraining and constructing accurate approximations, and to understanding their limitations. This task is greatly simplified by the fact that the total ground-state energy satisfies the variational principle. Many exact conditions use this in their derivation.

Let us quickly review some of the more prominent exact conditions. They almost all concern the energy functional, which, as mentioned above, is crucial for good KS-DFT calculations. We do not give original references here, but refer the interested reader to [Perdew 2003] for a thorough discussion.

### 11.2.1 Basic Conditions

These conditions are very elementary, and any sensible approximation should satisfy them.

- **Coordinate scaling:** By defining  $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$ , one can easily show

$$E_x[n_\gamma] = \gamma E_x[n]. \quad (11.1)$$

- **Virial theorem:**

$$E_{xc} + T_c = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_{xc}(\mathbf{r}), \quad (11.2)$$

where  $T_c$  is the kinetic contribution to the correlation energy.

- **Coupling constant:** In DFT, one imagines varying the strength of the electron-electron repulsion, while keeping the density fixed, and defines quantities as a function of  $\lambda$ . One finds:

$$E_{xc}^\lambda[n] = \lambda^2 E_{xc}[n_{(1/\lambda)}], \quad (11.3)$$

i.e., altering the coupling constant is simply related to scaling the density.

- **Adiabatic connection formula:** By using the Hellmann-Feynman theorem, one can show:

$$E_c[n] = \int_0^1 d\lambda U_c^\lambda[n]/\lambda, \quad (11.4)$$

where  $U_c^\lambda$  is the potential contribution to the correlation energy.

### 11.2.2 Finite Systems

The next set of conditions are derived for finite systems, just as the Hohenberg-Kohn theorem is.

- **Coordinate scaling:** Coordinate scaling of the correlation is less simple than exchange:

$$\begin{aligned} E_c[n_\gamma] &> \gamma E_c[n] && (\gamma > 1) \\ E_c[n_\gamma] &= E_c^{(2)}[n] + E_c^{(3)}[n]/\gamma + \dots && (\gamma \rightarrow \infty) \\ E_c[n_\gamma] &= \gamma B[n] + \gamma^{3/2} C[n] + \dots && (\gamma \rightarrow 0), \end{aligned} \quad (11.5)$$

where  $E_c^{(2)}[n]$ ,  $E_c^{(3)}[n]$ ,  $B[n]$  and  $C[n]$  are all scale-invariant functionals. Not all popular approximations satisfy these conditions.

- **Self-interaction:** For any one-electron system,

$$E_x[n] = -E_H[n], \quad E_c = 0 \quad (N = 1), \quad (11.6)$$

where  $E_H$  is the Hartree energy.

- **Asymptotic behavior of potential:** Far from a Coulombic system

$$v_{xc}(\mathbf{r}) \rightarrow -1/r \quad (r \rightarrow \infty), \quad (11.7)$$

and

$$\varepsilon_{\text{HOMO}} = -I, \quad (11.8)$$

where  $\varepsilon_{\text{HOMO}}$  is the eigenenergy of the highest occupied KS molecular orbital, and  $I$  the ionization potential. These results are intimately related to the self-interaction of one electron.

- **Lieb-Oxford bound:** For any density,

$$E_{xc} \geq 2.273 E_x^{\text{LDA}}. \quad (11.9)$$

### 11.2.3 Uniform and Nearly Uniform Gas

This last set of conditions involve the properties of the uniform or nearly uniform electron gas.

- **Uniform density:** When the density is uniform,  $E_{xc} = e_{xc}^{\text{unif}}(n) \mathcal{V}$ , where  $e_{xc}^{\text{unif}}(n)$  is the xc energy density of a uniform electron gas of density  $n$ , and  $\mathcal{V}$  is the volume.
- **Slowly varying density:** For slowly varying densities,  $E_{xc}$  should recover the gradient expansion.
- **Linear response of uniform gas:** Another generic limit is when a weak perturbation is applied to a uniform gas, and the resulting change in energy is given by the static response function,  $\chi(q, \omega = 0)$ . This function is known from accurate quantum Monte Carlo calculations [Moroni 1995], and approximations can be tested against it.

### 11.2.4 Finite Versus Extended Systems

Note the distinction above between extended systems (like the uniform gas or any bulk system) and finite systems. The basic theorems of DFT are proven for *finite* quantum mechanical systems, with densities that decay at large distances from the center. Their extension to extended systems, even those as simple as the uniform gas, requires careful thought. For ground-state properties, one can usually take results directly to the extended limit without change, but not always. For example, the high-density limit of the correlation energy in (11.5) fails for a uniform gas.

### 11.2.5 Types of Approximations

Despite a plethora of approximations [Perdew 2005], no present-day approximation satisfies all these conditions, and so one chooses which conditions to impose on a given approximate form. Nonempirical approaches attempt to

fix all parameters via exact conditions [Perdew 1996a, Perdew 1996b], while good empirical approaches might include one or two parameters that are fit to some data set [Becke 1988b, Lee 1988, Becke 1993b].

There are two basic flavors of approximations: pure density functionals, which are often designed to meet conditions on the uniform gas, and orbital-dependent functionals [Grabo 1998], which meet the finite-system conditions more naturally. The most sophisticated approximations being developed today use both [Tao 2003].

## 11.3 Conditions and Approximations

The time-dependent problem is much more diverse than the ground-state problem, making the known exact conditions more difficult to classify. We make the basic distinction between general time-dependent perturbations, of arbitrary strength, and weak fields, where linear response applies. The former give conditions on the xc potential for all time-dependent densities, the latter yield conditions directly on the xc kernel, which is a functional of the ground-state density alone. Of course, all of the former also yield conditions in the special case of weak fields.

### 11.3.1 Role of the Energy

In the time-dependent problem, we do not have the energy playing a central role. Formally, the action plays an analogous role (see Chap. 2), but in practice, we never evaluate the action in TDDFT calculations (as it is identically zero on the real time evolution). In TDDFT, our focus is truly the time-dependent density itself, and so, by extension, the potential determining that density. Thus many of our conditions are in terms of the potential.

Note also that most pure *density* functionals for the ground-state problem produce poor approximations for the details of the potential. Such approximations work well only for quantities integrated over space, such as the energy. Thus approximations that work well for ground-state energies are sometimes very poor as adiabatic approximations in TDDFT. For example their failure to satisfy (11.7) leads to large errors in the KS energies of higher-lying orbitals.

In place of the energy, there are a variety of physical properties that people wish to calculate. On the one hand, quantum chemists are most often focused on first few low-lying excitations, which might be crucial for determining the photochemistry of some biomolecule. Then the adiabatic generalization of standard ground-state approximations is often sufficient (see Chaps. 17, 22 and 23). At the other extreme, very often people who study matter in strong laser fields are very focused on ionization probabilities, and there the violation of (11.8) makes density approximations too crude, and requires orbital-dependent approximations instead.

### 11.3.2 Approximations

As we go through the various exact conditions, we will discuss whether the simplest approximations in present use satisfy them. The most important are:

- **ALDA:** Adiabatic local density approximation, the simplest pure density functional, commonly used in many calculations, and described in Chap. 1.
- **AA:** “Exact” adiabatic approximation, in which we imagine using the exact ground-state potential for a given density (see Chap. 1).
- **EXX:** Exact exchange, the orbital-dependent functional, treated as an implicit density functional (see Chap. 9).

A key aim of today’s methodological development is to build in correlation memory effects. Exact exchange (for more than two unpolarized electrons) has some memory when considered as a density functional. We will discuss two attempts at memory inclusion, both limited to the linear response regime:

- **GK:** The Gross-Kohn approximation is simply to use the local frequency-dependent kernel of the uniform gas,  $f_{xc}^{unif}(q \rightarrow 0, \omega)$  instead of its adiabatic limit as used in ALDA.
- **VK:** The Vignale-Kohn approximation is simply the gradient expansion in the current density for a slowly-varying gas (see Chap. 5).

The approximations suggested in the rest of this Part (Chaps. 8 and 10) could be tested for satisfaction of the conditions below, and perhaps improved.

## 11.4 General Conditions

In this section, we discuss conditions that apply no matter how strong the time-dependent potential is.

### 11.4.1 Adiabatic Limit

The most essential exact condition in TDDFT is the adiabatic limit. For any finite system, or an extended system with a finite gap, the deviation from the instantaneous ground-state during a perturbation (of arbitrary strength) can be made arbitrarily small, by slowing down the time-evolution, i.e., if the perturbation is  $v(t)$ , replacing it by  $v(t/\tau)$  and making  $\tau$  sufficiently large. This is the adiabatic theorem of quantum mechanics.

Similarly, as the time-dependence becomes very slow (or equivalently, as the frequency becomes small), for such system the functionals reduce to their ground-state counterparts:

$$v_{xc}(\mathbf{r}, t) \rightarrow v_{xc}[n(t)](\mathbf{r}) \quad (\tau \rightarrow \infty) \quad (11.10)$$

where  $v_{xc}[n](\mathbf{r})$  is the exact ground-state xc potential of density  $n(\mathbf{r})$ .

Clearly, any adiabatic approximation satisfies this theorem, and so also does EXX, by reducing to their ground-state analogs for slow variations. On the other hand, if an approximation to  $v_{xc}(\mathbf{r}, t)$  were devised that was not based on ground-state DFT, this theorem could be used in reverse to *define* the corresponding ground-state functional.

### 11.4.2 Equations of Motion

In this section, we discuss some elementary conditions that any reasonable TDDFT approximation should satisfy. Because almost all approximations do satisfy these conditions, they are best applied as tests of propagation schemes (see Part III). Satisfaction of these conditions by propagation schemes can be used to interpret their quality. For schemes that do not automatically satisfy a given condition, then a numerical check of its validity provides a test on the accuracy of the solution. A simple analog is the check of the virial theorem in ground-state DFT in a finite basis.

These conditions are all found via a very simple procedure. They begin with some operator that depends only on the time-dependent density, such as the total force on the electrons. The equations of motion for the operator in both the interacting and the KS systems are written down, and subtracted. Since the time-dependent density is the same in both systems, the difference vanishes. Usually, the Hartree term also separately satisfies the resulting equation, and so can be subtracted from both sides, yielding a condition on the xc potential alone. This procedure is well-described in Chap. 5 for the zero xc force theorem.

**Zero xc Force and Torque:** These are very simple conditions saying that interaction among the particles cannot generate a net force [Vignale 1995a, Vignale 1995b]:

$$\int d^3r n(\mathbf{r}, t) \nabla v_{xc}(\mathbf{r}, t) = 0 \quad (11.11a)$$

$$\int d^3r n(\mathbf{r}, t) \mathbf{r} \times \nabla v_{xc}(\mathbf{r}, t) = \int d^3r \mathbf{r} \times \frac{\partial \mathbf{j}_{xc}(\mathbf{r}, t)}{\partial t}, \quad (11.11b)$$

where  $\mathbf{j}_{xc}(\mathbf{r}, t)$  is the difference between the interacting current density and the KS current density [van Leeuwen 2001]. The second condition says that there is no net xc torque, *provided* the KS and true current densities are identical. This is not guaranteed in TDDFT (but is in TDCDFT).

**xc Power and Virial:** By applying the same methodology to the equation of motion for the Hamiltonian, we find [Hessler 1999]:

$$\int d^3r \frac{dn(\mathbf{r}, t)}{dt} v_{xc}(\mathbf{r}, t) = \frac{dE_{xc}}{dt}. \quad (11.12)$$

while another equation of motion yields the virial theorem, which intriguingly has the exact same form as in the ground state, (11.2):

$$E_{\text{xc}}[n](t) + T_{\text{c}}[n](t) = - \int d^3r n(\mathbf{r}, t) \mathbf{r} \cdot \nabla v_{\text{xc}}[n](\mathbf{r}, t). \quad (11.13)$$

These conditions are so basic that they are trivially satisfied by any reasonable approximation, including the ALDA, AA, and EXX. Thus they are more useful as detailed checks on a propagation scheme. The correlation contribution to the latter is very small, and makes a very demanding test. But because the energy does not play the same central role as in the ground-state problem (and the action is *not* simply the time-integral of the energy – see Chap. 2), that is all they are used for so far.

### 11.4.3 Self-Interaction

For any One-Electron System,

$$v_{\text{x}}(\mathbf{r}, t) = - \int d^3r' \frac{n(\mathbf{r}, t')}{|\mathbf{r} - \mathbf{r}'|}, \quad v_{\text{c}}(\mathbf{r}, t) = 0, \quad (N = 1). \quad (11.14)$$

These conditions are automatically satisfied by EXX, but are violated by ALDA, GK, and VK.

### 11.4.4 Initial State Dependence

There is a simple condition based on the principle that *any* instant along a given density history can be regarded as the initial moment [Maitra 2002b, Maitra 2005a] (see Chap. 4). This follows very naturally from the fact that the time-dependent Schrödinger equation is first order. When applied to both interacting and non-interacting systems, we find:

$$v_{\text{xc}}[n_{t'}, \Psi(t'), \Phi(t')](\mathbf{r}, t) = v_{\text{xc}}[n, \Psi(0), \Phi(0)](\mathbf{r}, t) \quad \text{for } t > t', \quad (11.15)$$

This is discussed in much detail in Chap. 4. Here we just mention that any adiabatic approximation, by virtue of its lack of memory and lack of initial-state dependence, automatically satisfies it. Interestingly, although EXX is instantaneous in the orbitals, it will have memory (and so initial-state dependence) as a density functional (when applied to more than two unpolarized electrons).

But this condition provides very difficult tests for any functional with memory. Consider any two known evolutions of an interacting system, which after some time,  $\tilde{t}$ , become identical. This result states they must have identical xc potentials at that time and forever after, even though they had different histories before then. An approximate functional with memory is unlikely, in general, to produce such identical potentials.

### 11.4.5 Coupling-Constant Dependence

Because of the lack of a variational principle for the energy, there is no simple analog of the adiabatic connection formula, (11.4), or definite results as limits are approached, (11.5). But there remains a simple connection between scaling and the coupling constant [Hessler 1999]. For exchange, analogous to (11.1), the relation is linear:

$$v_x[n_\gamma, \Phi_\gamma(0)](\mathbf{r}, t) = \gamma v_x[n, \Phi(0)](\gamma\mathbf{r}, \gamma^2t), \quad (11.16)$$

where  $\Phi(0)$  is the initial state of the Kohn-Sham system and, for time-dependent densities,

$$n_\gamma(\mathbf{r}, t) = \gamma^3 n(\gamma\mathbf{r}, \gamma^2t). \quad (11.17)$$

There is no simple correlation scaling, but we can relate the coupling constant to scaling and find, analogous to (11.4):

$$v_c^\lambda[n, \Psi(0), \Phi(0)](\mathbf{r}, t) = \lambda^2 v_c[n_{(1/\lambda)}, \Psi_{(1/\lambda)}(0), \Phi_{(1/\lambda)}(0)](\lambda\mathbf{r}, \lambda^2t), \quad (11.18)$$

where  $\Psi(0)$  is the initial state of the interacting system. It seems likely that, taking the limit  $\lambda \rightarrow 0$ , makes the exchange term dominant for finite systems (just as in the ground-state) [Hessler 2002], but this has yet to be proven.

### 11.4.6 Translational Invariance

Consider a rigid boost  $\mathbf{R}(t)$  of a system starting in its ground state at  $t = 0$ , with  $\mathbf{R}(0) = d\mathbf{R}/dt(0) = 0$ . Then the exchange-correlation potential of the boosted density will be that of the unboosted density, evaluated at the boosted point, i.e.,

$$v_{xc}[n'](\mathbf{r}, t) = v_{xc}[n](\mathbf{r} - \mathbf{R}(t), t), \quad n'(\mathbf{r}, t) = n(\mathbf{r} - \mathbf{R}(t), t), \quad (11.19)$$

This condition is universally valid [Vignale 1995a], and played a crucial role in the development of the VK approximation.

## 11.5 Linear Response

In the special case of linear response, all information is contained in the kernel. All the general conditions of Sect. 11.4 also yield results for the xc kernel.

### 11.5.1 Adiabatic Limit

For any finite system, the exact kernel satisfies:

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega \rightarrow 0) \rightarrow \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \quad (11.20)$$

where  $E_{xc}$  is the exact xc energy. Obviously, any approximate functional satisfies this, with its corresponding ground-state approximation on the right.

### 11.5.2 Zero Force and Torque

The exact conditions on the potential of Sect. 11.4.2 also yield conditions on  $f_{xc}$ , when applied to an infinitesimal perturbation (see Chap. 5). Taking functional derivatives of (11.11a) yields

$$\int d^3r n(\mathbf{r}) \nabla f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\nabla' v_{xc}(\mathbf{r}') \quad (11.21)$$

and

$$\int d^3r n(\mathbf{r}) \mathbf{r} \times \nabla f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\mathbf{r}' \times \nabla' v_{xc}(\mathbf{r}'), \quad (11.22)$$

the latter again assuming no xc transverse currents.

Again, these are satisfied by ground-state DFT with the static xc kernel, so they are automatically satisfied by any adiabatic approximation. Similarly, in the absence of correlation, they hold for EXX.

The equations employing energies do not produce directly useful results in the linear response regime, because the functional derivative of the exact time-dependent xc energy is not the xc potential.

### 11.5.3 Self-Interaction Error

For one electron, functional differentiation of (11.14) yields:

$$f_x(\mathbf{r}, \mathbf{r}', \omega) = -\frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad f_c(\mathbf{r}, \mathbf{r}', \omega) = 0, \quad (N = 1) \quad (11.23)$$

These conditions are trivially satisfied by EXX, but violated by the density functionals ALDA, GK, and VK.

### 11.5.4 Initial-State Dependence

The initial-state condition, (11.15), leads to very interesting restrictions on  $f_{xc}$  for arbitrary densities. But the information is given in terms of the initial-state dependence, which is very difficult to find.

### 11.5.5 Coupling-Constant Dependence

The exchange kernel scales linearly with coordinates, as found by differentiating (11.16):

$$f_x[n_\gamma](\mathbf{r}, \mathbf{r}', \omega) = \gamma f_x[n](\gamma\mathbf{r}, \gamma\mathbf{r}', \omega/\gamma^2). \quad (11.24)$$

A functional derivative and Fourier-transform of (11.18) yields [Lein 2000b]

$$f_c^\lambda[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', \omega) = \lambda^2 f_c[n_{0,(1/\lambda)}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2). \quad (11.25)$$

A similar condition has recently been derived for the coupling-constant dependence of the vector potential in TDCDFT [Dion 2005].

These conditions are trivial for EXX. They can be used to test the derivations of correlation approximations in cases where the coupling-constant dependence can be easily deduced. More often, they can be used to *generate* the coupling constant dependence when needed, such as in the adiabatic connection formula of (11.4).

### 11.5.6 Symmetry

Because the susceptibility is symmetric, so must also be the kernel:

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}', \mathbf{r}, \omega). \quad (11.26)$$

This innocuous looking condition is satisfied by any adiabatic approximation by virtue of the kernel being the second derivative of an energy, and is obviously satisfied by EXX.

### 11.5.7 Kramers-Kronig

The kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$  is an analytic function of  $\omega$  in the upper half of the complex  $\omega$ -plane and approaches a real function  $f_{xc}(\mathbf{r}, \mathbf{r}', \infty)$  for  $\omega \rightarrow \infty$ . Therefore, defining the function

$$\Delta f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}, \mathbf{r}', \omega) - f_{xc}(\mathbf{r}, \mathbf{r}', \infty), \quad (11.27)$$

we find

$$\Re \Delta f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \mathbb{P} \int \frac{d\omega'}{\pi} \frac{\Im f_{xc}(\mathbf{r}, \mathbf{r}', \omega')}{\omega' - \omega} \quad (11.28)$$

$$\Im f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = -\mathbb{P} \int \frac{d\omega'}{\pi} \frac{\Re \Delta f_{xc}(\mathbf{r}, \mathbf{r}', \omega')}{\omega' - \omega}, \quad (11.29)$$

where  $\mathbb{P}$  denotes the principal part of the integral. Also, since  $f_{xc}(\mathbf{x}, \mathbf{x}')$  is real-valued,

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}^*(\mathbf{r}, \mathbf{r}', -\omega). \quad (11.30)$$

The simple lesson here is that any adiabatic kernel (no frequency dependence) is purely real, and any kernel with memory has an imaginary part (or else is not sensible). Putting it the other way round, to produce a complex kernel requires memory.

Thus, any adiabatic approximation must have a real kernel, which they do. And EXX, to the extent that it has any frequency-dependence (for more than 2 electrons), must have a complex kernel. Both GK and VK have complex kernels satisfying these conditions.

### 11.5.8 Adiabatic Connection

A beautiful condition on the exact xc kernel is given simply by the adiabatic connection formula for the ground-state correlation energy:

$$-\frac{1}{2} \int d^3r \int d^3r' v_{ee}(\mathbf{r}', \mathbf{r}) \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{\pi} [\chi_\lambda(\mathbf{r}, \mathbf{r}', i\omega) - \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', i\omega)] = E_c \quad (11.31)$$

Combined with the Dyson-like equation of Chap. 1 for  $\chi_\lambda$  as a function of  $\chi_{\text{KS}}$  and  $f_{\text{xc}}$ , this is being used to generate new and useful approximations to the ground-state correlation energy (see Chaps. 28, 29 and 30), although at considerable computational cost.

But it provides an obvious exact condition on any approximate xc kernel for *any* system. Thus *every* system for which the correlation energy is known can be used to test approximations for  $f_{\text{xc}}$ . Note that, e.g., using ALDA for the kernel does *not* yield the corresponding  $E_{\text{xc}}^{\text{LDA}}$ , but rather a much more sophisticated functional. Even insertion of  $f_{\text{x}}$  yields correlation contributions to all orders in  $E_c$ . And lastly, even the exact adiabatic approximation,  $f_{\text{xc}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', \omega = 0)$ , does not yield the exact  $E_{\text{xc}}[n_{\text{GS}}]$ . In Chap. 28, this condition is used to test several approximations, but only for the uniform gas.

## 11.6 Finite Versus Extended Systems, and Currents

As mentioned in Sect. 11.2.4, care must be taken when extending exact ground-state DFT results to extended systems. This is even more the case for TDDFT. The first half of the RG theorem (Chap. 1) provides a one-to-one correspondence between potentials and *current* densities, but a surface condition must be invoked to produce the necessary correspondence with densities. With hindsight, this is very suggestive that time-dependent functionals may contain a non-local dependence on the details at a surface. As such, they are more amenable to local approximations in the current rather than the density.

As discussed elsewhere (Chap. 5) and first pointed out by Dobson [Dobson 1994a], the frequency-dependent LDA (GK approximation) violates the translational invariance condition of Sect. 11.4.6. One can trace this failure back to the non-locality of the xc functional in TDDFT. But, by going to a current formulation, everything once again becomes reasonable. The gradient expansion in the current, for a slowly varying gas, was first derived by Vignale and Kohn [Vignale 1996], and later simplified by Vignale, Ullrich, and Conti [Vignale 1997], and is discussed in much detail in Chap. 5.

For our purposes, the most important point is that, by construction, VK satisfies translational invariance. The frequency-dependence shuts off (it reduces to ALDA) when the motion is a rigid translation, but turns on when there is a true (non-translational) motion of the density [Vignale 1996].

### 11.6.1 Gradient Expansion in the Current

Any functional with memory should recover the VK gradient expansion in this limit, or justify why it does not. However, the VK approximation is *only* the gradient expansion. In the ground-state, the gradient expansion in the density was found to give poor results, and afterwards discovered to violate several important sum rules [Burke 1998a]. Fixing those sum-rules led to the development of generalized gradient approximations.

### 11.6.2 Response to Homogeneous Field

A decade ago, GGG [Gonze 1995b] caused a stir by pointing out that the periodic density in an insulating solid in an electric field is insufficient to determine the one-body potential, in apparent violation of the Hohenberg-Kohn theorem [Hohenberg 1964]. In fact, this effect appears straightforwardly in TDCDFT, and is even estimated by calculations using the VK approximation [van Faassen 2003a, Maitra 2003a]. When translated back to TDDFT language, one finds a  $1/q^2$  dependence in  $f_{xc}$ , where  $q$  is the wavevector corresponding to  $\mathbf{r} - \mathbf{r}'$  (see Chaps. 10 and 20). Thus this effect arises naturally in the static limit of TDCDFT (see Chaps. 5 and 19).

However, it implies a need for a kernel that has the same degree of non-locality as the Hartree kernel, and this is missed by any local or semilocal approximation, such as ALDA, but *is* built in to EXX [Kim 2002a] or AA and many-body derived kernels (see Chap. 10).

## 11.7 Odds and Ends

### 11.7.1 Functional Derivatives

A TDDFT result ought to come from a TDDFT calculation, but this is not always the case. By a TDDFT calculation, we mean the result of an evolution of the TDKS equations with some approximation for the xc potential that is a functional of the density. This implies that the xc kernel should be the functional derivative of some xc potential, which also reduces to the ground-state potential in the adiabatic limit.

All the approximations discussed here satisfy this rule. But calculations that intermix kernels with potentials in the solution of Casida's equations violate this condition, and run the risk of violating underlying sum-rules.

### 11.7.2 Infinite Lifetimes of Eigenstates

This may seem like an odd requirement. When TDDFT is applied to calculate a transition to an excited state, the frequency should be real. This is obviously true for ALDA and EXX, but not so clear when memory approximations are

used. As shown in Sect. 11.5.7, Kramers-Kronig relations mean that memory implies imaginary xc kernels, and these can yield imaginary contributions to the transition frequencies. Exactly these effects were seen in calculations using the VUC for atomic transitions [Ullrich 2004]. Indeed, very long lifetimes were found when VUC was working well, and much shorter ones occurred when VUC was failing badly.

### 11.7.3 Single-Pole Approximation for Exchange

This is another odd condition, in which two wrongs make something right. Using Görling-Levy perturbation theory [Görling 1993a], one can calculate the exact exchange contributions to excited state energies [Filippi 1997, Zhang 2004a]. To recover these results using TDDFT, one does *not* simply use  $f_x$ , and solve the Dyson-like equations. As noted in Sect. 11.5.8, the infinite iteration yields contributions to all orders in the coupling constant.

However, the single-pole approximation (SPA) truncates this series after one iteration, and so drops all other orders. Thus, the correct exact exchange results are recovered in TDDFT from the SPA solution to Casida's equations, and *not* by a full solution [Gonze 1999]. This procedure can be extended to the next order [Appel 2003].

## 11.8 Memory Correlation Approximations

The first approximation that went beyond adiabatic is the Gross-Kohn approximation, as mentioned above, which was replaced by the VK approximation, when it was realized that it violated translational invariance.

### 11.8.1 Double Excitations and Branch Cuts

Maitra et al. [Maitra 2004, Cave 2004] argued that a strong  $\omega$ -dependence in  $f_{xc}$  allows double excitation solutions to Casida's equations. Similarly, the second ionization of the He atom implies a branch cut in its  $f_{xc}$  at the frequency needed [Burke 2005a]. Under limited circumstances, this frequency dependence can be estimated, but a generalization [Casida 2005] has been proposed. It would be interesting to check its compliance with the conditions listed in this chapter.

### 11.8.2 Beyond Linear Response

A major point of interest is to go beyond the linear response regime for non-adiabatic approximations. The first such attempt was the bootstrap approach of [Dobson 1997]. More recent attempts are described in Chap. 8 and in [Kurzweil 2004].

## 11.9 Summary

What lessons can we take away from this brief survey?

1. In the ground-state theory, the xc energy dominates, and many conditions are proven for that functional. This is not so for TDDFT.
2. The adiabatic approximation satisfies many exact conditions by virtue of its lack of memory. Inclusion of memory may lead to violations of conditions that adiabatic approximations satisfy. This is reminiscent of the ground-state problem, where the gradient expansion approximation violates several key sum rules respected by the local approximation. Explicit imposition of those rules led to the development of generalized gradient approximations.
3. Explicit density functionals have poor quality potentials, but it is the time-dependent density that counts. The potential is a far more sensitive functional of the density than vice versa. Thus, while we have enumerated many conditions on the xc potential, it is important to determine which conditions significantly affect the density.

As shown in several chapters in this book, many people are presently testing the limits of our simple approximations, and very likely, these or other exact conditions will provide guidance on how to go beyond them.

## Acknowledgments

I gratefully acknowledge support of NSF grant CHE-0355405 and DOE grant DE-FG02-01ER45928, and thank Hardy Gross, Robert van Leeuwen, Giovanni Vignale, and Neepta Maitra for helpful discussions.