

# 1 Basics

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## 1.1 Introduction

Suppose you are given some piece of matter, such as a molecule, cluster, or solid, and you have already solved the ground-state electronic problem highly accurately. You now ask, how can we best calculate the behavior of the electrons when some time-dependent perturbation, such as a laser field, is applied? The direct approach to this problem is to solve the time-dependent Schrödinger equation. But this can be an even more demanding task than solving for the ground state, and becomes prohibitively expensive as the number of electrons grows, due to their Coulomb repulsion.

We will show in this chapter that, under certain quite general conditions, there is a one-to-one correspondence between time-dependent one-body densities  $n(\mathbf{r}, t)$  and time-dependent one-body potentials  $v_{\text{ext}}(\mathbf{r}, t)$ , for a given initial state. That is, a given evolution of the density can be generated by at most one time-dependent potential. This statement, first proven by Runge and Gross [Runge 1984] (RG), is the time-dependent analog of the celebrated Hohenberg-Kohn theorem [Hohenberg 1964]. Then one can define a fictitious system of noninteracting electrons moving in a time-dependent effective potential, whose density is precisely that of the real system. This effective potential is known as the time-dependent Kohn-Sham potential. Just as in ground-state density functional theory (DFT), it consists of an external part, the Hartree potential, and the exchange-correlation potential,  $v_{\text{xc}}(\mathbf{r}, t)$ , which is a functional of the entire history of the density,  $n(\mathbf{r}, t)$ , the initial interacting wavefunction,  $\Psi(0)$ , and the initial Kohn-Sham wavefunction,  $\Phi(0)$ . This functional is a very complex one, much more so than the ground-state case. Knowledge of it implies solution of all time-dependent Coulomb-interacting problems.

In practice, we always need to approximate unknown functionals. An obvious and simple choice for TDDFT is the adiabatic local density approximation (ALDA), sometimes called time-dependent LDA, in which we use the ground-state potential of the uniform gas with that instantaneous and local density, i.e.,  $v_{\text{xc}}^{\text{ALDA}}[n](\mathbf{r}, t) = v_{\text{xc}}^{\text{unif}}(n(\mathbf{r}, t))$ . This gives us a working Kohn-Sham scheme, just as in the ground state. We can then apply this DFT technology to every problem involving time-dependent electrons. These applications fall into three general categories: nonperturbative regimes, linear (and

higher-order) response, and ground-state applications. The rapidly growing number of such applications, and the diversity of systems, ranging from chemistry to biology to materials science, forms the motivation for this book.

The first of these applications involves atoms and molecules in strong laser fields [Marques 2004], in which the field is so intense that perturbation theory does not apply. In these situations, the perturbing electric field is comparable to or much greater than the static electric field due to the nuclei. Experimental aims would be to enhance, e.g., the 27th harmonic, i.e., the response of the system at 27 times the frequency of the perturbing electric field [Christov 1997], or to cause a specific chemical reaction to occur (quantum control) [Rice 2000]. Previously, only one and two electron systems could be handled computationally, as full time-dependent wavefunction calculations are very demanding [Parker 2000]. Crude and unreliable approximations had to be made to tackle larger systems. But with the advent of TDDFT, larger systems with more electrons can now be tackled (see Chaps. 22, 23, 26 and 27).

When the perturbing field is weak, as in typical spectroscopic experiments, perturbation theory applies. Then, instead of needing knowledge of the functional  $v_{xc}[n](\mathbf{r}, t)$  at densities that are changing significantly with time, which might differ substantially from a ground-state density, we only need to know this potential in the vicinity of the initial state, which we take to be a nondegenerate ground-state. These changes are characterized by a new functional, the exchange-correlation kernel [Gross 1985]. The exchange-correlation kernel is much more manageable than the full time-dependent exchange-correlation potential, because it is a functional of the ground-state density alone. Analysis of the linear response then shows [Appel 2003] that the latter is (usually) dominated by the response of the ground-state Kohn-Sham system, but corrected by TDDFT via matrix elements of the exchange-correlation kernel. In the absence of Hartree-exchange-correlation effects, the allowed transitions are exactly those of the ground-state Kohn-Sham potential. But the presence of the kernel shifts the transition frequencies away from the Kohn-Sham values to the true values. The intensities of the optical transitions are also affected by the kernel [Petersilka 1996a, Casida 1996, Rubio 1996].

Several approaches to extracting excitations from TDDFT for atoms, molecules, and clusters are currently being used. The standard approach in quantum chemistry is to very efficiently convert the search for poles of response functions into a large eigenvalue problem [Casida 1996, Görling 1999a, Furche 2005a], in a space of the single-particle excitations of the system. The eigenvalues yield transition frequencies, while the eigenvectors yield oscillator strengths. This allows use of many existing fast algorithms to extract the lowest few excitations (see Chap. 23). In this way, TDDFT has been programmed into most standard quantum chemical packages [Bauernschmitt 1996a] and, after a molecule's structure has been found, it is usually not too costly to extract its low-lying spectrum [Furche 2005c]. Physicists, on the other hand,

tend to solve the time-dependent Kohn-Sham equations by evolving the system in real time in the presence of a weak field [Yabana 1996]. Fourier-transform of the time-dependent dipole matrix element then yields the optical spectrum. Using either methodology, the number of these TDDFT response calculations for transition frequencies is growing exponentially at present [Burke 2005a]. Overall, results tend to be fairly good (0.1 to 0.2 eV errors, typically), but little is understood about their reliability [Furche 2005c]. Challenges remain for the application of TDDFT to solids [Onida 2002], because the present generation of approximate functionals (local and semi-local) lose important effects in the thermodynamic limit, but much work (some reported in this book) is currently in progress.

The last class of application of TDDFT is, perhaps surprisingly, to the ground-state problem. One can extract the ground-state exchange-correlation energy from a response function, in the same fashion as perturbation theory yields expressions for ground-state contributions in terms of sums over excited states, i.e., via the DFT version of the fluctuation-dissipation theorem [Langreth 1975, Gunnarsson 1976]. Thus, any approximation for the exchange-correlation kernel of TDDFT yields an approximation to the exchange-correlation energy,  $E_{xc}$ , of *ground-state* DFT. Although such calculations are significantly more demanding than regular ground-state DFT calculations [Furche 2001c, Fuchs 2002], they produce a natural method for incorporating time-dependent fluctuations in the exchange-correlation energy. In particular, as a system is pulled apart into fragments, this approach includes correlated fluctuations on the two separated pieces. While in principle all this is included in the exact ground-state functional, in practice TDDFT provides a natural methodology for modeling these fluctuations [van Gisbergen 1995, Kohn 1998, Lein 1999].

## 1.2 One-to-One Correspondence

The Runge-Gross paper is usually cited as the beginning of modern TDDFT. There were several calculations before this, including those of Ando [Ando 1977a, Ando 1977b], Peuckert [Peuckert 1978], and of Zangwill and Soven [Zangwill 1980a], as well as proofs of the one-to-one correspondence under more limited conditions [Deb 1982]. But the RG paper established this correspondence for a sufficiently general class of problems to make TDDFT rigorous for most of the subsequent applications.

The evolution of the wavefunction is governed by the time-dependent Schrödinger equation:

$$\hat{H}(t)\Psi(t) = i\frac{d\Psi(t)}{dt}, \quad \Psi(0) \text{ given} \quad (1.1)$$

where  $\hat{H}(t)$  is the Hamiltonian operator. Because this is a first-order differential equation in time, the initial wavefunction must be specified. We consider

$N$  nonrelativistic electrons, mutually interacting via the Coulomb repulsion, in a time-dependent external potential. We write

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (1.2)$$

for the kinetic energy, where the label  $i$  denotes the particle coordinates  $\mathbf{r}_i$ . We use atomic units throughout this chapter ( $e^2 = \hbar = m = 1$ ) and so all distances are in Bohr and energies in Hartrees ( $1 \text{ H} = 27.21 \text{ eV} = 627.5 \text{ kcal/mol}$ ). The electron-electron repulsion is given by

$$\hat{V}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1.3)$$

where the sum is over all pairs, and the factor of  $1/2$  avoids double counting. Last, we denote the one-body potential as

$$\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i, t), \quad (1.4)$$

which differs from problem to problem. For a hydrogenic atom with nuclear charge  $Z$  in an alternating electric field of strength  $\mathcal{E}$  oriented along the  $z$ -axis and of frequency  $\omega$ ,  $v_{\text{ext}}(\mathbf{r}, t) = -Z/r + \mathcal{E} \cdot z \cos(\omega, t)$ . An important point to note is that *only*  $v_{\text{ext}}(\mathbf{r}, t)$  and the particle number differ in the many problems we address; the interparticle repulsion and statistics never change. As the system evolves in time from some initial point (say  $t = 0$ ), its one-particle density changes. This electron density is given by

$$n(\mathbf{r}, t) = N \int d^3r_2 \dots \int d^3r_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t)|^2, \quad (1.5)$$

and has the interpretation that  $n(\mathbf{r}, t)d^3r$  is the probability of finding any electron in a region  $d^3r$  around  $\mathbf{r}$  at time  $t$ . The density is normalized to the number of electrons

$$\int d^3r n(\mathbf{r}, t) = N. \quad (1.6)$$

The analog of the Hohenberg-Kohn theorem for time-dependent problems is the one-to-one correspondence proven by RG [Runge 1984]. We consider  $N$  nonrelativistic electrons, mutually interacting via the Coulomb repulsion, in a time-dependent external potential. The theorem states that the densities  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  evolving from a common initial state  $\Psi(t = 0)$  under the influence of two potentials  $v_{\text{ext}}(\mathbf{r}, t)$  and  $v'_{\text{ext}}(\mathbf{r}, t)$  (both Taylor expandable about the initial time 0) eventually differ if the potentials differ by more than a purely time-dependent ( $\mathbf{r}$ -independent) function:

$$\Delta v_{\text{ext}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t) \neq c(t). \quad (1.7)$$

Under these conditions, there is a one-to-one mapping between densities and potentials, which implies that the potential is a *functional* of the density.

We prove this theorem by first showing that the corresponding current densities must differ. The current density is given by

$$\mathbf{j}(\mathbf{r}, t) = N \int d^3r_2 \dots \int d^3r_N \Im \{ \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \nabla \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \}, \quad (1.8)$$

where  $\Im f$  denotes the imaginary part of  $f$ . One can easily prove continuity from the time-dependent Schrödinger equation, (1.1):

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad (1.9)$$

Return now to the problem of two different systems [i.e.,  $\Delta v_{\text{ext}}(\mathbf{r}, t) \neq c(t)$ ]. Because the corresponding Hamiltonians differ only in their one-body potentials, the equation of motion for the difference of the two current densities is, at  $t = 0$ :

$$\begin{aligned} \frac{\partial}{\partial t} \{ \mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t) \}_{t=0} &= -i \langle \Psi_0 | \left[ \hat{\mathbf{j}}(\mathbf{r}, t), \{ \hat{H}(0) - \hat{H}'(0) \} \right] | \Psi_0 \rangle \\ &= -i \langle \Psi_0 | \left[ \hat{\mathbf{j}}(\mathbf{r}), \{ v_{\text{ext}}(\mathbf{r}, 0) - v'_{\text{ext}}(\mathbf{r}, 0) \} \right] | \Psi_0 \rangle \\ &= -n_0(\mathbf{r}) \nabla \{ v_{\text{ext}}(\mathbf{r}, 0) - v'_{\text{ext}}(\mathbf{r}, 0) \}, \end{aligned} \quad (1.10)$$

where  $n_0(\mathbf{r}) = n(\mathbf{r}, 0)$  is the initial density. Thus we see that if, at the initial time, the two potentials differ (by more than just a constant), the first derivative of the currents must differ. Then the currents will change infinitesimally soon thereafter. One can go further, by repeatedly using the equation of motion, and considering  $t = 0$ , to find [Runge 1984]

$$\frac{\partial^{k+1}}{\partial t^{k+1}} \{ \mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t) \}_{t=0} = -n_0(\mathbf{r}) \nabla \frac{\partial^k}{\partial t^k} \{ v(\mathbf{r}, t) - v'(\mathbf{r}, t) \}_{t=0}. \quad (1.11)$$

If (1.7) holds, and the potentials are Taylor expandable about  $t = 0$ , then there must be some finite  $k$  for which the right hand side of (1.10) does *not* vanish, so that

$$\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t). \quad (1.12)$$

For two Taylor-expandable potentials that differ by more than just a trivial constant, the corresponding currents must be different. This is the first part of the theorem, which establishes a one-to-one correspondence between current densities and external potentials.

In the second part, we extend the proof to the densities. Taking the gradient of both sides of (1.11), and using continuity, (1.9), we find

$$\frac{\partial^{k+2}}{\partial t^{k+2}} \{ n(\mathbf{r}, t) - n'(\mathbf{r}, t) \}_{t=0} = \nabla \cdot \left[ n_0(\mathbf{r}) \nabla \frac{\partial^k}{\partial t^k} \{ v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t) \}_{t=0} \right]. \quad (1.13)$$

Now, if not for the divergence on the right-hand-side, we would be done, i.e., if  $f(\mathbf{r}) = \partial^k \{v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t)\} / \partial t^k|_{(t=0)}$  is nonconstant for some  $k$ , then the density difference must be nonzero.

Does the divergence allow some escape from this conclusion? The answer is no, for any physical density in a finite system. To see this, write

$$\int d^3r f(\mathbf{r}) \nabla \cdot [n_0(\mathbf{r}) \nabla f(\mathbf{r})] = \int d^3r \{ \nabla \cdot [f(\mathbf{r}) n_0(\mathbf{r}) \nabla f(\mathbf{r})] - n_0(\mathbf{r}) |\nabla f(\mathbf{r})|^2 \}. \quad (1.14)$$

The first term on the right may be written as a surface integral at  $r = \infty$ , and vanishes for all realistic potentials (which fall off at least as fast as  $-1/r$ ). If we imagine that  $\nabla f$  is nonzero somewhere, then the second term on the right is definitely negative, so that the integral on the left cannot vanish, and its integrand must be nonzero somewhere. Thus there is no way for  $\nabla f$  to be nonzero, and yet have  $\nabla(n_0 \nabla f)$  vanish everywhere [Gross 1990].

Since the density determines the potential up to a time-dependent constant, the wavefunction is in turn determined up to a time-dependent phase, that in turn cancels out of the expectation value of any operator. Thus the expectation value of any operator is a functional of the time-dependent density and initial state, completing our proof.

### 1.3 Time-Dependent Kohn-Sham Equations

Having established that the one-body potential is a functional of the density and initial state, we next define a fictitious system of noninteracting electrons that satisfy time-dependent Kohn-Sham equations:

$$i \frac{\partial \varphi_j(\mathbf{r}, t)}{\partial t} = \left[ -\frac{\nabla^2}{2} + v_{\text{KS}}[n](\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t), \quad (1.15)$$

whose density,

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}, t)|^2, \quad (1.16)$$

is defined to be precisely that of the real system. By virtue of the one-to-one correspondence proven in the previous section, the potential  $v_{\text{KS}}(\mathbf{r}, t)$  yielding this density is unique. We then *define* the exchange-correlation potential via:

$$v_{\text{KS}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_{\text{H}}(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t), \quad (1.17)$$

where the Hartree potential has the usual form,

$$v_{\text{H}}(\mathbf{r}, t) = \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (1.18)$$

but for a time-dependent density. The exchange-correlation potential is then a functional of the entire history of the density,  $n(\mathbf{r}, t)$ , the initial interacting wavefunction  $\Psi(0)$ , and the initial Kohn-Sham wavefunction,  $\Phi(0)$ . This functional is a very complex one, much more so than the ground-state case. Knowledge of it implies solution of all time-dependent Coulomb interacting problems.

By the arguments of the previous section, if both the interacting and KS initial wavefunctions are nondegenerate ground states, the xc potential is a functional of the time-dependent density alone.

In ground-state DFT, the exchange-correlation potential is the functional derivative of  $E_{xc}[n]$ . It would be nice to find a functional of  $n(\mathbf{r}, t)$  for which  $v_{xc}(\mathbf{r}, t)$  was the functional derivative, called the exchange-correlation action. A plausible action was given in the RG paper [Runge 1984]. However, it turned out later [Gross 1995a] that this action leads to a paradox, namely that the resulting exchange-correlation kernel (see next section) violates causality. Two different solutions to this problem are offered in this volume (see Chaps. 2 and 7). In either case, some generalization of the space of densities is required.

Several extensions and further advances on the Runge-Gross paper will appear later in this book, or have appeared in the literature. Here we make several points:

- **Construction of Potential:** The one-to-one correspondence tells us only that the potential is a functional of the density and initial state, but not what that functional is. Van Leeuwen gives a constructive procedure for finding such a potential, thereby “solving” the representability problem for the time-dependent case (see Chap. 2).
- **Currents:** The first part of the proof produced a one-to-one correspondence between currents and potentials, while to get a density functional, we needed to invoke a surface condition. This renders the application of TDDFT to extended systems nontrivial. We will see later in the book that the first step is easily generalized to produce a one-to-one correspondence between currents and any vector potential (producing time-dependent current density functional theory) and that some effects are indeed highly nonlocal, when expressed as density functionals (see Chap. 5).
- **Allowed Time-Dependence:** The one-to-one correspondence does not apply to the adiabatic switching often assumed in perturbation theory,  $\exp(\gamma t)$ , where  $\gamma \rightarrow 0$ . Such potentials are singular around their initial time ( $-\infty$  in this case). But one can take the adiabatic limit of well-behaved potentials, as described in Sect. 11.4.1.
- **Initial-State Dependence:** Later in this book, it is shown that, while for one electron the initial state wavefunction is completely fixed by requiring it to yield a given density, for two or more electrons, it is possible to find more than one initial wavefunction, thereby producing two different KS potentials for a given evolution (see Chap. 4).

- **Removal of Initial-State Dependence:** Note that a dependence on the initial wavefunction would render TDDFT useless in practice, as we would need a different density functional for every possible initial wavefunction. However, if the initial state is a nondegenerate ground state, then, by virtue of the *Hohenberg-Kohn* theorem, its wavefunction is a functional of the ground-state density alone. Then the time-dependent potential is a functional of the time-dependent density alone. This is the case for almost all practical applications (see Parts IV and V of this volume).

## 1.4 Linear Response

In this section, we show how the TDKS equations, with a given approximation for the xc potential, can be used to extract the electronic excitations of a system. This is a powerful tool for studying, e.g., photoluminescence in biological molecules (see Chap. 23), where the quantitative treatment of the absorption spectrum can be key to identifying the underlying mechanism.

In principle, we already have sufficient technology to do these calculations. Simply perturb the system at time  $t = 0$  with a weak electric field, and then propagate the TDKS equations for a while, evaluating the dipole of interest as you go. The Fourier transform of that function of time is precisely the optical absorption spectrum. In fact, this procedure is followed in many real-time codes, as described in later chapters. However, it is very enlightening and fruitful to analyze the situation in detail using standard linear response theory.

When the perturbing field is weak, as in normal spectroscopic experiments, perturbation theory applies. Instead of needing knowledge of  $v_{\text{xc}}$  for densities that are changing significantly with time, we need only know this potential for densities close to that of the initial state, which we take to be a nondegenerate ground-state. Writing  $n(\mathbf{r}, t) = n_{\text{GS}}(\mathbf{r}, t) + \delta n(\mathbf{r}, t)$ , we have

$$v_{\text{xc}}[n_{\text{GS}} + \delta n](\mathbf{r}, t) = v_{\text{xc}}[n_{\text{GS}}](\mathbf{r}) + \int dt' \int d^3r' f_{\text{xc}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', t - t') \delta n(\mathbf{r}', t'), \quad (1.19)$$

where  $f_{\text{xc}}$  is called the exchange-correlation kernel, evaluated on the ground-state density:

$$f_{\text{xc}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', t - t') = \left. \frac{\delta v_{\text{xc}}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n=n_{\text{GS}}}. \quad (1.20)$$

While still more complex than the ground-state exchange-correlation potential, the exchange-correlation kernel is much more manageable than the full time-dependent exchange-correlation potential, because it is a functional of the ground-state density alone. To understand why  $f_{\text{xc}}$  is important for linear response, define the point-wise susceptibility  $\chi[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', t - t')$  as the

response of the ground state to a small change in the external potential:

$$\delta n(\mathbf{r}, t) = \int dt' \int d^3 r' \chi[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', t - t') \delta v_{\text{ext}}(\mathbf{r}', t'), \quad (1.21)$$

i.e., if you make a small change in the external potential at point  $\mathbf{r}'$  and time  $t'$ ,  $\chi$  tells you how the density will change at point  $\mathbf{r}$  and later time  $t$ . The ground-state Kohn-Sham system has its own analog of  $\chi$ , which we denote by  $\chi_{\text{KS}}$ . This function tells you how the noninteracting KS electrons would respond to  $\delta v_{\text{KS}}(\mathbf{r}', t')$ , which is quite different from the interacting case. But both must yield the same density response:

$$\delta n(\mathbf{r}, t) = \int dt' \int d^3 r' \chi_{\text{KS}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', t - t') \times \{ \delta v_{\text{ext}}(\mathbf{r}', t') + \delta v_{\text{H}}(\mathbf{r}', t') + \delta v_{\text{xc}}(\mathbf{r}', t') \}. \quad (1.22)$$

Equating this density change with that of the interacting system, (1.21), and using the definition of the xc kernel, (1.20), we find the central equation of TDDFT linear response (in frequency space):

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) &= \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) \\ &+ \int d^3 r_1 \int d^3 r_2 \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}_1, \omega) \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right\} \chi(\mathbf{r}_2, \mathbf{r}', \omega), \end{aligned} \quad (1.23)$$

where all objects are functionals of the ground-state density. This is a Dyson-like equation, because it has the same mathematical form as the Dyson equation which relates the one-particle Green's function to its free counterpart via a kernel that is the self-energy.

This equation contains the key to electronic excitations via TDDFT. When  $\omega$  matches a true transition frequency of the system, the response function  $\chi$  blows up, i.e., has a pole as a function of  $\omega$ . Likewise  $\chi_{\text{KS}}$  has a set of such poles, at the single-particle excitations of the KS system:

$$\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) = 2 \lim_{\eta \rightarrow 0^+} \sum_q \left\{ \frac{\xi_q(\mathbf{r}) \xi_q^*(\mathbf{r}')}{\omega - \omega_q + i\eta} - \frac{\xi_q^*(\mathbf{r}) \xi_q(\mathbf{r}')}{\omega + \omega_q - i\eta} \right\} \quad (1.24)$$

where  $q$  is a double index, representing a transition from occupied KS orbital  $i$  to unoccupied KS orbital  $a$ ,

$$\omega_q = \varepsilon_a - \varepsilon_i, \quad (1.25)$$

and

$$\xi_q(\mathbf{r}) = \varphi_i^*(\mathbf{r}) \varphi_a(\mathbf{r}), \quad (1.26)$$

where  $\varepsilon_j$  is the eigenenergy of the KS state  $\varphi_j$ . Thus  $\chi_{\text{KS}}$  is purely a product of the ground-state KS calculation. In the absence of Hartree-exchange-correlation effects,  $\chi = \chi_{\text{KS}}$ , and so the allowed transitions are exactly those

of the ground-state KS potential. But the presence of the kernel in (1.23) shifts the transitions away from the KS values to the true values. Moreover, the strengths of the poles can be simply related to optical absorption intensities (oscillator strengths) and so these are also affected by the kernel.

Casida showed that, for frequency-independent kernels, finding the poles of  $\chi$  is equivalent to solving the eigenvalue problem [Casida 1996]:

$$\sum_{q'} R_{qq'} F_{q'} = \Omega_q^2 F_q, \quad (1.27)$$

The matrix is

$$R_{qq'} = \omega_q^4 \delta_{qq'} + 4\sqrt{\omega_q \omega_{q'}} K_{q,q'}, \quad (1.28)$$

where

$$K_{q,q'} = \int d^3r \int d^3r' \xi_q^*(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \xi_{q'}(\mathbf{r}'). \quad (1.29)$$

In this equation,  $f_{\text{Hxc}}$  is the Hartree-exchange-correlation kernel:

$$f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}'). \quad (1.30)$$

The solution of (1.27) yields the excitation energies  $\Omega$ , while the oscillator strengths can be obtained from the eigenvectors [Casida 1996]. Efficient algorithms exist for extracting just the lowest transitions. It is in this form that most quantum chemical codes extract TDDFT excitations.

A simple approximate solution to the TDDFT linear response equations is the single-pole approximation (SPA) [Petersilka 1996a], in which the TDDFT corrections to a given transition are included, but not its coupling to the other KS transitions. This amounts to neglecting all other poles in  $\chi_{\text{KS}}$ , or simply taking the diagonal matrix elements in Casida's equations:

$$\Omega^4 \approx \omega_q^4 + 4 \omega_q K_{q,q}, \quad (1.31)$$

While not needed numerically, the SPA yields much insight into how and why TDDFT produces the results it does [Appel 2003], and will be used in several occasions in this book.

## 1.5 Adiabatic Connection Formula

Lastly, we discuss how TDDFT produces sophisticated approximations to the *ground-state* exchange-correlation energy. Almost thirty years ago, the fluctuation-dissipation theorem was applied carefully in DFT. The resulting adiabatic connection fluctuation-dissipation formula is:

$$E_{\text{xc}}[n_{\text{GS}}] = -\frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ \times \int_0^\infty \frac{d\omega}{\pi} \{ \chi_\lambda[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', \omega) + n_{\text{GS}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \} \quad (1.32)$$

where the coupling-constant  $\lambda$  is defined to multiply the electron-electron repulsion in the Hamiltonian, but the external potential is adjusted to keep the density fixed [Langreth 1975, Gunnarsson 1976].

This intriguing formula means that approximations in TDDFT can be used to yield approximations to the ground-state xc energy functional, by constructing  $\chi_\lambda$  from the  $\lambda$ -dependent generalization of (1.23). This scheme is much more computationally demanding than a regular ground-state DFT calculation with, e.g., a GGA, but can naturally accommodate effects that are difficult to capture with simple ground-state functionals. For example, van der Waals interactions are very naturally described in this scheme [Kohn 1998], as the correlated fluctuations between distant atoms or molecules are correctly described by the frequency-dependent contributions. Furthermore, ground-state DFT has difficulty describing how bonds break as a function of bond length, because the single Slater determinant of KS DFT is a poor representation of the interacting (Heitler-London) wavefunction of separated atoms [Perdew 1995]. But TDDFT treatments of the adiabatic connection formula can yield the entire dissociation curve [Fuchs 2002].

## 1.6 Adiabatic Approximation

Although the one-to-one correspondence has given us in principle an exact description of many-electron quantum mechanics in a time-dependent potential, it yields no hint of the missing density functional. By constructing a set of time-dependent KS equations, a significant fraction of that missing functional is included exactly. But the scheme is incomplete without some approximation to the missing xc potential.

As we have noted, the exact exchange-correlation potential depends on the entire history of the density, as well as the initial wavefunctions of both the interacting and the Kohn-Sham systems:

$$v_{\text{xc}}[n, \Psi(0), \Phi(0)](\mathbf{r}, t) = v_{\text{KS}}[n, \Psi(0), \Phi(0)](\mathbf{r}, t) - v_{\text{ext}}(\mathbf{r}, t) - v_{\text{H}}[n](\mathbf{r}, t). \quad (1.33)$$

However, in the special case of starting from a nondegenerate ground state (both interacting and noninteracting), the initial wavefunctions themselves are functionals of the initial density, and so the initial-state dependence disappears. This is the usual case in which TDDFT is used. But even then, the exchange-correlation potential at  $\mathbf{r}$  and  $t$  has a functional dependence not just on  $n(\mathbf{r}, t)$  but on all  $n(\mathbf{r}, t')$  for  $0 \leq t' \leq t$ , and for arbitrary points  $\mathbf{r}'$  in space. Thus the potential *remembers* the density's past, and we say it has memory.

The adiabatic approximation is one in which we ignore all dependence on the past, and allow only a dependence on the instantaneous density:

$$v_{\text{xc}}^{\text{adia}}[n](\mathbf{r}, t) = v_{\text{xc}}^{\text{approx}}[n(t)](\mathbf{r}), \quad (1.34)$$

i.e., it approximates the functional as being local in time. If the time-dependent potential changes very slowly (adiabatically), this approximation will be valid. But the electrons will remain always in their instantaneous ground state. To make the adiabatic approximation exact for the only systems for which it can be exact, we require

$$v_{\text{xc}}^{\text{adia}}[n](\mathbf{r}, t) = v_{\text{xc}}^{\text{GS}}[n_{\text{GS}}](\mathbf{r})|_{n_{\text{GS}}(\mathbf{r}')=n(\mathbf{r}', t)}, \quad (1.35)$$

where  $v_{\text{xc}}^{\text{GS}}[n_{\text{GS}}](\mathbf{r})$  is the *exact* ground-state exchange-correlation potential of the density  $n_{\text{GS}}(\mathbf{r})$ . This is the analog of the argument made to determine the function used in LDA calculations for the ground-state energy: The only sensible choice there is the xc energy of the uniform electron gas. Throughout this book, we will see many successes of this approximation, but some striking failures also.

In practice, the spatial nonlocality of the functional is also approximated, since we do not know the exact xc energy functional, even in the static case. As mentioned above, the ALDA is the mother of all TDDFT density approximations, but any ground-state functional, such as a GGA or hybrid, automatically yields an adiabatic approximation for use in TDDFT calculations.

The adiabatic approximation is particularly simple for linear response, yielding an xc kernel of the form:

$$f_{\text{xc}}^{\text{adia}}[n_{\text{GS}}](\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta v_{\text{xc}}^{\text{GS}}[n_{\text{GS}}](\mathbf{r})}{\delta n_{\text{GS}}(\mathbf{r}')} \delta(t - t'), \quad (1.36)$$

i.e., it is completely local in time. When Fourier-transformed, this implies that  $f_{\text{xc}}^{\text{adia}}(\omega)$  is *frequency-independent*.

By construction, ALDA should work only for systems with very small density gradients in space and time. It may seem like a drastic approximation to neglect all nonlocality in time. However, the success of modern ground-state density functional theory can be traced to how well LDA works beyond its obvious range of validity, due to satisfaction of sum rules, etc., and how its success was built upon with GGA's and hybrids [Perdew 2005]. We will see in the chapters concerned with applications that some of the same magic applies in TDDFT ALDA calculations.

## 1.7 Relation to Ground-State DFT

Time-dependent DFT is *not* a simple extension of ground-state DFT. It is an application of DFT philosophy to the world of driven systems, i.e., to

the time-dependent Schrödinger equation, a first-order differential equation in time. Thus while many of the statements look similar, the functionals themselves contain greatly different physics.

On the other hand, TDDFT calculations enhance our knowledge and understanding gained from ground-state DFT calculations. One of the most important applications is to produce a spectroscopic signature of a given molecule, not just its thermochemistry and geometric structure. An important example is the interpretation of KS orbital eigenvalues. In ground-state DFT, it was often said that, apart from the highest occupied molecular orbital (HOMO), these had no direct physical significance. With the advent of TDDFT, we can see that they are a zero-order approximation to the optical excitation energies.

