WHAT IS TIME-DEPENDENT DENSITY FUNCTIONAL THEORY? SUCCESSES AND CHALLENGES

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Abstract We discuss ongoing projects in ground-state density functional theory (DFT) before introducing some basic concepts in time-dependent DFT (TDDFT). The accuracy of simple approximations to transition frequencies and oscillator strengths is analyzed, developing scattering theory within TDDFT is discussed, and the importance of memory in fully time-dependent calculations is emphasized.

1. Introduction: ground-state DFT

Since its birth in the 1960's (Hohenberg and Kohn, 1964) and especially with the developments in recent years (Kohn, 1999), density functional theory (DFT) has been enormously successful for calculating the electronic structure and properties of ground-state systems. Modern DFT is in principle an exact theory, built on the firm foundation of the Hohenberg-Kohn theorem (1964): the ground-state density $n(\mathbf{r})$ of an interacting N-electron system in a static external potential completely determines all of its properties (e.g. energy, bond lengths, excited states). From a practical point of view, the power of DFT lies in the mapping of the interacting system to a fictitious non-interacting system of the same ground-state density, the Kohn-Sham system. The Kohn-Sham orbitals experience a one-body effective potential functional $v_{\rm S}[n](\mathbf{r})$ and so the calculation reduces to solving self-consistently N one-particle Schrödinger equations, finally producing the exact density of the true interacting system. In practical calculations, the exact Kohn-Sham potential is unknown and approximations must be made. Popular approximate functionals include the local spin-density approximation (Kohn and Sham, 1965) (particularly ubiquitous in solid-state calculations), generalized gradient approximations such as PBE (Perdew,

Burke, and Ernzerhof, 1996) (becoming increasingly popular in quantum chemistry), and empirical hybrids such as B3LYP (Becke, 1998, 1993; Lee,Yang, and Parr, 1988) (perhaps the most used in quantum chemistry).

In the Rutgers DFT group, there are many projects underway to investigate and further improve the functionals used in ground-state DFT. We mention here a few of these projects. Consider the strictly correlated limit: studying what happens when electron-electron repulsion becomes infinite should help guide the construction of new functionals (Magyar, Terilla, Burke, 2001). We are calculating unambiguously the exchange-correlation energy density (Burke, Cruz and Lam, 1998) in molecules in order to visualize bond formation as well as to study functionals. We are studying properties of the non-interacting kinetic energy density (Larkin et al., 2001), to investigate the validity of the von Weisacker functional and to shed some light on the construction of a good kinetic energy functional. We are developing a new tool to study systems in which the spins are not equivalent, such as magnetic systems: by independently scaling the spin densities, one can analyze the behaviour of the correlation energy for various polarizations and test whether approximate functionals follow this behaviour (Whittingham, Magyar, and Burke, 2001). The problem of degenerate ground-states is being investigated through a superhamiltonian approach (Katriel, Zahariev and Burke, 2001).

2. What is TDDFT?

The time-dependent Schrödinger equation,

$$\hat{H}(t)\Psi(t) = i\dot{\Psi}(t), \tag{1}$$

where the dot indicates a time derivative, gives the solution to the many-body wavefunction for a given initial state $\Psi(0)$. The Hamiltonian $\hat{H}$ is the sum of the kinetic energy operator, the Coulomb repulsion, and an external time-varying one-body potential, $v_{\text{ext}}(\mathbf{r}, t)$. For more than very few electrons, the two-body Coulomb potential makes this a nightmare to solve.

The success of DFT methods for ground-state properties encouraged a search for a time-dependent theory of a similar flavor (TDDFT). This came to fruition with the Runge-Gross theorem (1984): for a given initial state, there is a unique mapping between the evolving density and the time-dependent potential. A non-interacting system of the same density may be defined, whose evolution is described by time-dependent Kohn-Sham equations where the orbitals evolve under a time-dependent one-

body potential functional $v_{\rm S}[n;\Phi(0)](\mathbf{r}t)$:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm S}[n;\Phi(0)](\mathbf{r},t)\right\}\phi_i(\mathbf{r}t) = i\dot{\phi}_i(\mathbf{r}t) \tag{2}$$

$$n(\mathbf{r}t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}t)|^2 \tag{3}$$

$$v_{\rm S}[n;\Phi(0)](\mathbf{r}t) = v_{\rm ext}[n;\Psi(0)](\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}[n;\Psi(0),\Phi(0)](\mathbf{r}t) \tag{4}$$

As in the ground-state case, this fictitious system of non-interacting electrons is far faster to solve than the full interacting problem, and, in principle, yields everything we would want to know about the exact interacting problem. Any quantity that depends only on the time-dependent density is given exactly, while exact formulas for other expectation values can be written down. In any practical calculation, we must make approximations for the exchange-correlation potential. The most popular in use today is the adiabatic local density approximation (ALDA), which uses the potential for a uniform gas of electrons of density $n(\mathbf{r}t)$:

$$v_{\rm XC}^{\rm ALDA}(\mathbf{r}t) = v_{\rm XC}^{\rm unif}(n(\mathbf{r}t)), \tag{5}$$

as was used in the historic calculations of Zangwill and Soven (1980), and Ando (1977). This approximation should work well for a system beginning in its ground state which varies slowly in time and space. It is on shaky ground in the general case however: in particular, because it has no memory. We shall come back to this point shortly, and demonstrate a drastic consequence of this lack of memory.

3. Applications of TDDFT

There is an exponentially increasing use of TDDFT in chemistry and in physics as described in the recent reviews of Burke and Gross (1998), and Maitra et al. (2001). Most of the calculations are in the linear response regime, which is discussed in the next section. For example, there are many calculations of electronic excitations in atoms and molecules (Appel, Burke, and Gross (2001)) and this is now built into many commercial chemical codes such as Gaussian, where ALDA is used. There have been the first few optical response calculations in solids (Bertsch et al., 2000; Kootstra, de Boeij, and Snijders, 2000). Within TDDFT, one is now able to calculate van der Waal's forces (Andersson, Langreth, and Lunqvist, 1996), whose origin lies in small time-dependent fluctuations;

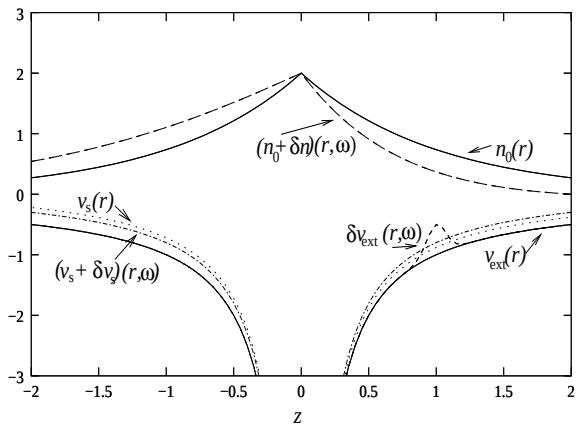

Figure 1. How TDDFT response works: A ground state density is perturbed by a frequency dependent change in the external potential. The change in the KS potential is defined to be that which causes the KS system to produce the same density change as the real system.

this is of great interest in biochemistry. Two years ago, Sundholm (1999) calculated the spectrum of chlorophyll A. One can improve on *ground-state* energies, including more non-local effects, through the adiabatic-connection-fluctuation-dissipation formula (Kurth and Perdew, 1999).

Far beyond linear response, TDDFT appears to be the only feasible approach to studying atoms in intense laser fields, and during energetic collisions (Burke and Gross, 1998). We are building a fully time-dependent Kohn-Sham code to calculate transport through molecular wires.

4. Linear response theory

Most of the applications of TDDFT have been in the linear response regime (Burke and Gross, 1998), where one turns on a small time-dependent perturbation on a system initially in its ground-state. This is illustrated in Fig. 1, where the perturbation is shown in the frequency domain. The change in the density may be written in terms of the susceptibility: for either the non-interacting Kohn-Sham or the physical system:

$$\delta n(\mathbf{r}\omega) = \int d^3r' \chi[n_0](\mathbf{r}\mathbf{r}'\omega)\delta v_{\rm ext}(\mathbf{r}'\omega) \quad (6)$$

$$= \int d^3r' \chi_s[n_0](\mathbf{r}\mathbf{r}'\omega)\delta v_{\rm S}(\mathbf{r}'\omega) \quad (7)$$

where the susceptibility $\chi[n_0](\mathbf{r}\mathbf{r}'\omega)$ is the response of the interacting system to a small change in the external potential. The second line follows since the density change is the same for the interacting system and the non-interacting system; $\chi_s[n_0](\mathbf{r}\mathbf{r}'\omega)$ is the Kohn-Sham susceptibility. It is convenient to write the change in the Kohn-Sham potential as

$$\delta v_{\mathrm{S}}(\mathbf{r}\omega) = \delta v_{\mathrm{ext}}(\mathbf{r}\omega) + \int d^3r' \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{XC}}[n_0](\mathbf{r}\mathbf{r}'\omega) \right) \delta n(\mathbf{r}'\omega) \quad (8)$$

where $f_{\mathrm{XC}}[n_0](\mathbf{r}\mathbf{r}'\omega)$ is known as the exchange-correlation kernel. In the time-domain,

$$f_{\mathrm{XC}}[n_0](\mathbf{r}\mathbf{r}', t-t') = \frac{\delta v_{\mathrm{XC}}[n_0](\mathbf{r}t)}{\delta n(\mathbf{r}'t')}. \quad (9)$$

These equations lead to the Dyson-type response equation

$$\chi(\mathbf{r}\mathbf{r}'\omega) = \chi_{\mathrm{S}}(\mathbf{r}\mathbf{r}'\omega) + \int d^3r_1 \int d^3r_2 \chi_{\mathrm{S}}(\omega)(\mathbf{r}\mathbf{r}_1\omega) f_{\mathrm{HXC}}[n_0](\mathbf{r}_1\mathbf{r}_2\omega)\chi(\mathbf{r}_2\mathbf{r}'\omega),$$

where $f_{\mathrm{HXC}} = 1/|\mathbf{r}-\mathbf{r}'| + f_{\mathrm{XC}}$. There are two key ingredients to composing the interacting response: first, the Kohn-Sham susceptibility, which may be written as a sum over Kohn-Sham orbitals:

$$\chi_{\mathrm{S}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{jk} (f_k - f_j) \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i0_+} \quad (10)$$

where the f_k are occupation numbers; and second, the exchange-correlation kernel, Eq. (9). Excitation energies lie at the poles of the true response function (Petersilka, Gossmann and Gross, 1996), and oscillator strengths are related to the pole strengths (Casida, 1996).

Both of the two ingredients mentioned above involve approximations: in obtaining the ground-state Kohn-Sham potential whose orbitals to use in Eq. (10), and in approximating f_{XC}. Which of these has the greater influence?

Petersilka, Gross and Burke (2000) found that an accurate *ground-state* Kohn-Sham potential is a vital starting point for these calculations. For atoms and molecules, KS eigenvalues and orbitals of valence states are well approximated with standard LDA and GGA potentials, but Rydberg states require the slow $-1/r$ decay of $v_{\mathrm{XC}}(r)$ far from a Coulomb system. This can be achieved via an exact exchange calculation or some grafting procedure for the long-range tail. In that article, the case of singlet excitations in Be was also studied. This case dramatically illustrates that the approximation for the ground-state potential used in calculating the Kohn-Sham response χ_s has a much bigger impact on the

positions of the higher-lying transitions than the approximation used for $f_{\rm XC}$.

The other key ingredient is the XC kernel, about which relatively little is known. This is almost always approximated by its ground-state limit, $\omega \to 0$. Again, the most popular approximation for the $f_{\rm XC}$ is the ALDA, completely local in space and in time:

$$f_{\rm XC}^{\rm ALDA} = \frac{d^2 e_{\rm XC}^{\rm unif}}{dn^2}(n(\mathbf{r}t))\delta^{(3)}(\mathbf{r}-\mathbf{r}')\delta(t-t') \tag{11}$$

Memory dependence gives the exact $f_{\rm XC}[n_0](\mathbf{r}\mathbf{r}'\omega)$ a frequency-dependence, neglected in any adiabatic approximation. Within this approximation, Filippi, Umrigar and Gonze (1997) found that the exact triplet and singlet excitation tends to sandwich the exact Kohn-Sham level. The triplet-singlet splitting is pretty well approximated by using $f_{\rm XC}$ in the ALDA approximation, but then the mean of the two is shifted. This motivated Burke, Petersilka, and Gross (2000) to develop a hybrid $f_{\rm XC}$ functional.

When are the bare Kohn-Sham transitions good approximations? Casida (1996) transformed the response equation Eq. (9) to a linear response problem. Using q as a double-index, we consider the basis $\Phi_q(\mathbf{r}) = \phi_i(\mathbf{r})\phi_a(\mathbf{r})$, where i labels an occupied state and a an unoccupied one, we obtain

$$\sum_{q'} \tilde{\Omega}_{qq'} v_{q'} = \Omega v_q \tag{12}$$

where $\Omega = \omega^2$, the square of the true transition frequency, and

$$\tilde{\Omega}_{qq'} = \delta_{qq'}\Omega_q + 2\sqrt{\omega_q \omega_{q'}}\langle q|f_{\rm HXC}|q'\rangle, \tag{13}$$

with $\Omega_q = \omega_q^2$ being the square of the KS transition frequency. The square arises naturally when both forward and back transitions are treated on an equal footing.

If we then do perturbation theory in the *distance from the diagonal* of the matrix (Appel, Burke, and Gross (2001)), we obtain, for transition frequencies that are only weakly shifted from their Kohn-Sham values,

$$\omega = \omega_q + \langle q|f_{\rm HXC}|q\rangle \left(1 + \sum_{q\neq q'} \frac{\langle q'|f_{\rm HXC}|q\rangle}{\omega_q - \omega_q'}\right) \tag{14}$$

Neglecting the sum over off-diagonal elements on the right-hand side constitutes the "single pole approximation" (SPA) (Petersilka, Gossmann, and Gross, 1996). For the oscillator strengths, we find

$$f = f_q \left(1 + \frac{\langle q'|f_{\rm HXC}|q\rangle}{\omega_q - \omega_q'}\sqrt{\frac{f_{q'}}{f_q}}\right). \tag{15}$$

The precise expressions for these corrections are given in the article cited just above.

Ignoring the corrections leads to the single-pole approximation of Petersilka, Gossmann and Gross (1996). Now we can see precisely when this is a good approximation. It requires the poles to be decoupled, in the sense that the the ratio of the matrix elements of the Hartree-XC kernel to the frequency separation must be small. Hence it is accurate in the limit of weak Coulomb interaction, but also in the limit of well-separated poles. Note also that, when it is accurate, it provides a simple formula for correcting KS transition frequencies, without solving further sets of equations. Finally, note that a signal for this SPA to be valid is that the KS oscillator strengths are accurate. In such circumstances, the corrections to the KS transition frequencies yield expectation values of the unknown XC kernel.

The single-pole approximation has proved to be very successful in predicting excitation energies for finite systems, such as atoms and molecules, when the bound states are well-separated and the off-diagonal elements are truly small. For solids however, the poles are no longer separated and this analysis cannot be used. There are subtleties involved in extracting the long wavelength limit of an extended system (de Boeij et al. , 2001).

5. Density Functional Scattering Theory

The Kohn-Sham potential for an N-electron system has proven to be a very accurate approximation of the effective optical potential felt by an electron in a Rydberg state orbiting in the field of the daughter (N-1)-electron system (Al-Sharif, Resta, and Umrigar, 1998). The natural question arises if the N-electron ground-state Kohn-Sham potential also produces accurate *continuum* states for an electron scattering off the corresponding (N-1)-electron system. In particular, when an electron collides at low energies with a neutral (N-1)-electron system, is it possible to get scattering information from the corresponding N-electron ground-state Kohn-Sham potential? The photoresponse problem has already been addressed by Zangwill and Soven (1980), but the electronic scattering one has not been formulated yet within the TDDFT framework.

Consider the example (in one dimension) of one electron scattering off a negative delta function potential $V(x) = -Z\delta(x)$ of strength Z. This potential admits one bound state, and its energy is $-Z^2/2$. The transmission coefficient must be singular at that energy, and should therefore be of the form $T(\varepsilon) = f(\varepsilon)/(\varepsilon + Z^2/2)$, where $f(\varepsilon)$ must go to zero

as $\varepsilon \to 0$ and to ε as $\varepsilon \to \infty$. The simplest guess $f(\varepsilon) = \varepsilon$ provides in fact the exact answer: $T(\varepsilon) = \varepsilon/(\varepsilon + Z^2/2)$. Notice how knowledge of the ground-state energy for an electron *bound* in an external potential was enough in this case to easily guess the transmission probability (1d-cross-section) for an electron *scattering* off that potential.

We can also obtain the same answer from the susceptibility, which for one electron in one dimension (arbitrary $V(x)$) is given by:

$$\chi(x, x', \varepsilon) = \sqrt{n(x)n(x')}[g^{>}(x, x', \varepsilon + \varepsilon_0) + g^{>*}(x, x', -\varepsilon + \varepsilon_0)], \quad (16)$$

where $n(x)$ is the ground-state density, ε_0 is the ground-state energy, and $g^{>}$ is the outgoing Green's function satisfying:

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial x^2} + V(x) - i\frac{\partial}{\partial t}\right) g^{>}(x, x'; t - t') = -i\delta(x - x')\delta(t - t'). \quad (17)$$

Eq. (16) can be proven in the following way: due to an external time-dependent perturbation $\delta v(x, t)$, the ground state $\phi_0(x)e^{-i\varepsilon_0 t}$ changes by an amount determined by the Green's function:

$$\delta\phi_0(x, t)e^{-i\varepsilon_0 t} = \int dx' \int dt' \phi_0(x')e^{-i\varepsilon_0 t'} g^{>}(x, x'; t - t')\delta v(x', t'), \quad (18)$$

and since for one electron $\delta n(x, t) = \phi_0(x, t)\delta\phi_0^*(x, t) + \phi_0^*(x, t)\delta\phi_0(x, t)$, taking the Fourier transform and using the definition of the susceptibility (eq. (7)), we get eq. (16).

Since at large distances only the continuum states contribute to the susceptibility (the bound states have decayed), it is possible to get the transmission amplitude $t(\varepsilon)$ for one electron scattering off any potential $V(x)$ by extracting the oscillating part of the susceptibility at large distances:

$$t(\varepsilon) = \lim_{x \to -\infty} \left(\frac{i\sqrt{2\varepsilon}}{n(x)}\chi^{osc}(x, -x; \varepsilon - \varepsilon_0)\right). \quad (19)$$

Eq. (19) can be readily tested for $V(x) = -Z\delta(x)$. In this case, the ground-state density is $n(x) = Ze^{-2Z|x|}$ and:

$$g^{>}(x, x', \varepsilon) = \frac{1}{i\sqrt{2\varepsilon}}\left(e^{i\sqrt{2\varepsilon}|x-x'|} - \frac{Ze^{i\sqrt{2\varepsilon}(|x|+|x'|)}}{i\sqrt{2\varepsilon} + Z}\right). \quad (20)$$

Using eqns. (16) and (19) we get (see also Fig. 2):

$$T(\varepsilon) = |t(\varepsilon)|^2 = \frac{\varepsilon}{\varepsilon + Z^2/2}. \quad (21)$$

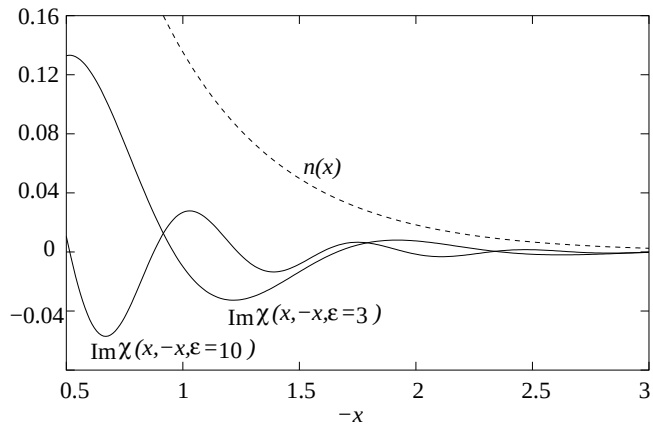

Figure 2. Although $\chi(x, -x, \varepsilon)$ decays exponentially (because the density decays exponentially), it oscillates at large distances, and the amplitude of these oscillations yields the transmission coefficient. $Z = 1$ in this plot.

The Rutgers group is exploring how general this prescription is. Can we always extract cross-sections from the Kohn-Sham susceptibility? Is it possible to relate the Kohn-Sham scattering amplitudes to the true amplitudes using the linear response formalism presented in the preceding section? These are some of the challenges that TDDFT will face in the near future.

6. Memory in TDDFT

There are two sources of memory in TDDFT. Functionals depend, in principle, on both the history of the density and on the initial-state of the system. Often the term memory is used to refer to the former, but we prefer to call it history-dependence to distinguish it from the other memory effect, initial-state dependence.

Very little is known about initial-state dependence and it is completely ignored in all functionals used today. Recently, we have begun to investigate the importance of initial-state dependence (Maitra and Burke, 2001). We found that for one electron, there is in fact *no* initial-state dependence: the time-evolving density uniquely specifies the time-dependent potential. Any attempt to find an alternative initial wavefunction that evolves with the same density as another, in a different potential, results in unphysical potentials which diverge at large distances. We also note that there is no initial-state dependence for the case of one electron scattering off a (many-electron) target (see

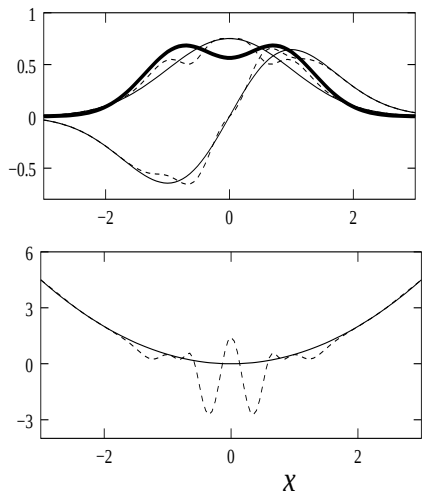

Figure 3. Initial-state dependence: the solid lines in the top panel are the two orbitals of one wavefunction, which happens to be a stationary state of the harmonic oscillator shown below as a solid line. The dashed lines are the orbitals of an alternative initial wavefunction which evolve with the same density (thick solid line in top figure) in the potential which at time 0 is shown as the dashed line in the bottom figure.

Sec. 5). Assuming the target to be initially in its ground-state reduces the initial-state dependence problem to that of one electron, for which knowledge of the density is enough to pin down the potential (and the wavefunction).

For more than one electron, however, the initial-state question is alive and kicking. Using van Leeuwen's construction (1999), we constructed an example for two non-interacting electrons, where two different initial wavefunctions were made to evolve in two different potentials with the same density. An example is given in Fig. 3, where the simple case of two non-interacting electrons in one dimension are considered. If we consider the density in the top panel to be that of an interacting system of two electrons, then the difference between the two potentials in the lower panel corresponds to the difference in the exchange-correlation potential for the two different choices of initial KS state.

The dependence of functionals on the history of the density has been dramatically illustrated in a recent work of Hessler, Maitra and Burke (2001). There we studied exactly numerically, time-dependent Hooke's atom: two interacting electrons in a harmonic well with a time-varying

force constant. We began in the ground-state. We could compare the exact correlation energy with an exact adiabatic approximation (i.e. using the exact ground-state functional). We found major qualitative differences in the behaviour of the correlation energy, including positivity of $E_{\rm C}$ which can never occur in any adiabatic approximation due to the ground-state variational principle. In particular, we found very strong history effects: there were two time slices in which the density evolved essentially identically but in which the correlation potential looked completely different. The density at time t and right around time t is not enough to specify the correlation potential; $v_{\rm C}$ is a highly non-local functional in time.

In fact the two memory effects are intimately connected. Maitra, Burke and Woodward (2001) derive a memory formula:

$$v_{\rm XC}[n_{t'};\Psi(t'),\Phi(t')](\mathbf{r}t) = v_{\rm XC}[n_0;\Psi(0),\Phi(0)](\mathbf{r}t), \quad t > t' > 0 \qquad (22)$$

where $n_{t'}(\mathbf{r}t) = n_0(\mathbf{r}t)$, $t > t'$ and is undefined for $t < t'$. This follows from a very simple statement in quantum mechanics, saying that it doesn't matter what we consider to be the "initial" time. We just need to adjust the arguments of the functionals consistently. But it has profound consequences for TDDFT, providing a stringent test of any functional with memory. Notice that ALDA satisfies it trivially, since it has no memory of any sort, but any of the recent functionals which attempt to capture some of the memory (Vignale and Kohn, 1996; Vignale, Ullrich and Conti, 1997; Dobson, Bünner and Gross, 1997) will not. These have history dependence but no initial-state dependence. By functional differentiation of Eq. (22), one obtains a relation expressing the exchange-correlation kernel $f_{\rm XC}$ entirely in terms of initial-state dependence. The memory formula translates the two memory effects into each other; indeed, if one can find a "pseudo-prehistory" (Maitra, Burke and Woodward, 2001) during which the initial state evolves into a non-degenerate ground-state, initial-state dependence can be completely absorbed into a history effect. This is discussed in much detail in the article above.

7. Excited-state densities in TDDFT

We now encounter a conundrum: what are excited state densities in TDDFT, and what is the nature of the Kohn-Sham state when an interacting system is in an excited state? Let us consider the specific case of a single singlet excitation in He. Suppose we find some $v_{\rm ext}(\mathbf{r}t)$ which starts with the He atom in the ground state $1s^2$, with wavefunction $\Psi(0)$ and brings it in a finite time to the first excited singlet state, 1s2p, along a history $n_0(\mathbf{r}t)$. What is an exact Kohn-Sham potential

for this problem? Since the Kohn-Sham system begins in a single Slater determinant, with one occupied spatial orbital, it will remain in a single (time-dependent) orbital throughout the history that brings it to the excited state. This means that the excited state density for 1s2p state is represented in the KS system by *one* orbital! Now, consider the case that $v_{\rm S}$ becomes static once the interacting excited state is reached: the density and $v_{\rm ext}(\mathbf{r}t)$ become static, and the KS state is an eigenstate of the static $v_{\rm S}(\mathbf{r})$. Clearly, this one-orbital KS eigenstate would be rather unpleasant to deal with, being of a completely different nature to the two-orbital 1s2p state it is representing. On the other hand, with $v_{\rm XC}$ ultra-nonlocal in time, consider the case that the KS wavefunction and potential continue to evolve even as the density remains static. In either situation, it is hard to imagine ALDA being a useful approximation.

8. Summary

TDDFT is a promising theory, generalizing ground-state DFT to include time-dependent systems. Most applications are so far in the linear response regime where, for example, it is being used to get electronic excitations of molecules. For systems with well-separated transition frequencies, the single-pole approximation is accurate for transition frequencies and the Kohn-Sham oscillator strengths are good. We discuss a new idea for developing scattering theory within TDDFT, based on properties of response functions. However TDDFT is not limited to linear response.

Much has yet to be learnt about properties of functionals, one of which is memory. Functionals depend in principle on both the initial-state of the system as well as the entire history of the density. Until very recently little was known about the two effects. Recently it has been shown that initial-state dependence can be significant, as can the dependence on the history. The two memory effects are inextricably intertwined and often initial-state dependence can be completely absorbed into a history dependence. Finally, we discussed an important challenge to TDDFT: representing certain excited states fully within TDDFT (not just in the linear response regime).

Acknowledgments

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References

A. I. Al-Sharif, R. Resta, C.J. Umrigar, *Evidence of physical reality in the Kohn-Sham potential: The case of atomic Ne*, Phys. Rev. A **57**, 2466 (1998).

Y. Andersson, D.C. Langreth, and B.I. Lunqvist, *van der Waals Interactions in Density-Functional Theory*, Phys. Rev. Lett. **76**, 102 (1996).

T. Ando, *Inter-subband optical absorption in space-charge layers on semiconductor surfaces.*, Z. Phys. B. **26**, 263 (1977).

H. Appel, K. Burke, and E.K.U. Gross, *Oscillator strengths in density functional theory*, in preparation.

A.D. Becke, *Density-functional exchange-energy approximation with correct asymptotic behavior*, Phys. Rev. A **38**, 3098 (1988).

A.D. Becke, *Density-functional thermochemistry. III. The role of exact exchange*, J. Chem. Phys. **98**, 5648 (1993).

G.F. Bertsch, J.-I. Iwata, A. Rubio, and K. Yabana, *Real-space, real-time method for the dielectric function*, Phys. Rev. B **61**, 7998 (2000).

P. L. de Boeij, F. Kootstra, J. A. Berger, R. van Leeuwen, and J. G. Snijders, *Current density functional theory for optical spectra: A polarization functional*, J. Chem. Phys. **115**, 1995 (2001).

K. Burke, F.G. Cruz, and K.C. Lam, *Unambiguous exchange-correlation energy density*, J. Chem. Phys. **109**, 8161 (1998).

K. Burke and E.K.U. Gross, *A guided tour of time-dependent density functional theory*, in *Density functionals: Theory and applications*, ed. D. Joubert (Springer, Berlin, 1998).

K. Burke, M. Petersilka, and E.K.U. Gross, *A hybrid functional for the exchange-correlation kernel in time-dependent density functional theory*, in *Recent advances in density functional methods, vol. III*, ed. P. Fantucci and A. Bencini (World Scientific Press, 2000).

M.E. Casida, *Time-dependent density functional response theory of molecular systems: Theory, computational methods, and functionals*, in *Recent developments and applications in density functional theory*, ed. J.M. Seminario (Elsevier, Amsterdam, 1996).

J.F. Dobson, M. Bünner, and E.K.U. Gross, *Time-dependent density functional theory beyond linear response: An exchange-correlation potential with memory*, Phys. Rev. Lett. **79**, 1905 (1997).

C. Filippi, C.J. Umrigar, and X. Gonze, *Excitation energies from density functional perturbation theory*, J. Chem. Phys., **107**, 9994 (1997).

P. Hessler, N.T. Maitra, and K. Burke, *Dynamic effects in time-dependent density functional theory* submitted (2001).

P. Hohenberg and W. Kohn, *Inhomogeneous electron gas*, Phys. Rev. **136**, B 864 (1964).

J. Katriel, F. Zahariev, and K. Burke, *Symmetry and degeneracy in density functional theory* to appear in Int. J. Quantum Chem. (2001).

W. Kohn, *Nobel Lecture: Electronic structure of matter - wave functions and density functionals*, Rev. Mod. Phys. **71**, 1253 (1999).

W. Kohn and L.J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. **140**, A 1133 (1965).

F. Kootstra, P.L. de Boeij, and J.G. Snijders, *Efficient real-space approach to time-dependent density functional theory for the dielectric response of nonmetallic crystals*, J. Chem. Phys. **112**, 6517 (2000).

S. Kurth and J.P. Perdew, *Density-functional correction of random-phase-approximation correlation with results for jellium surface energies*, Phys. Rev. B **59**, 10461 (1999).

J. Larkin, C. Bock, N.T. Maitra, and K. Burke, *A new tool for studying the kinetic energy density functional*, in prep., Fall 2001.

C. Lee, W. Yang, and R.G. Parr, *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density*, Phys. Rev. B **37**, 785 (1988).

R. van Leeuwen, *Mapping from Densities to Potentials in Time-Dependent Density-Functional Theory*, Phys. Rev. Lett. **82**, 3863, (1999).

R. Magyar,B. Terilla, and K. Burke, *Extrapolating the adiabatic connection*, in preparation for Chem. Phys. Letts., Fall 2001.

N.T. Maitra and K. Burke, *Demonstration of initial-state dependence in time-dependent density functional theory*, Phys. Rev. A **63**, 042501 (2001); (E) **64**, 039901 (2001).

N.T. Maitra, K. Burke, H. Appel, E.K.U. Gross, and R. van Leeuwen, *Ten topical questions in time-dependent density functional theory*, to appear in *Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R.G. Parr*, ed. K.D. Sen (World Scientific, 2001).

N.T. Maitra, K. Burke, and C. Woodward, *Memory in time-dependent density functional theory*, submitted (2001).

J.P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997) (E).

M. Petersilka, E.K.U. Gross, and K. Burke, *Excitation energies from time-dependent density functional theory using exact and approximate functionals*, Int. J. Quantum Chem. **80**, 534 (2000).

M. Petersilka, U.J. Gossmann, and E.K.U. Gross, *Excitation energies from time-dependent density-functional theory*, Phys. Rev. Lett. **76**, 1212 (1996).

E. Runge and E.K.U. Gross, *Density-functional theory for time-dependent systems*, Phys. Rev. Lett. **52**, 997 (1984).

D. Sundholm, *Density functional theory calculations of the visible spectrum of chlorophyll a*, Chem. Phys. Lett., **302**, 480 (1999).

G. Vignale and W. Kohn, *Current-Dependent Exchange-Correlation Potential for Dynamical Linear Response Theory*, Phys. Rev. Lett. **77**, 2037 (1996).

G. Vignale, C.A. Ullrich, and S. Conti, *Time-dependent density functional theory beyond the adiabatic local density approximation*, Phys. Rev. Lett. **79**, 4878 (1997).

T. Whittingham, R.J. Magyar, and K. Burke, *Scaling one spin density at a time*, in prep, Fall 2001.

A. Zangwill and P Soven, *Density-functional approach to local-field effects in finite systems: Photoabsorption in the rare gases*, Phys. Rev. A **21**, 1561 (1980).