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# Time-dependent density functional theory: Past, present, and future

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Time-dependent density functional theory (TDDFT) is presently enjoying enormous popularity in quantum chemistry, as a useful tool for extracting electronic excited state energies. This article discusses how TDDFT is much broader in scope, and yields predictions for many more properties. We discuss some of the challenges involved in making accurate predictions for these properties.

Kohn-Sham density functional theory [1, 2, 3] is the method of choice to calculate ground-state properties of large molecules, because it replaces the interacting many-electron problem with an effective single-particle problem that can be solved much faster. Time-dependent density functional theory (TDDFT) applies the same philosophy to time-dependent problems. We replace the complicated many-body time-dependent Schrödinger equation by a set of time-dependent single-particle equations whose orbitals yield the same time-dependent density $n(\mathbf{r}, t)$. We can do this because the Runge-Gross theorem[4] proves that, for a given initial wavefunction, particle statistics and interaction, a given time-dependent density $n(\mathbf{r}, t)$ can arise from at most one time-dependent external potential $v_{\rm ext}(\mathbf{r}, t)$. We define time-dependent Kohn-Sham (TDKS) equations that describe $N$ non-interacting electrons that evolve in $v_{\rm S}(\mathbf{r}, t)$, but produce the same $n(\mathbf{r}, t)$ as that of the interacting system of interest. Development and applications of TDDFT have enjoyed exponential growth in the last few years[5, 6, 7, 8], and we hope this merry trend will continue.

The scheme yields predictions for a huge variety of phenomena, that can largely be classified into three groups: (i) the non-perturbative regime, with systems in laser fields so intense that perturbation theory fails, (ii) the linear (and higher-order) regime, which yields the usual optical response and electronic transitions, and (iii) back to the ground-state, where the fluctuation-dissipation theorem produces *ground-state* approximations from TDDFT treatments of excitations.

In the first, **non-perturbative regime**, we have systems in intense laser fields with electric field strengths that are comparable to or even exceed the attractive Coulomb field of the nuclei[5]. The time-dependent field cannot be treated perturbatively, and even solving the time-dependent Schrödinger equation for the evolution of two interacting electrons is barely feasible with present-day computer technology[9]. For more electrons in a time-dependent field, wavefunction methods are prohibitive, and in the regime of (not too high) laser intensities, where the electron-electron interaction is still of importance TDDFT is essentially the only practical scheme available. With the recent advent of atto-second laser pulses, the electronic time-scale has become accessible. Theoretical tools to analyze the dynamics of excitation processes on the attosecond time scale will become more and more important. An example of such a tool is the time-dependent electron localization function (TDELF) [10, 11]. This quantity allows the **time-resolved** observation of the **formation, modulation, and breaking of chemical bonds**, thus providing a visual understanding of the dynamics of excited electrons (for an example see Fig.1 and Ref. [12]). The natural way of calculating the TDELF is from the TDKS orbitals. Recent applications in the beyond perturbative regime range from above-threshold ionization of metal clusters[13] to coherent control of quantum wells[14] to multiharmonic generation in benzene[15].

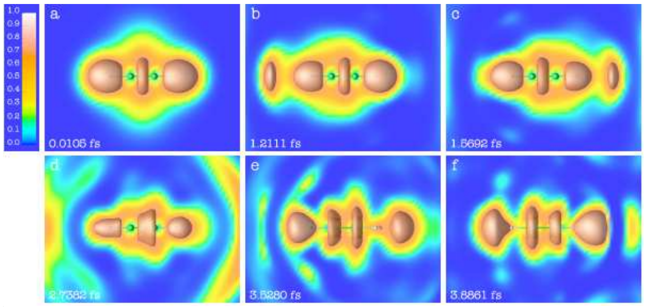

FIG. 1: Snapshots of the time-dependent ELF for the excitation of acetylene by a 17.5 eV laser pulse[12]. The pulse had a total length of 7 fs, an intensity of $1.2 \times 10^{14}$Wcm$^{-2}$, and was polarized along the molecular axis. Ionization and the transition from the bonding $\pi$ state to the anti-bonding $\pi^*$ state are clearly visible.

A much larger group of applications in chemistry is the linear response to a spatially uniform electric field, i.e., the **optical response** in the dipole approximation[16, 17]. Formal analysis of this situation shows that TDDFT yields predictions for electronic excitations, both their position (transition frequency) and intensity (oscillator strength). These are corrections to transitions between occupied and unoccupied levels of the ground-state KS potential, thus providing a simple interpretation of those levels[18]. In the area of calculating electronic excitations, TDDFT is rapidly becoming a standard tool, complimentary to existing wavefunction techniques[19]. Just as in the ground-state case, it has the advantage in computational speed, allowing study of larger systems than with traditional methods, and the usual disadvantage (or excitement) of being unsystematic and artful. A final application is to write the **ground-state XC energy** in terms of the frequency-dependent response function, and so linear response TDDFT yields approximate treatments of the ground-state problem[20, 21, 22, 23].

A random walk through some of 2004's papers using TDDFT gives some feeling for the breadth of applications. Most are in the linear response regime. In inorganic chemistry, the optical response of many transition metal complexes[24, 25, 26, 27, 28, 29] has been calculated, and even some X-ray absorption[30]. In organic chemistry, the response of thiouracil[31] and s-tetrazine[32], and annulated porphyrins[33] were investigated. In photobiology, potential energy curves for the trans-cis photo-isomerization of protonated Schiff base of retinal[34] have been calculated. For these and other systems, there is great interest in charge-transfer excitations[35, 36, 37, 38, 39, 40], but (as we later discuss) intermolecular charge transfer is a demanding problem for TDDFT. Another major area of application is clusters, large and small, covalent and metallic, and everything inbetween[41, 42, 43, 44, 45, 46, 47], including Met-Cars[48]. Several studies include solvation, for example, the behavior of metal ions in explicit water[49]. TDDFT in linear response can also be used to calculate both electronic and magnetic circular dichroism[50, 51], and has been applied to helical aromatics[52], and to artemisinin complexes in solution[53]. There have also been applications in materials[54, 55] and quantum dots[56] but, as discussed below, the optical response of solids requires some non-local approximations[57]. Beyond the linear regime, there is also growing interest in second- and third-order response[58, 59, 60, 61] in all these fields.

A wonderful aspect of TDDFT is that a single approximation to the time-dependent XC potential implies predictions for all these quantities. This is analogous to the ground-state case, where a single approximation to $E_{\rm XC}$ can be applied to all ground-state properties of all electronic systems, such as dissociation energies, bond lengths and angles, vibrational frequencies, etc., of atoms, molecules, clusters, and solids. The starting point of most TDDFT approximations is the adiabatic local density approximation (ALDA), which approximates the XC potential at point $\mathbf{r}$ and time $t$ by that of a ground-state uniform electron gas of density $n(\mathbf{r}t)$. This is clearly accurate when the density varies sufficiently slowly in time and space, but works surprisingly well beyond that limit for many systems and properties, just as LDA does for most ground-state problems.

We make an important distinction here between the mature subject of ground-state DFT, and the developing one of TDDFT. In the former, there is general consensus on which properties are captured by which functionals, and the aim is toward higher accuracy[62]. One expects chemical bonds to form in modern KS DFT calculations, and one hopes to use better functionals to produce better accuracy and reliability[63]. But time-dependent quantum mechanics probes a far more diverse range of electronic phenomena, and in TDDFT, we are still exploring even which properties are captured at all by the presently available approximate functionals. Quantitative accuracy is less of an issue as yet. Most data on the performance of TDDFT are for systems driven by some external field. Practically nothing is known about how TDDFT performs in the description of relaxation processes, i.e., on the time evolution of large systems starting from a non-equilibrium initial condition[64]. A closely related question is the description of density fluctuations within TDDFT[65].

At this point, we introduce a few equations, to make the discussion more precise. We use atomic units throughout, and suppress spin indices. For brevity, we drop commas between arguments wherever the meaning is clear. We write the TDKS equations as

$$i\frac{d\phi_j(\mathbf{r}t)}{dt} = \left(-\frac{\nabla^2}{2} + v_{\rm S}[n](\mathbf{r}t)\right)\phi_j(\mathbf{r}t) \quad . \qquad (1)$$

whose density $n(\mathbf{r}t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r}t)|^2$ is precisely that of the real system. We *define* the exchange-correlation potential via

$$v_{\rm S}(\mathbf{r}t) = v_{\rm ext}(\mathbf{r}t) + \int d^3r' \; \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}(\mathbf{r}t). \qquad (2)$$

The exchange-correlation potential, $v_{\rm XC}(\mathbf{r}t)$ is in general 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. If we always begin in a non-degenerate ground state[66], the initial-state dependence can be subsumed by the Hohenberg-Kohn theorem[1], and the only unknown part of $v_{\rm S}(\mathbf{r}t)$, the exchange-correlation (XC) potential, is a functional of $n(\mathbf{r}t)$ alone.

In the special case of the response of the ground state to a weak external field, the system's response is characterized by the non-local susceptibility

$$\delta n(\mathbf{r}t) = \int dt' \int d^3r' \chi[n_0](\mathbf{r},\mathbf{r}';t-t') \; \delta v_{\rm ext}(\mathbf{r}'t'). \quad (3)$$

$\chi$ is a functional of the *ground-state* density, $n_0(\mathbf{r})$. The central equation of TDDFT linear response[16] is a Dyson-like equation for the true $\chi$ of the system:

$$\begin{aligned}\chi(\mathbf{r}\mathbf{r}'\omega) &= \chi_{\rm S}(\mathbf{r}\mathbf{r}'\omega) + \int d^3r_1 \int d^3r_2\ \chi_{\rm S}(\mathbf{r}\mathbf{r}_1\omega) \\ &\times \left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + f_{\rm XC}(\mathbf{r}_1\mathbf{r}_2\omega)\right)\chi(\mathbf{r}_2\mathbf{r}'\omega), \quad (4)\end{aligned}$$

Here $\chi_{\rm S}$ is the *Kohn-Sham* response function, constructed from KS energies and orbitals:

$$\chi_{\rm S}(\mathbf{r}\mathbf{r}'\omega) = 2\sum_q \frac{\Phi_q(\mathbf{r})\ \Phi_q^*(\mathbf{r}')}{\omega - \omega_q + i0_+} + c.c.(\omega \to -\omega) \quad (5)$$

where $q$ is a double index, representing a transition from occupied KS orbital $i$ to unoccupied KS orbital $a$, $\omega_q = \epsilon_a - \epsilon_i$, and $\Phi_q(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_a(\mathbf{r})$. Thus $\chi_{\rm S}$ is purely a product of the ground-state KS calculation. On the other hand, the XC kernel is defined as

$$f_{\rm XC}[n_0](\mathbf{r}\mathbf{r}', t-t') = \delta v_{\rm XC}(\mathbf{r}t)/\delta n(\mathbf{r}'t')|_{n_0}. \quad (6)$$

This is a much simpler quantity than $v_{\rm XC}[n](\mathbf{r}t)$, since the functional is only evaluated at the ground-state density. It is non-local in both space and time. The non-locality in time manifests itself as a frequency dependence in the Fourier transform, $f_{\rm XC}(\mathbf{r}\mathbf{r}'\omega)$.

Next, we introduce Casida's equations[17], in which the poles of $\chi$ are found as the solution to an eigenvalue problem:

$$\sum_{q'} \tilde{\Omega}_{qq'}(\omega)\ a_{q'} = \omega^2\ a_q, \quad (7)$$

where

$$\tilde{\Omega}_{qq'}(\omega) = \omega_q^2\delta_{qq'} + 2\sqrt{\omega_q\omega_q'}\langle q|f_{\rm HXC}(\omega)|q'\rangle. \quad (8)$$

and $\langle q|f_{\rm HXC}(\omega)|q'\rangle$ is the matrix element of the (Hartree)-XC kernel in the set of functions $\Phi_q(\mathbf{r})$. Eigenvalues yield the square of transition frequencies, while eigenvectors yield oscillator strengths. Ignoring off-diagonal matrix elements can yield much insight into the nature of the TDDFT corrections to the KS transitions[18].

Lastly, we mention how TDDFT produces sophisticated approximations to the *ground-state* exchange-correlation energy. The adiabatic connection fluctuation-dissipation formula is:

$$\begin{aligned}E_{\rm XC}[n_0] &= -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r'\ \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\ &\int_0^\infty \frac{d\omega}{\pi}\left\{\chi l[n_0](\mathbf{r}\mathbf{r}'\omega) + n_0(\mathbf{r})\delta^{(3)}(\mathbf{r}-\mathbf{r}')\right\} (9)\end{aligned}$$

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[67, 68]. So any model for $f_{\rm XC}$, even setting it to zero (called the Random Phase Approximation), yields a sophisticated approximation to $E_{\rm XC}$, by solving Eq. (4) for $\chi$ (at each $\lambda$) and inserting in Eq. (9).

All the above equations are formally exact. In any practical DFT calculation, approximations must be made. The most common approximation in TDDFT is the *adiabatic* approximation, in which

$$v_{\rm XC}^{\rm adia}[n](\mathbf{r}t) = v_{\rm XC}^{\rm gs}[n_0](\mathbf{r})|_{n_0(\mathbf{r})=n(\mathbf{r}t)}, \quad (10)$$

i.e., the XC potential at any time depends only on the density at that time, not on its entire history. This becomes exact for slow variations in time. Most applications, however, are not in this slowly varying regime. Nevertheless, results obtained within the adiabatic approximation are, in most cases, rather accurate. Any ground-state approximation (LDA, GGA, hybrid) automatically provides an adiabatic approximation (e.g., ALDA) in TDDFT. Moreover, the XC kernel is frequency-independent in the adiabatic approximation, taking its $\omega \to 0$ value.

As mentioned above, TDDFT is proving very useful in predicting optical response properties of molecules. The Casida equations have been encoded in most standard quantum chemical packages, and efficient algorithms developed to extract the lowest-lying excitations. A small survey is given by Furche and Ahlrichs[19]. Typical chemical calculations are done with the B3LYP[69] functional, and typical results are transition frequencies within 0.4 eV of experiment, and structural properties of excited states are almost as good as those of ground-state calculations (bond lengths to within 1%, dipole moments to within 5%, vibrational frequencies to within 5%). Most importantly, this level of accuracy appears sufficient in most cases to qualitatively identify the nature of the most intense transitions, often debunking cruder models that have been used for interpretation for decades. This is proving especially useful for the photochemistry of biological molecules[70]. An alternative implementation, often favored by physicists, is to propagate the TDKS equations in real time, having given the system an initial weak perturbation. Such calculations either use a real-space-grid[71, 72] or plane waves[73].

This article is *not* about the (admittedly) gratifying successes of TDDFT calculations, which are dicussed in recent reviews[5, 6] and the recent literature. We begin from there, and explore a much wider arena. To do this, in Fig. 2 we have drawn a cartoon (literally, a stick figure) to represent the information in a typical calculation. Each line represents a transition, with its position denoting the transition frequency and its height proportional to the oscillator strength. For the He atom, the 2s→2p singlet transition is at 21.2 eV, while for the $N_2$ molecule, the $^3\Pi_\gamma$ transition is at 7.4 eV. Many applications of TDDFT report only the positions of the few lowest optically-allowed transitions, while some report also their oscillator strengths.

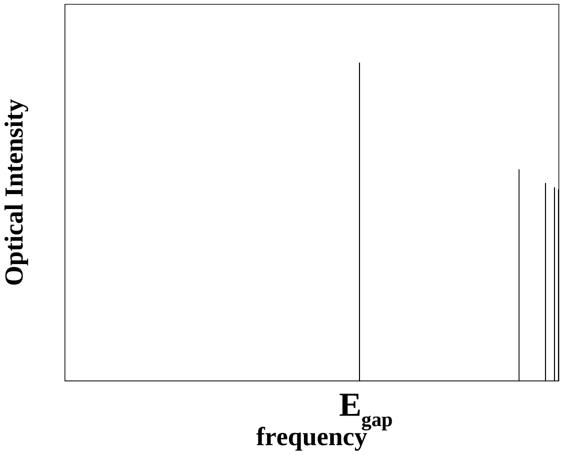

FIG. 2: Cartoon of the exact optical absorption spectrum of an atom or molecule, with discrete transitions represented by straight lines (see text).

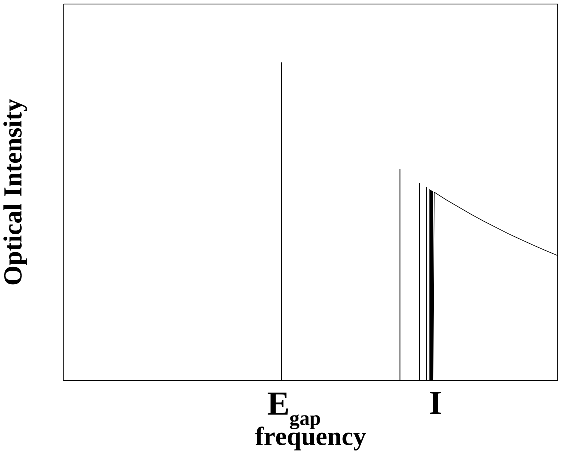

FIG. 3: Same as Fig. 2, but showing higher frequencies, including the infinite Rydberg series of states as the ionization threshold is approached.

To help our analysis, we list qualitatively different sources of error in the predictions from any TDDFT calculation. We refer to them as the four deadly sins:

- The sin of the **ground-state**: Errors in the underlying *ground-state* DFT calculation. If the KS orbital energies are wrong to begin with, TDDFT corrections cannot produce accurate results.

- The sin of **locality**: Errors due to local (or gradient-corrected) approximations to an adiabatic $f_{\rm XC}(\mathbf{rr}')$, i.e., properties that require non-locality in $|\mathbf{r}-\mathbf{r}'|$.

- The sin of **forgetfulness**: Phenomena missing when the adiabatic approximation is made, i.e., properties that require non-locality in time, i.e., memory.

- The sin of the **wavefunction**: Even if the *exact* $v_{\rm XC}(\mathbf{r}t)$ is used, solution of the TDKS equations only yields the TDKS non-interacting wavefunction. The true wavefunction may differ so dramatically from the KS wavefunction that observables evaluated on the latter may be inaccurate.

The remainder of this essay is a discussion of the various areas of TDDFT applications and development, and the challenges presently facing us. We begin in the middle, with the linear response regime, where most of the applications presently are, then go to non-perturbative phenomena, and end with ground-state applications.

We start with applications to the **excitations of atoms and molecules**. An important point we wish to emphasize here is the wealth of prediction made by any TDDFT approximation. The simplest real system of interacting electrons is the He atom, and even it has a rich and complex optical absorption spectrum. Returning to Fig. 2, we note that a calculation of the optical spectrum of the bare ground-state KS system, often[18] looks quite similar to the exact one, with TDDFT corrections merely shifting and resizing peaks. In Fig. 3, we zoom out a little, and see the ionization threshold at $\omega = I$ and the infinite Rydberg series of excitations just to its left. If one calculates the optical response of $N$ non-interacting electrons in the exact KS ground-state potential, i.e., what we call the KS response, its ionization threshold is in *exactly* the right place, by virtue of the DFT version of Koopman's theorem[74].

From the very earliest calculations of transition frequencies[16, 17], it was recognized that the inaccuracy of standard density functional approximations (LDA, GGA, hybrids) for the ground-state XC potential leads to inaccurate KS eigenvalues. Because the approximate KS potentials have **incorrect asymptotic behavior** (they decay exponentially, instead of as $-1/r$), the KS orbital eigenvalues are insufficiently negative, the ionization threshold is far too low, and Rydberg states are often unbound. This is therefore a *ground-state* sin.

Given this disastrous behavior, many methods have been developed to asymptotically correct potentials[75, 76]. Any corrections to the ground-state potential are dissatisfying, however, as the resulting potential is *not* a functional derivative of an energy functional. Even mixing one approximation for $v_{\rm XC}(\mathbf{r})$ and another for $f_{\rm XC}$ has become popular. A more satisfying route is to use the optimized effective potential (OEP) method[77, 78] and include exact exchange or other self-interaction-free functionals. This produces a far more accurate KS potential, with the correct asymptotic behavior. The chief error is simply the correlation contribution to the position of the HOMO, i.e, a small shift. All the main features below and just above $I$ are retained.

Why has the poor quality of ground-state potentials not impeded the rapid growth of TDDFT calculations for excitations in quantum chemistry? For many molecules, the lowest excitations are not Rydberg in character, and the orbitals do not depend on the large-$r$ behavior of the potential. But there are important cases where the problem does show up. The 'fruitfly' of TDDFT benchmarks is the $\pi \to \pi^*$ transition in benzene. This occurs at about 5 eV in a ground-state LDA calculation, and ALDA shifts it correctly to about 7 eV[79]. Unfortunately, this is in the LDA continuum, which starts at about 6.5 eV! So how is it possible to get this right in ALDA?

The answer is that ALDA usually yields good oscillator strengths, even for states pushed into the continuum[80]. The reason is simple, and was suggested long ago in early photoabsorption calculations by Zangwill and Soven[81]. The KS LDA potential looks very much like the exact one (especially in the interior, as the occupied orbitals yield a good approximation to the true density), shifted up by a constant, due to the lack of derivative discontinuity[74]. The shift pushes the Rydberg states into the continuum, but retains their contribution to the optical spectrum. Likewise for the benzene transition. Hence ALDA can still be used and trusted for that transition. Moral: *Just because it's in the continuum, doesn't mean it's not right.*

The cartoon of Fig. 2 changes when bonds are stretched. Of particular interest in biochemistry are **charge-transfer excitations**, especially between weakly bonded molecules. Capturing these seems unnatural within TDDFT, for the simple reason that the numerator in $\chi$ in Eq. (5) vanishes as the molecular separation goes to infinity. Thus, in the density-density response, the oscillator strength for these transitions is exponentially small. Recently[82], it has been shown how to build an empirical approximation to an adiabatic $f_{\rm XC}$ that can capture these effects, but it is one that *grows* exponentially with $|\mathbf{r}-\mathbf{r}'|$. Thus this is a sin of *locality*, in which local approximations to $f_{\rm XC}$ miss a qualitative feature.

A presently open question is the extraction of **double excitations**[83, 84]. In the adiabatic approximation, these are lost from the linear response equations. When a double excitation lies close to a single excitation, elementary quantum mechanics shows that $f_{\rm XC}$ must have a strong frequency dependence [85]. Thus this problem is due to the adiabatic approximation: a sin of *forgetfulness*. Recently, a post-adiabatic TDDFT methodology has been developed[85, 86] for including a double excitation when it is close to an optically-active single excitation, and works well for small dienes[87]. It had been hoped that, by going beyond linear response, non-trivial double excitations would be naturally included in, e.g., TDLDA, but it has recently been proven that, in the higher-order response in TDLDA, the double excitations occur simply at the sum of single-excitations. Thus we do not currently know how best to approximate these excitations. This problem is particularly severe for quantum dots, where the external potential is parabolic, leading to multiple near degeneracies between levels of excitation.

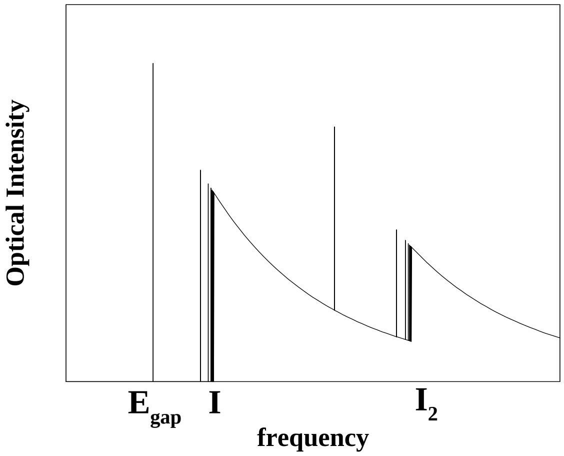

FIG. 4: Same as Fig. 3, but now including the second ionization threshold

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Concerns about both ionization potentials and double excitations are combined when we consider more of the optical response of the He atom. Zooming out just a little more in Fig. 4, we see that there is of course a **second** ionization potential, when a second electron is stripped off the atom or molecule. For reference, in a He atom, $I = 24.2$ eV, and $I_2 = 54$ eV. But the bare KS response contains *only* the first threshold. It has no structure at all in the region of the second ionization. Our simple density functional approximations to $f_{\rm XC}$ tend to shift and resize peak positions. It is very difficult to imagine *density* or orbital functional approximations to $f_{\rm XC}$ that can build in the $\omega$-dependence needed to create a second threshold.

Lastly in this section, we mention recent progress in developing a theory for **electron scattering** from molecules. This was one of the original motivations for developing TDDFT. One approach would be to evolve a wavepacket using the TDKS equations, but a more direct approach has been developed[88], in terms of the response function $\chi$ of the $N+1$ electron system (assuming it is bound). This uses similar technology to the discrete transition case. Initial results for the simplest case, electron scattering from He$^+$, suggest a level of accuracy comparable to bound-bound transitions, at least for low energies (the most difficult case for traditional methods, due to bound-free correlation[89]).

A key question that often arises is the need for **time-dependent current DFT (TDCDFT)**, or not. The Runge-Gross theorem proceeds by first proving a one-to-one correspondence between currents and scalar potentials. Obviously, the current is needed in the presence of time-dependent magnetic fields, but in their absence, is it necessary? By continuity, $dn/dt = -\nabla \cdot \mathbf{j}(\mathbf{r}t)$, so that the density is uniquely determined by the current (up to its initial value), but not vice versa. It would seem preferable to stay within the simpler density functional theory where possible. A careful examination of the conditions of applicability of the Runge-Gross theorem to finite systems[90] shows that all atoms and molecules satisfy the necessary conditions of potentials vanishing sufficiently rapidly as $r \to \infty$. However, early work showed that the gradient expansion (the origin of GGA's for the ground state) fails within TDDFT, but behaves reasonably within the current theory, yielding the Vignale-Kohn approximation[91, 92] for the response kernel, which has frequency dependence.

These questions become relevant to the **optical response of bulk insulators**. The Dyson-like Eq. (4) becomes a matrix equation with indices of the reciprocal lattice vectors $\mathbf{G}$ for each perturbation of wavevector $\mathbf{q}$. As $q \to 0$, to find the optical response, any local approximation to $f_{\text{XC}}$ produces a negligible correction to the RPA response ($f_{\text{XC}} = 0$), as the Hartree contribution (correctly) blows up as $1/q^2$. Thus, to have a noticable effect, the XC kernel must have a $1/q^2$ component as $q \to 0$. While this effect is sometimes referred to as 'ultra'-non-local, we prefer to call it simply non-local, as the range of non-locality is precisely that of the Hartree contribution. The optical response of the solid can be found within TDDFT by perturbing the system with a long-wavelength perturbation of wavevector $q$, and by carefully taking $q \to 0$. This requires extending the RG theorem to periodic Hamiltonians[93]. On the other hand, a $q = 0$ calculation, with just the period of the lattice, is possible within TDCDFT, and the non-local contribution in TDDFT appears as a local contribution within TDCDFT, with no unusual non-locality needed in the current density. For example, the VK approximation produces a finite correction, whereas LDA and GGA do not. Thus, in this and other cases, TDCDFT is not strictly necessary, but provides a more direct description and a route to extract quantities that are non-local in TDDFT. Similar observations apply to the **polarizabilities of long organic polymers**. ALDA and GGA greatly overestimate these quantities, but VK often does much better.

In this context, an important challenge is the proper description of **excitonic peaks** in the optical spectra of insulators. It was recently demonstrated[94, 95, 96] that with complicated orbital-dependent approximations for $f_{\text{XC}}$, which were derived from the Bethe-Salpeter equation, excitonic effects can be described perfectly. However, the presently available schemes require a GW calculation in the first place. There remains the challenge to find *sufficiently simple* (possibly current-dependent) approximations that are able to describe excitonic effects.

Another interesting question in the optical response of insulators is the one of the **gap**. It is well-known from ground-state DFT that the gap in the spectrum of KS eigenvalues (the KS gap) differs from the true gap by a quantity called the derivative discontinuity[3]. Ignoring excitons within the gap, shouldn't TDDFT correct the KS gap to yield the true gap? The answer is, yes, but again the XC kernel that does this must be very sophisticated, just as in our double ionization example. Since $\chi_{\text{S}}$ develops an imaginary part for frequencies above the KS gap, the kernel must have a branch cut that exactly suppresses this in order to widen the gap. There is a close analogy to the problem of charge-transfer excitations: Remove an electron from the donor to infinity. This costs the ionization energy $I_{\text{DON}}$. Then move the electron from infinity to the acceptor. In this way one gains the energy $-A_{\text{ACC}}$. So the excitation energy is $\Delta E = I_{\text{DON}} - A_{\text{ACC}} = \epsilon_{\text{ACC}}^{\text{LUMO}} - \epsilon_{\text{DON}}^{\text{HOMO}} + \Delta_{\text{XC}}^{(\text{ACC})}$, where $\Delta_{\text{XC}}^{(\text{ACC})}$ is the discontinuity in the ground-state $v_{\text{XC}}(\mathbf{r})$ of the acceptor. This formula is reminiscent of the band gap in insulators[3]. Furthermore, the next-order correction is the Coulomb-interaction between the electron on the acceptor and the hole on the donor which, in solids, corresponds to the exciton binding energy.

On the boundary between extended systems and molecules is **transport through single molecules** connected to bulk metal leads[97]. There is enormous interest in this as a key component in future nanotechnology. Present formulations use ground-state density functionals to describe the stationary non-equilibrium current-carrying state[98]. But several recent suggestions consider this as a time-dependent problem[64, 99, 100, 101, 102], and use TD(C)DFT for a full description of the situation. Only time will tell if TDDFT is really needed for an accurate description of these devices. In the special case of weak bias, XC corrections to the Landauer formula are missed by local approximations, the sin of *locality* [103].

Next we turn our attention to beyond-perturbative regimes. Due to advances in laser technology over the past decade, many experiments are now possible in regimes where the laser field is stronger than the nuclear attraction. There are a whole host of phenomena that TDDFT might be able to predict: high harmonic generation, multi-photon ionization, above-threshold ionization, above-threshold dissociation, etc. For **high harmonic generation**, TDDFT calculations have been rather succesful for atoms [104, 105] and molecules [15, 106]. In the near future, this might become very important for the generation of atto-second laser pulses [107, 108, 109]. For **multi-photon ionization**, the relative proportion of double to single ionization for He, while given much better in approximate TDDFT calculations than in previous calculations assuming a sequential mechanism, still does not show the same pronounced features (the 'knee') seen in experiments [110, 111]. The electron spectra from **above-threshold ionization** have recently been calculated within TDDFT [13, 112]. Since the ionization yields and above-threshold ionization spectra depend on probabilities extracted directly from the wavefunction, these errors are suspected to be sins of the *wavefunction*, mentioned above. An important task for the future will be the design of more realistic expressions for ionization probabilities or, more generally, transition probabilities as functionals of the time-dependent density or the time-dependent KS orbitals. First steps in this direction can be found in Ref. [110].

While the need for more accurate KS potentials was first noticeable in calculating excitations, it is even more acute in strong laser fields. To ensure an atom or molecule ionizes accurately in an approximate TDKS calculation, Koopmans' theorem ($I = -\epsilon_{HOMO}$) should be well-satisfied, and this again requires using OEP exact exchange[77, 78] or other self-interaction-free functionals.

The field of **quantum control** has, so far, mainly concentrated on manipulating the motion of the nuclear wave packet on a given set of precalculated potential energy surfaces, the ultimate goal being the femto-second control of chemical reactions [113]. With atto-second pulses available, the control of electronic dynamics has come within reach. A marriage of optimal-control theory with TDDFT appears to be the ideal theoretical tool to tackle this situation. However, it will bring with it its own difficulties and challenges for approximate functionals. Using the functional algorithms developed by Rabitz and others [114, 115], we can find the optimal pulse that drives a He atom from its ground state to its first excited state, $1s2p$. (In practice, we do not reach exactly 100% occupation, due to a finite penalty factor).

Now repeat this experiment on non-interacting electrons sitting in the same potential. Such a pulse cannot be found, i.e., the non-interacting system is not controllable, whereas the interacting system is. The two non-interacting electrons must follow the same time evolution as they start from the same initial 1s orbital and are exposed to the same laser field. Hence the time-dependent wave function of the two non-interacting electrons must have the form:

$$\Phi(r_1, \sigma_1, r_2, \sigma_2, t) = \varphi(\mathbf{r}_1, t)\varphi(\mathbf{r}_2, t)\chi_S(\sigma_1, \sigma_2) \tag{11}$$

where $\chi_S(\sigma_1, \sigma_2)$ represents the (antisymmetric) spin-singlet part of the wavefunction. But we want to maximize the occupation

$$|< \Phi(T)|\Phi_{1s,2p} >|^2 \tag{12}$$

of the time-propagated wavefunction $\Phi(T)$ at the end, $T$, of the laser pulse in the lowest excited state

$$\Phi_{1s,2p} = \frac{1}{\sqrt{2}}(\varphi_{1s}(\mathbf{r}_1)\varphi_{2p}(\mathbf{r}_2) + \varphi_{2p}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2))\chi_S(\sigma_1, \sigma_2) \tag{13}$$

Expanding the final wavefuntion $\Phi(T)$ in the complete set of single-particle orbitals representing the eigenfunctions of the unperturbed system, one sees that the best possible occupation is 50%.

If TDDFT is used to describe the multi-electron dynamics, how would one properly define the control target, i.e., the functional to be maximized? Choosing, as control target, the overlap with an excited-state Kohn-Sham determinant does not seem to be a good idea in view of the above dilemma. If, on the other hand, the time-dependent density of a fully controlled $(1s)^2$ to $(1s, 2p)$ transition of the interacting system is given, would an exact TDKS calculation reproduce such an optimal evolution? The answer is yes, but $v_{\text{XC}}(\mathbf{r}t)$ must be very special to do so. To see this, take the density evolution from the exact Schrödinger equation, and invert the TDKS equation for the single (doubly-occupied) time-dependent orbital. The final state KS potential is very odd, producing the density of two orbitals of different symmetry from a single doubly-occupied orbital[116].

For a subset of cases in which molecules are exposed to strong fields, the nuclear motion can be treated classically. The electrons then feel the Coulomb field of classically moving nuclei as well as the laser field. In this case, the electronic motion is well described by ordinary TDDFT. However, **when nuclear trajectories split**, e.g., when a molecule has a 50% chance of dissociation in a given laser pulse, the classical treatment fails. A multicomponent TDDFT[117, 118, 119] has been developed for electrons and nuclei which, in principle, handles such a situation. In practice, one needs to develop appropriate approximations that can build in the appropriate physics of, e.g., dissociating nuclei. Again, in this case, orbital-dependent functionals appear crucial[117, 119].

Finally, and fondly, we return to the ground state. The last general application mentioned was the odd-sounding process of **using TDDFT to generate ground-state approximations**, via Eq. (9). By inserting an approximation for $f_{\text{XC}}$, we get an approximation to $E_{\text{XC}}$. Most importantly for biological systems, Eq. (9) provides a route to **van der Waals** forces for separated pieces of matter, and so is being much studied by developers. In particular, the coefficient in the decay of the energy between two such pieces ($C_6$ in $E \to -C_6/R^6$, where $R$ is their separation) can be accurately (within about 20%) evaluated using a local approximation to the frequency-dependent polarizability[21, 120, 121, 122]. Recent work shows that the response functions of TDDFT can yield extremely accurate dispersion energies of monomers[123]. More recently, the frequency integral in Eq. (9) has been done approximately, yielding an explicit non-local density functional[23] applicable at all separations.

One can go the other way, and try using Eq. (9) for all bond lengths[124, 125]. Such calculations are costly, as the functional is very high up on Jacob's ladder of sophistication, including both occupied and unoccupied

KS orbitals[63]. However, they have the merit of being entirely non-empirical and, where successful, can be used as a starting point for new approximations. In fact, Eq (9) provides a KS density functional that allows **bond-breaking** without artifical symmetry breaking[22]. In the paradigm case of the $H_2$ molecule, the binding energy curve has no Coulson-Fischer point, and the dissociation occurs correctly to two isolated H atoms. Unfortunately, simple approximations, while yielding correct results near equilibrium and at infinity, produce an unphysical repulsion at large but finite separations. This can be traced back[22] to the lack of double excitations in any adiabatic $f_{XC}$.

We end with a **summary**. Most importantly, TDDFT has become extremely popular as a method for calculating electronic excited-state energies in chemistry. In this arena, it has become as robust (or as flaky, depending on your perspective) as ground-state DFT, and is being used to really understand the photochemistry of many interesting problems. Furthermore, our favorite crude density functional approximations from the ground-state serve well here. We are very thankful for this, and it has led to tremendous interest in further methodological development.

In principle, however, TDDFT yields predictions for an enormous variety of phenomena, and electronic excitations are only the tip of an iceberg. We have mentioned a few. Even limiting ourselves to linear response, there are double excitations, second ionization thresholds, optical response of solids, gaps in solids, transport through single molecules. Combining with the fluctuation-dissipation theorem, TDDFT yields a route to van der Waals forces and bond-breaking with symmetry problems. In strong fields, there are high harmonic generation, multi-photon ionization, above-threshold ionization, quantum control, and quantum nuclear motion.

For some of these areas, simple application of density functionals within the adiabatic approximation, works well, but for many, such methods miss some qualitative features (e.g., double excitations, or non-locality in the response of solids). A now standard step upward in sophistication is to use orbital-dependent functionals (at least, among developers), and these cure some of the difficulties (e.g., the first ionization threshold or the polarizability of long-chain polymers). But such functionals are unlikely to cure all of the problems (e.g., inclusion of double excitations or defining the target in quantum control) for properties that are of interest experimentally and technologically. We happily look forward to many interesting years of development to come.

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