Chapter XX. Time-dependent density functional theory in quantum chemistry

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Time-dependent density functional theory (TDDFT) is increasingly popular for predicting excited state and response properties of molecules and clusters. We review the present state-of-the-art, focusing on recent developments for excited states. We cover the formalism, computational and algorithmic aspects, and the limitations of present technology. We close with some promising developments. Extensive reviews on many aspects of TDDFT exist [1] [2] [3] [4] [5], and no pretence at comprehensive coverage is made here; instead, we rely heavily on our own work and that of our collaborators.

BACKGROUND

Standard (i.e., ground-state) density functional theory (DFT) is derived from traditional wavefunction-based quantum mechanics. The Hohenberg-Kohn (HK) theorem is a simple rewriting of the Rayleigh-Ritz variational principle [6]. Time-dependent DFT is based on a different theorem [7], which is a simple consequence of the *time-dependent* Schrödinger equation. For a given initial wavefunction and particle interaction, a time-dependent one-electron density $\rho(\mathbf{r}\ t)$ can be generated by at most one time-dependent external (i.e., one-body) potential. By starting in a non-degenerate ground-state, the dependence on the initial wavefunction can be absorbed into the density dependence, by virture of HK.

We define a set of time-dependent Kohn-Sham (TDKS) equations that reproduce $\rho(\mathbf{r}\ t)$, from a unique time-dependent Kohn-Sham (KS) potential. This consists of the external potential, the Hartree potential, and the unknown time-dependent exchange-correlation (XC) potential $v_{xc}[\rho](\mathbf{r}\ t)$. This is a much more sophisticated object than the ground-state $v_{xc}[\rho](\mathbf{r})$, as it encapsulates all the quantum mechanics of all electronic systems subjected to all possible time-dependent perturbations.

ELECTRONIC EXCITATIONS

To extract electronic excitations, apply a weak electric field, and ask how the system responds, as in standard perturbation theory. We don't need the entire $v_{xc}[\rho](\mathbf{r}\ t)$, but only its value close to the ground state. This is captured in the XC kernel, $f_{xc}(\mathbf{r}\ \mathbf{r}';\ t\text{-}t')=\delta v_{xc}[\rho](\mathbf{r}\ t)/\delta\rho(\mathbf{r}'\ t')$. This is a *new* functional introduced by the time-dependence. Its Fourier transform, $f_{xc}(\mathbf{r}\ \mathbf{r}';\ \omega)$, reduces to the ground-state value as $\omega \rightarrow 0$. The standard *adiabatic* approximation ignores the frequency dependence, and uses the second-derivative of the ground-state XC energy functional. Typical examples are the local density approximation (LDA), generalized gradient approximation (GGA) and hybrids, such as B3LYP.

Several practical routes have been adopted for extracting excitation energies from TDDFT response theory. In 1995, Casida converted the optical response problem into the solution of an eigenvalue problem (EVP) [2] whose indices are the single-particle transitions of the ground-state Kohn-Sham potential:

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - \Omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}\right] \begin{pmatrix} X_n \\ Y_n \end{pmatrix} = 0$$

The matrices **A** and **B** are the Hessians of the electronic energy. The dominant contributions to the **A** matrix are the Kohn-Sham transition frequencies along the diagonal. The transition vectors (X_n Y_n) correspond to collective eigenmodes of the TDKS density matrix with eigenfrequencies Ω_n. The Hartree and XC kernels produce both diagonal and off-diagonal contributions to **A** and **B**, correcting the transitions between occupied and unoccupied levels of the ground-state KS potential into the true transitions of the system. If the different Kohn-Sham transitions do not couple strongly to one-another, a useful approximation is to take only the diagonal elements of **A**. One can view the KS transition as being corrected by an integral over $f_{xc}(\mathbf{r}\ \mathbf{r}'\ ,\omega)$ on the transition matrix elements, and the KS oscillator strengths will be good approximations to the true ones [8].

Alternatively, many physicists propagate the TDKS equations in real time, usually on a real-space grid inside a large sphere. They calculate the time-dependent dipole moment of their system, whose Fourier-transform yields the optical response.

COMPUTATIONAL ASPECTS

The response theory outlined above can be re-cast in variational form [9]. To this end, one defines a Lagrangian L which is stationary with respect to *all* its parameters at the excited state energies. L depends on the ground state KS molecular orbitals (MOs), on the excitation vector; and three Lagrange multipliers. This is convenient for excited state property calculations, because the Hellmann-Feynman theorem holds for L. The LCAO(linear combination of atomic orbitals)-MO expansion reduces the computation of excited state energies and properties to a finite-dimensional optimization problem for L, which can be handled algebraically. The stationarity conditions for L lead to the following problems which have to be solved subsequently in an excited state calculation.

(i) **Ground state KS equations in a finite basis**; results are the ground state KS MOs and their eigenvalues. Computational strategies to solve this problem have been developed over decades, e.g., direct SCF (self-consistent field), RI (resolution of the identity), and linear scaling methods. Efficient excited state methods take advantage of this technology as much as possible.

(ii) **The finite-dimensional TDKS EVP (Casida's equations)** [10] [11]; results are the excitation energies and transition vectors. They are used (a) to compute transition moments and (b) to analyze the character of a transition in terms of occupied and virtual MOs. Complete solution of the TDKS EVP for all excited states leads to a prohibitive $O(N^6)$ scaling of CPU time and to $O(N^5)$ I/O (N is the dimension of the one-particle basis). In most applications only the lowest states are of interest; iterative diagonalization methods such as the Davidson method are therefore the first choice [12] [13] [14]. In these iterative procedures, the time-determining step is a single matrix-vector operation per excited state and iteration, which can be cast into a form closely resembling a ground state Fock matrix construction [15]. In this way, a single-point excitation energy can be computed with similar effort as a single-point ground state energy. Block algorithms lead to additional savings if several states are computed at the same time [16]. Sometimes, the Tamm-Dancoff approximation is used [3], which amounts to constraining Y to zero in the variation of L.

(iii) **The "Z-vector equation"**; results are the TDKS "relaxed" excited state density and energy weighted density matrices. Excited state properties such as dipole moments and atomic populations can be computed from the excited state density matrix; analytical gradients of the excited state energy with respect to the nuclear positions require the energy weighted density matrix as well. Using iterative methods similar to those above, the cost for computing the Z-vector is again in the range of the cost for a single-point ground state energy. Geometry optimizations for excited states are therefore not significantly more expensive than for ground states.

Flexible Gaussian basis sets developed for ground states are usually suited for excited state calculations. The smallest recommendable basis sets are of split valence quality and have polarization functions on all atoms except H, e.g., SV(P) or 6-31G*. Especially in larger systems, these basis sets can give useful accuracy, e.g., for simulating UV spectra (see below). However, excitation energies are typically overestimated by 0.2-0.5 eV, and individual oscillator strengths may be qualitatively correct only. A useful (but not sufficient) indicator of the quality is the deviation between the oscillator strengths computed in the length and in the velocity gauge, which approaches zero in the basis set limit. Triple-zeta valence basis sets with two sets of polarization functions, e.g., cc-pVTZ or TZVPP, usually lead to basis set errors well below the functional error; larger basis sets are used to benchmark. Higher excitations and Rydberg states may require additional diffuse functions.

PERFORMANCE

Vertical excitation and CD spectra – So far, simulation and assignment of vertical electronic absorption spectra has been the main task of TDDFT calculations in chemistry. Most benchmark studies agree that low-lying valence excitations are predicted with errors of ca. 0.4 eV by LDA and GGA functionals [10] [17] [18]. Hybrid functionals can be more accurate, but display a less systematic error pattern. Traditional methods such as time-dependent Hartree-Fock (TDHF) or configuration interaction singles (CIS) often produce errors of 1-2 eV at comparable or higher computational cost. Bearing in mind that UV-VIS spectra of larger molecules are mostly low-resolution spectra recorded in solution, and in view of the relatively low cost of a TDDFT calculation, errors in the range of 0.4 eV are acceptable for many purposes.

Calculated oscillator strengths may be severely in error for individual states, but the global shape of the calculated spectra is often accurate. Because semi-local functionals often predict the onset of the continuum to be 1-2 eV too low (due to the lack of derivative discontinuity), this is especially true for excitations in the continuum (excitation energy > |HOMO energy|) [19]. Rotatory strengths which determine electronic circular dichroism (CD) spectra can be computed from magnetic transition moments in the density matrix based approach to TDDF response theory [20]. The simulated CD spectra predict the absolute configuration of chiral compounds in a simple and mostly reliable way. In particular, TDDFT also works well for inherently chiral chromophores [21] and transition metal compounds [22] where semi-empirical methods tend to fail.

Successful applications of TDDFT vertical excitation and CD spectra have been reported in various areas of chemistry, including metal clusters, fullerenes, aromatic compounds, porphyrins and corrins, and many other organic chromophores. As an example, we show the simulated and measured CD spectra of the chiral fullerene C_{76} in Fig. 1 [16]. We used the Becke-Perdew86 GGA together with the RI-J approximation and a SVP basis set augmented with diffuse *s* functions; a uniform blue-shift of 0.4 eV was applied to all excitation energies to correct systematic errors of the calculation and solvent effects. The computed spectrum reproduces the main features of the experimental spectrum, even the intensities are in the right range. The absolute configuration of C_{76} can be determined in this way, because the measured spectrum can be assigned to one of the two enantiomers whose CD spectra differ by their sign only. The simulated spectrum involves 240 excited states; its calculation took 30h on a single processor 1.2 Ghz Athlon PC using TURBOMOLE V5-4 [23].

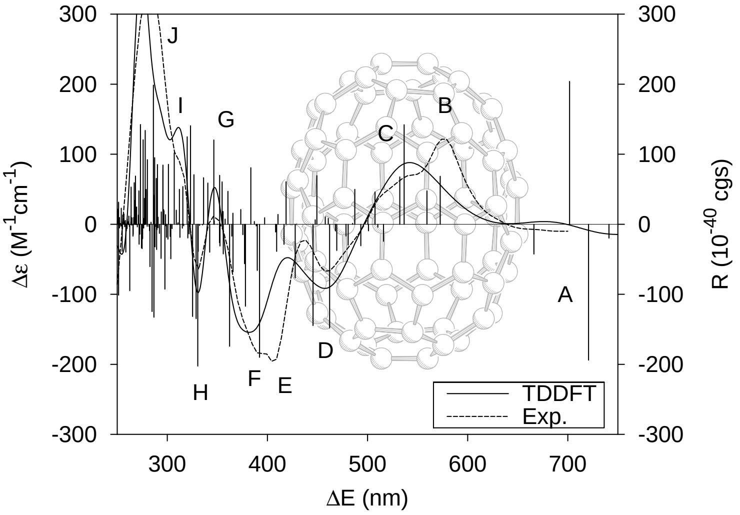

Figure 1: The simulated CD spectrum of fullerene C_{76} compared to experiment.

Excited state structure and dynamics – An adequate description of most photophysical and photochemical properties requires information on excited potential energy surfaces beyond vertical excitation energies. Early benchmark studies indicated at least qualitative agreement of excited potential surfaces calculated using TDDFT and correlated wavefunction methods [24] [25]. An increasing number of excited state reaction path calculations using TDDFT have been reported. A limitation of most studies is that the reaction paths do not correspond to minimum energy paths (MEPs), i.e., the internal degrees of freedom other than the reaction coordinate are not optimized.

Analytical gradients of the excited state energy with respect to the nuclear positions are a basic prerequisite for systematic studies of excited state potential energy surfaces even in small systems. Implementations have become available only recently [26] [2] [27]. While errors in adiabatic excitation energies are similar to errors in vertical excitation energies, the calculated excited state structures, dipole moments, and vibrational frequencies are relatively accurate, with errors in the range of those observed in ground state calculations. The traditional CIS method, which has almost exclusively been used for excited state optimizations in larger systems, is comparable in cost, but significantly less accurate. Moreover, the KS reference is much less sensitive to stability problems than the HF reference, which is an important advantage especially if the ground and excited state structures differ strongly.

Individual excited states of larger molecules can be selectively investigated by pump-probe experiments. The resulting time-dependent absorption, fluorescence, IR, and resonance Raman spectra can be assigned by TDDFT excited state calculations. First applications show that calculated vibrational frequencies are accurate enough to determine the excited state structure by comparison with experiment [28]. The combination of TDDFT and transient spectroscopy methods a promising strategy for excited state structure elucidation in larger systems. Computed normal modes of excited states can be used to study the vibronic structure of UV spectra within the Franck-Condon and Herzberg-Teller approximation [29]. For a detailed understanding of photochemical reactions beyond MEPs, excited state nuclear dynamics simulations including non-adiabatic couplings are necessary. The first steps towards this ambitious goal have already been made [30] [31].

QUALITATIVE LIMITATIONS OF PRESENT FUNCTIONALS

Next we discuss situations where today's approximations in TDDFT produce much larger errors, or entirely miss important aspects of the optical response.

Inaccurate ground-state KS potentials – It had been well-known for many years that the XC potentials of LDA and GGA are inaccurate. At large distances, they decay exponentially rather than as the correct -1/r. This can be a severe problem for TDDFT, since the orbital energies can be very sensitive to the details of the potential. This is not a problem if only low-lying valence excitations of large molecules are required, but the energy of low-lying diffuse states is often considerably underestimated, while higher Rydberg states are completely missing in the bound spectrum [32].

There now exist several schemes for imposing the correct asymptotic decay of the XC potential [33]. But such potentials are not the functional derivative of any XC energy. While this has no direct effect on vertical excitation energies, other excited state properties are not well-defined. Exact exchange DFT methodology is developing rapidly (see next section), which does not suffer from this problem. Furthermore, when correctly interpreted, even the physicists' TDLDA calculations recover the correct oscillator strength despite these difficulties.

Adiabatic approximation – The frequency-dependence of the XC kernel is ignored in most calculations. A simple approximation is to use the ω-dependent XC kernel of the uniform gas [34]. However, any collective motion of the electrons that does not deform the density, e.g., an overall boost, should not excite the electrons, but a frequency-dependent kernel violates this exact condition (whereas adiabatic approximations do not) [35].

Multiple excitations – In principle, the exact electronic response functions contain all levels of excitation. But Casida's equations span the space of KS single-particle excitations only, and this is unchanged by a frequency-independent XC kernel, i.e., within the adiabatic approximation.

Extended systems – Unlike ground-state DFT, there are non-trivial complications when TDDFT is applied to bulk systems. These arise because the XC kernel has long-range contributions, comparable to the Hartree $1/|\mathbf{r}-\mathbf{r}'.|$ However, our usual local and semilocal approximations yield XC kernels that are of the form $\delta^{(3)}(\mathbf{r}-\mathbf{r}')$, or derivatives thereof. Thus they have *little effect* on the calculated optical response of extended systems.

Charge transfer problems – Charge transfer (CT) excitations are notoriously predicted too low in energy by up to 1 eV or more [36]. In chain-like systems such as polyenes, polyacenes, or other conjugated polymers, the error in CT excitation energies increases with the chain length [37,38]. In the limit of complete charge separation, this can be related to the lack of derivative discontinuities in semi-local functionals [36]. To correct CT excitation energies, methods have been suggested that estimate the derivative discontinuity from a ΔSCF calculation [36,39]. The validity of this approach depends on assumptions such as complete charge separations that may rarely be justified in real systems.

PROMISING DEVELOPMENTS

Here we discuss several promising paths to overcome present limitations.

Exact exchange: Many problems are related to spurious self-interaction, which affects energies and potentials computed with semi-local functionals. The self-interaction free exact exchange functional leads to a potential with the correct -1/r tail,. greatly improving the description of Rydberg states [40,41]. Moreover, the absence of self-interaction is a prerequisite for a correct derivative discontinuity, as has been demonstrated numerically. The use of exact exchange potentials improves the description of optical properties of conjugated polymers. Unfortunately, exchange alone is not enough. So far, calculations employing the full frequency-dependent exchange kernel have been reported for solids only [42]. Excitation energies of valence states obtained with exchange-only potentials plus ALDA kernel are not systematically better than those from GGA calculations. Moreover, the neglect of correlation effects generally leads to an overestimation of the energy of ionic states, as is well known, e.g., from TDHF. Adding an LDA or GGA correlation potential to the x only potential leads to marginal improvements only, because the error compensation between approximate exchange and correlation is lost. In practice, one often resorts to hybrid functionals, which contain a (relatively small) fraction of exact exchange only. Thus, moderately diffuse states and certain CT excitations can still be handled [43]. A more fundamental solution may require correlation functionals compatible with exact exchange.

Beyond the adiabatic approximation: Higher-order excitations are accounted for by dramatic frequency-dependence in f_{xc}, and building it into the kernel allows one to recover, e.g., a double excitation close to a single. In fact, the usual adiabatic approximation simply combines both into one peak, which will be a good approximation to the total oscillator strength [44] [45].

Over the last year, it has been shown that incorporation of the essential terms of the polarizability from the Bethe-Salpeter equation (i.e., an orbital-dependent functional) recovers excellent excitonic peak shifts in semiconductors [46] [47]. Chemists with long molecules should be aware of this, as the standard methodology misses these effects.

TD current DFT: The Runge-Gross theorem in fact establishes that the potential is a functional of the current density, $\mathbf{j}(\mathbf{r})$. This approach allowed Vignale and Kohn [48] to construct a gradient expansion in $\mathbf{j}(\mathbf{r})$ that goes beyond the adiabatic approximation without violating exact conditions for boosts. This formulation leads naturally to ultra non-local functionals that can shift exciton peaks and correct polarizability problems [49], but no accurate approximation is yet available.

OUTLOOK

TDDFT in its present incarnation works remarkably well for many systems and properties. The number of papers is growing exponentially. While most are focused on extracting electronic transitions, there are many other promising applications. For example, atoms and molecules in intense laser fields can be handled with this formalism. Recently, it has been shown that scattering cross-sections can also be extracted [50].

This is a golden-age of TDDFT in quantum chemistry, in which we are right now discovering which systems and properties can be handled routinely, where our favorite approximations fail, and how to fix these failures. We anticipate several more exciting years.

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