A simplified time-dependent density functional theory approach for electronic ultraviolet and circular dichroism spectra of very large molecules

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ARTICLE INFO

ABSTRACT

We present a simplified time-dependent density functional theory approach (sTD-DFT) that allows fast computation of electronic ultraviolet (UV) or circular dichroism (CD) spectra of molecules with 500–1000 atoms. The matrix elements are treated in the same way as in the recently proposed simplified Tamm-Dancoff approach (sTDA, S. Grimme, J. Chem. Phys., 138 (2013), 244104) but instead of applying the Tamm-Dancoff approximation, the standard linear-response density functional theory problem is solved. Compared to sTDA, the method leads to an increase in computation time (typically a factor of 2–5 compared to the corresponding sTDA) which is justified since the resulting transition dipole moments are in general of higher quality. This becomes important if spectral intensities (e.g. single-photon oscillator and rotatory transition strengths) are of interest. Comparison of UV and CD spectra obtained from sTD-DFT and sTDA for some typical systems employing standard hybrid functionals shows that both yield very similar excitation energies but the advantage of using the former approach for transition moments. In order to show the applicability of sTD-DFT to systems which are far beyond the scope of conventional TD-DFT, we present the CD spectrum of a substituted, chiral fullerene over a range of almost 1200 excited states. We propose this method as a more reliable alternative for the prediction especially of the more challenging CD spectra.

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1. Introduction

Kohn-Sham density functional theory (KS-DFT) is now the most widely used method for electronic structure calculations of larger molecules in the electronic ground state. For the calculation of excited state properties and electronic spectra of fairly large systems (about 100 atoms), time-dependent density functional theory (TD-DFT) [1–4] based on a KS-DFT ground state determinant has become the most important method (see e.g. Refs. [5–9] for reviews). For TD-DFT calculations of ground state properties like dispersion coefficients see e.g. Refs. [10,11].

It is generally assumed in TD-DFT that the density changes only slowly with time. For this reason, the time-dependent exchange-correlation (XC) kernel is replaced by a time-independent one which is then evaluated using the time-dependent density. This so-called adiabatic approximation [1,2] allows one to make use of ground state XC potentials in TD-DFT. The states of common

interest are often valence states far below the first ionization potential for which this approximation works fairly well [3].

The accuracy of TD-DFT for vertical excitation energies is roughly comparable to that of KS-DFT for relative ground state energies (about 0.2–0.3 eV for TD-DFT, 2–5 kcal/mol for KS-DFT) [12,13]. There are some well-known deficiencies of TD-DFT such as the description of excitations with double excitation or multiplet character which are problematic for any single-reference method. Density functionals of the general gradient approximation (GGA) type, have an XC potential of an incorrect asymptotic form [7] and suffer also from the self-interaction error (SIE) [14–17] and the related integer discontinuity problem [18,17]. General implications are underestimated ionization potentials, overestimated electron affinities and too small energy gaps between Kohn-Sham orbitals. Due to these deficiencies TD-DFT/GGA severely underestimates charge-transfer (CT) and Rydberg excitations [7,19,20,18,21]. This artificially introduces many states with low oscillator strength ('ghost states') to the low energetic part of the spectrum. Even though they are often not observed in a simulated ultraviolet-visible (UV-Vis) spectrum, they may cause

artificial mixing of configurations and 'contaminate' the bright states which can then corrupt spectra considerably.

Since Hartree-Fock (HF) does not suffer from SIE and exhibits the correct asymptotic potential, admixing certain amounts of non-local Fock exchange to the GGA exchange, as done in global hybrids (e.g. B3LYP [22–24]), partially alleviates the SIE as well as the CT problem in TD-DFT. Such functionals are more reliable in an excited state treatment than pure GGAs on the one hand and HF based single-excitation methods on the other. The advantage of (hybrid) TD-DFT over the latter are the implicitly 'correlated' Kohn-Sham orbitals. Since semi-empirical methods are typically less reliable and wave-function based methods which include double and higher excitations are too costly to be applied to large systems, hybrid TD-DFT has become one of the most widely used methods to describe excited states systems up to about 100 atoms.

The amount of non-local Fock exchange for typical hybrid functionals lies in the range of 10–25%, but can be as high as 50% like in the BHLYP functional [22]. In a systematic study, it has been found that on average admixing 40% of non-local Fock exchange yields the best excitation energies of fairly large organic molecules [25], although the correct treatment of some larger systems required higher amounts of Fock exchange up to 50% or more. A commonly applied class of functionals in TD-DFT calculations nowadays are the range-separated-hybrid (RSH) functionals that, starting with no or low amounts of Fock exchange, asymptotically employ 100% non-local Fock exchange (65% in the case of CAM-B3LYP) [26–29]. With these functionals, the correct asymptotic behaviour is achieved. Nevertheless, we will employ exclusively global hybrids in this work and make use of the BHLYP functional in large systems where the description of CT states may become problematic. The extension of the here proposed method to RSH functionals is straightforward (see below) and will be discussed elsewhere.

Even though TD-DFT can deal with systems beyond the scope of traditional wave function based methods, the theoretical treatment of an entire UV-Vis electronic spectrum in a typical excitation energy range from 2 to 7 eV for systems with several hundreds up to about 1000 atoms remains a challenge. Recently, a simplified Tamm-Dancoff approach to time-dependent density functional theory (sTDA) has been proposed which allows routine computations of UV-Vis or circular dichroism (CD) spectra of such large systems [30]. The drastic simplifications are on the one hand, the evaluation of the two-electron integrals as short-range damped Coulomb interactions between (transition) charge density monopoles and a massive truncation of the single excitation expansion space on the other. Solving the Tamm-Dancoff approximated problem (TDA) [31,32] instead of the TD-DFT equation requires the solution of only one eigenvalue problem and along with the simplifications mentioned above, this makes the sTDA approach extremely fast even for large molecules.

While the TDA typically gives quite similar excitation energies to TD-DFT, it suffers from the fact that it is not gauge invariant and oscillator and rotatory strengths obtained from TDA do not satisfy the respective sum rules [4,7,33]. These shortcomings can become particularly problematic if one is interested in calculating rotator strengths for CD spectra. TD-DFT, on the other hand, does not suffer from these shortcomings. Therefore, a simplified time-dependent density functional theory approach (sTD-DFT) is presented here which makes use of the same simplifications as made in sTDA while the full TD-DFT problem is solved.

This paper is structured in the following way: After a brief outline of the basic theory followed by a short summary of the sTDA method, we will recapitulate the dipole length and the dipole velocity formalisms for transition moments. Then the sTD-DFT is discussed. Finally, we will compare the performance of sTD-DFT to sTDA and conventional TD-DFT for the computation of excitation energies as well as UV and CD spectra for various systems.

2. Theory

2.1. TD-DFT and TDA

The full TD-DFT response problem is given by the following non-Hermitian eigenvalue problem [1,7].

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \omega & 0 \\ 0 & -\omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{1}$$

where $\mathbf{A}$ and $\mathbf{B}$ are the so-called orbital rotation Hessian matrices with eigenfunctions $\mathbf{X}$ and $\mathbf{Y}$ and ω is a vector with the dimension of the number of roots (nroots) that contains the respective eigenvalues. In wave function theory, this equation corresponds to time-dependent Hartree-Fock (TD-HF, also called random-phase approximation, RPA). For a global hybrid density functional in the spin-restricted case, the elements of the matrices $\mathbf{A}$ and $\mathbf{B}$ take the form

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia\,|\,jb) - a_x(ij\,|\,ab) + (1-a_x)(ia\,|\,f_{XC}\,|\,jb) \tag{2}$$

and

$$B_{ia,jb} = 2(ia\,|\,bj) - a_x(ib\,|\,aj) + (1-a_x)(ia\,|\,f_{XC}\,|\,bj). \tag{3}$$

Here, ϵ_a and ϵ_i are the orbital energies of the virtual and occupied orbitals obtained from the respective ground state calculation. The two-electron integrals are given in the so-called chemists' notation, i.e., $(ia\,|\,jb) = \psi_i(r_1)\psi_a(r_1)\frac{1}{r_{12}}\psi_j(r_2)\psi_b(r_2)dr_1 dr_2$ (ij stand for occupied, ab for virtual orbitals). a_x is the amount of non-local Fock exchange that is mixed into the XC funtional [22] such that

$$E_{XC}^{hybrid} = (1-a_x)E_X^{GGA} + a_x E_X^{Fock} + E_C^{GGA} \tag{4}$$

where E_X^{GGA} and E_X^{Fock} denote semi-local GGA and non-local Fock exchange terms, respectively and E_C^{GGA} is the GGA correlation energy. For $a_x = 1$ the above equations correspond to the HF/RPA case [3]. The other extreme (i.e. $a_x = 0$) corresponds to semi-local TD-DFT equations [1]. The terms $2(ia\,|\,jb)$ and $2(ia\,|\,bj)$ in the matrix elements of $\mathbf{A}$ and $\mathbf{B}$, respectively, are of exchange type and result from the response of the Coulomb integrals in the ground state. The response of the XC functional is given by the terms $(ia\,|\,f_{XC}\,|\,jb)$ and $(ia\,|\,f_{XC}\,|\,bj)$, respectively, and its contribution is scaled by the amount of (semi-)local density functional exchange used in the ground state (first term on the right-hand side of Eq. 4). Accordingly, the terms scaled by a_x correspond to the response of the non-local Fock exchange. While this term is of exchange type in the $\mathbf{B}$ matrix elements, it is of Coulomb type in the $\mathbf{A}$ matrix elements. This term alleviates the incorrect description of CT states by GGA based TD-DFT.

Since the used orbitals are usually real, instead of the non-Hermitian eigenvalue problem in Eq. (1), the Hermitian one

$$(\mathbf{A}-\mathbf{B})^{\frac{1}{2}}(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B})^{\frac{1}{2}}\mathbf{Z} = \omega^2\mathbf{Z} \tag{5}$$

with

$$\mathbf{Z} = (\mathbf{A}-\mathbf{B})^{-\frac{1}{2}}(\mathbf{X}+\mathbf{Y}) \tag{6}$$

can be solved [1,3]. The matrix $(\mathbf{A}-\mathbf{B})$ is diagonal in the case of a pure GGA [7,34] but not in TD-HF and hybrid TD-DFT. Thus, in order to take the square-roots a unitary transformation needs to be performed which involves a diagonalization in the full configuration space. To circumvent this step, Hirata and Head-Gordon have applied the Tamm-Dancoff approximation [31] to TD-DFT in which the contribution of the $\mathbf{B}$ matrix is neglected [32]. Instead of solving two eigenvalue problems as in hybrid TD-DFT, only one eigenvalue problem needs to be solved:

$$\mathbf{A}\mathbf{t} = \omega_{TDA}\mathbf{t} \tag{7}$$