



Assessment of dressed time-dependent density-functional theory for the low-lying valence states of 28 organic chromophores

Miquel Huix-Rotllant^{a,*}, Andrei Ipatov^a, Angel Rubio^{b,c,d}, Mark E. Casida^a

^a Laboratoire de Chimie Théorique, Département de Chimie Moléculaire (DCM, UMR CNRS/UJF 5250), Institut de Chimie Moléculaire de Grenoble (ICMG, FR2607), Université Joseph Fourier (Grenoble I), 301 rue de la Chimie, BP 53, F-38041 Grenoble Cedex 9, France

^b Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre, Departamento de Física de Materiales, Universidad del País Vasco, E-20018 San Sebastián, Spain

^c Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, E-20018 San Sebastián, Spain

^d Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

ARTICLE INFO

Article history:

Available online 30 March 2011

Keywords:

Time-dependent density-functional theory
Exchange-correlation kernel
Adiabatic approximation
Frequency dependence
Many-body perturbation theory
Excited states
Organic chromophores

ABSTRACT

Almost all time-dependent density-functional theory (TDDFT) calculations of excited states make use of the adiabatic approximation, which implies a frequency-independent exchange-correlation kernel that limits applications to one-hole/one-particle states. To remedy this problem, Maitra et al. [N.T. Maitra, F. Zhang, R.J. Cave, K. Burke, Double excitations within time-dependent density functional theory linear response theory, *J. Chem. Phys.* 120 (2004) 5932] proposed dressed TDDFT (D-TDDFT), which includes explicit two-hole/two-particle states by adding a frequency-dependent term to adiabatic TDDFT. This paper offers the first extensive test of D-TDDFT, and its ability to represent excitation energies in a general fashion. We present D-TDDFT excited states for 28 chromophores and compare them with the benchmark results of Schreiber et al. [M. Schreiber, M.R. Silva-Junior, S.P.A. Sauer, W. Thiel, Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3, *J. Chem. Phys.* 128 (2008) 134110]. We find the choice of functional used for the A-TDDFT step to be critical for positioning the 1h1p states with respect to the 2h2p states. We observe that D-TDDFT without HF exchange increases the error in excitations already underestimated by A-TDDFT. This problem is largely remedied by implementation of D-TDDFT including Hartree–Fock exchange.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Time-dependent density-functional theory (TDDFT) is a popular approach for modeling the excited states of medium- and large-sized molecules. It is a formally exact theory [1], which involves an exact exchange-correlation (xc) kernel with a role similar to the xc-functional of the Hohenberg–Kohn–Sham ground-state theory. Since the exact xc-functional is not known, practical calculations involve approximations. Most TDDFT applications use the so-called adiabatic approximation which supposes that the xc-potential responds instantaneously and without memory to any change in the self-consistent field [1]. The adiabatic approximation limits TDDFT to one hole-one particle (1h1p) excitations (i.e., single excitations), albeit dressed to include electron correlation effects [2]. Overcoming this limitation is desirable for applications of TDDFT to systems in which 2h2p excitations (i.e., double excitations) are required, including the excited states of polyenes, open-shell molecules, and many common photochemical reactions

* Corresponding author.

E-mail addresses: Miquel.Huix@UJF-Grenoble.Fr (M. Huix-Rotllant), Mark.Casida@UJF-Grenoble.Fr (M.E. Casida).

[3–5]. Burke and coworkers [6,7] proposed the dressed TDDFT (D-TDDFT) model, an extension to adiabatic TDDFT (A-TDDFT) which explicitly includes 2h2p states. The D-TDDFT kernel adds frequency-dependent terms from many-body theory to the adiabatic xc-kernel. While initial results on polyenic systems appear encouraging [7–9], no systematic assessment has been made for a large set of molecules. The present article reports the first systematic study of D-TDDFT for a large test set namely, the low-lying excited states of 28 organic molecules for which benchmark results exist [10,11]. This study has been carried out with several variations of D-TDDFT implemented in a development version of the density-functional theory (DFT) code deMon2k [12].

The formal foundations of TDDFT were laid out by Runge and Gross (RG) [1] which put on rigorous grounds the earlier TDDFT calculations of Zangwill and Soven [13]. The original RG theorems showed some subtle problems [14], which have been since re-examined, criticized, and improved [15–17] providing a remarkably well-founded theory (for a recent review see [18].) A key feature of this formal theory is a time-dependent Kohn–Sham equation containing a time-dependent xc-potential describing the propagation of the density after a time-dependent perturbation is applied to the system. Casida used linear response (LR) theory to

derive an equation for calculating excitation energies and oscillator strengths from TDDFT [19]. The resultant TDDFT response equations [19] are

$$\begin{bmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ -\mathbf{B}^*(\omega) & -\mathbf{A}^*(\omega) \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}. \quad (1.1)$$

Here $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ explicitly include the Hartree (H) and xc kernels,

$$\begin{aligned} A_{a\sigma,bj\tau} &= (\epsilon_a^\sigma - \epsilon_j^\sigma) \delta_{ij} \delta_{ab} \delta_{\sigma\tau} + (ia|f_{Hxc}^{\sigma,\tau}(\omega)|bj) \\ B_{a\sigma,bj\tau} &= (ia|f_{Hxc}^{\sigma,\tau}(\omega)|jb), \end{aligned} \quad (1.2)$$

where ϵ_p^σ is the KS orbital energy for spin σ , and

$$(pq|f(\omega)|rs) = \int d^3r \int d^3r' \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) f(\mathbf{r}, \mathbf{r}'; \omega) \phi_r^*(\mathbf{r}') \phi_s(\mathbf{r}'). \quad (1.3)$$

Here and throughout this paper we use the following indexes notation: $i, j, \dots$ are occupied orbitals, $a, b, \dots$ are virtual orbitals, and $p, q, \dots$ are orbitals of unspecified nature.

In chemical applications of TDDFT, the Tamm–Dancoff approximation (TDA) [20],

$$\mathbf{A}(\omega)\mathbf{X} = \omega\mathbf{X} \quad (1.4)$$

improves excited state potential energy surfaces [21,22], though sacrificing the Thomas–Reine–Kuhn sum rule. Although the standard random-phase approximation (RPA) equations [23] provide only 1h1p states, the exact LR-TDDFT equations include also 2h2p states (and higher-order n hnp states) through the ω -dependence of the xc part of the kernel $f_{xc}^{\sigma,\tau}(\omega)$. However, the matrices $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ are supposed ω -independent in the adiabatic approximation to the xc-kernel, thereby losing the non-linearity of the LR-TDDFT equations and the associated 2h2p (and higher) states.

Double excitations are essential ingredients for a proper description of several physical and chemical processes. Though they do not appear directly in photo-absorption spectra, (i.e., they are dark states), signatures of 2h2p states appear indirectly through mixing with 1h1p states, thereby leading to the fracturing of main peaks into satellites [24,25]. In open-shell molecules such mixing is often required in order to maintain spin symmetry [2,26,27]. Perhaps more importantly dark states often play an essential important role in photochemistry and explicit inclusion of 2h2p states is often considered necessary for a minimally correct description of conical intersections [5]. A closely-related historical, but still much studied, problem is the location of 2h2p states in polyenes [28,3,29–35], partly because of the importance of the polyene retinal in the photochemistry of vision [36–38].

It is thus manifest that some form of explicit inclusion of 2h2p states is required within TDDFT when attacking certain types of problems [39]. This has lead to various attempts to include 2h2p states in TDDFT. One partial solution was given by spin-flip TDDFT [40,41] which describes some states which are 2h2p with respect to the ground state by beginning with the lowest triplet state and including spin-flip excitations [42–45]. However, spin-flip TDDFT does not provide a general way to include double excitations. Strengths and limitations of this theory have been discussed in recent work [46].

The present article focuses on D-TDDFT, which offers a general model for including explicitly 2h2p states in TDDFT. D-TDDFT was initially proposed by Maitra, Zhang, Cave and Burke as an *ad hoc* many-body theory correction to TDDFT [6]. They subsequently tested it on butadiene and hexatriene with encouraging results [7]. The method was then reimplemented and tested on longer polyenes and substituted polyenes by Mazur et al. [8,9].

In the present work, we consider several variants of D-TDDFT, implement and test them on the set of molecules proposed by Schreiber et al. [10,11] The set consists of 28 organic molecules

whose excitation energies are well characterized both experimentally or through high-quality *ab initio* wavefunction calculations.

This paper is organized as follows. Section 2 describes D-TDDFT in some detail and the variations that we have implemented. Section 3 describes technical aspects of how the formal equations were implemented in deMon2k, as well as additional features which were implemented specifically for this study. Section 4 describes computational details such as basis sets and choice of geometries. Section 5 presents and discusses results. Finally, Section 6 concludes.

2. Formal equations

D-TDDFT may be understood as an approximation to exact equations for the xc-kernel [47]. This section reviews D-TDDFT and the variations which have been implemented and tested in the present work.

An *ab initio* expression for the xc-kernel may be derived from many-body theory, either from the Bethe–Salpeter equation or from the polarization propagator (PP) formalism [2,48]. Both equations give the same xc-kernel,

$$\begin{aligned} f_{xc}(\mathbf{x}, \mathbf{x}'; \omega) &= \int d^3x_1 \int d^3x_2 \int d^3x_3 \\ &\times \int d^3x_4 A_s(\mathbf{x}; \mathbf{x}_1, \mathbf{x}_2; \omega) K(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_3, \mathbf{x}_4; \omega) A^\dagger(\mathbf{x}_3, \mathbf{x}_4; \mathbf{x}'; \omega), \end{aligned} \quad (2.1)$$

where $x_p = (\mathbf{r}_p, \sigma_p)$, K is defined as

$$K(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_3, \mathbf{x}_4; \omega) = \Pi_s^{-1}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_3, \mathbf{x}_4; \omega) - \Pi^{-1}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_3, \mathbf{x}_4; \omega) \quad (2.2)$$

and Π and Π_s are respectively the interacting and non-interacting polarization propagators, which contribute to the pole structure of the xc-kernel. The interacting and non-interacting localizers, A and A_s , respectively, convert the 4-point polarization propagators into the 2-point TDDFT quantities (4-point and 2-point refer to the space coordinates of each kernel.) The localization process introduces an extra ω -dependence into the xc-kernel. Interestingly, Gonze and Scheffler [49] noticed that, when we substitute the interacting by the non-interacting localizer in Eq. (2.1), the localization effects can be neglected for key matrix elements of the xc-kernel at certain frequencies, meaning that the ω -dependence exactly cancels the spatial localization. More importantly, removing the localizers simply means replacing TDDFT with many-body theory terms. To the extent that both methods represent the same level of approximation, excitation energies and oscillator strengths are unaffected, though the components of the transition density will change in a finite basis representation. In Ref. [2], Casida proposed a PP form of D-TDDFT without the localizer. In Ref. [47], Huix-Rotllant and Casida gave explicit expressions for an *ab initio* ω -dependent xc-kernel derived from a Kohn–Sham-based second-order polarization propagator (SOPPA) formula. Equivalent expressions were derived by Zhang and Burke in Ref. [50], in which they calculated the excitation energy by truncating to second-order the Görling–Levy perturbation theory.

The calculation of the xc-kernel in SOPPA can be cast in RPA-like form. In the TDA approximation, we obtain

$$[\mathbf{A}_{11} + \mathbf{A}_{12}(\omega\mathbf{1}_{22} - \mathbf{A}_{22})^{-1}\mathbf{A}_{21}]\mathbf{X} = \omega\mathbf{X}, \quad (2.3)$$

which provides a matrix representation of the second-order approximation of the many-body theory kernel $K(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_3, \mathbf{x}_4; \omega)$. The blocks $\mathbf{A}_{11}$, $\mathbf{A}_{21}$ and $\mathbf{A}_{22}$ couple respectively single excitations among themselves, single excitations with double excitations and double excitations among themselves. In Appendix A we give explicit equations for these blocks in the case of a SOPPA calculation based on

Download English Version:

<https://daneshyari.com/en/article/5374667>

Download Persian Version:

<https://daneshyari.com/article/5374667>

[Daneshyari.com](https://daneshyari.com)