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Time-dependent density functional theory within the Tamm–Dancoff approximation

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Abstract

A computationally simple method for molecular excited states, namely, the Tamm–Dancoff approximation to time-dependent density functional theory, is proposed and implemented. This method yields excitation energies for several closed- and open-shell molecules that are essentially of the same quality as those obtained from time-dependent density functional theory itself, when the same exchange-correlation functional is used. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In the last several years, time-dependent density functional theory (TDDFT) [1–4] has emerged as an attractive alternative to the conventional Hartree–Fock (HF)-based single-excitation theories such as configuration interaction with single substitutions (CIS) or random-phase approximation (RPA). The computational costs and complexity of TDDFT are roughly comparable to those of CIS and RPA, and hence TDDFT is applicable to fairly large systems for which accurate but computationally more demanding excited-state theories are not feasible. Although TDDFT is a formally exact theory for molecular excited states, it is in practice an approximate method the performance of which should be assessed by numerical applications, due to the approximate nature of the exchange-correlation functionals used. The numerical data reported so far indicate that TDDFT, using current approximate functionals and the so-called adiabatic approximation, performs significantly better than CIS and RPA for several

low-lying valence excited states [5–10], although there remains much room for improvement in the description of Rydberg states [11,12].

In this Letter, we propose a computationally simple method for molecular excited states, which amounts to the so-called Tamm–Dancoff approximation [13] to TDDFT. We demonstrate that the performance of this method, which we call TDDFT/TDA, is essentially the same as TDDFT itself. The working equation of this method closely resembles the CIS working equation, and hence the efficient and robust algorithms employed in the current implementation of the CIS method can be straightforwardly generalized to solve the TDDFT/TDA equation. We apply this method to calculate the vertical excitation energies of several closed-shell (N_2, CO, water, formaldehyde, and ethylene) and open-shell (BeF, BeH, CO^+, CN, and methyl radical) molecules employing local, gradient-corrected, hybrid, and asymptotically corrected functionals. It is found that TDDFT/TDA yields excitation energies which are usually very close to the corresponding TDDFT values, and that

these two methods are interchangeable from a practical point of view.

2. Theory

In Section 2, we review time-dependent response theory [4,14] for the purpose of defining the TDDFT/TDA method and of clarifying the nature of the approximation assumed in this method. We start with the following time-dependent Kohn–Sham (KS) equation

$$\sum_q \{ F_{pq\sigma} P_{qr\sigma} - P_{pq\sigma} F_{qr\sigma} \} = i \frac{\partial P_{pr\sigma}}{\partial t}, \qquad (1)$$

with the idem-potency condition

$$\sum_q P_{pq\sigma} P_{qr\sigma} = P_{pr\sigma}, \qquad (2)$$

where F and P are the KS Hamiltonian and density matrices, respectively, represented by orthonormal basis functions $\{\phi_p(r)\}$, and p,q,r are basis set indexes, and σ denotes spin. The KS Hamiltonian matrix elements are written explicitly as

$$F_{pq\sigma} = \int \phi_{p\sigma}^*(r) \left(-\frac{1}{2}\nabla^2 + \sum_A \frac{-Z_A}{|r - R_A|} \right.$$
$$\left. + \int \frac{\rho(r')}{|r - r'|} \, dr' + \frac{\delta E_{XC}}{\delta \rho_\sigma(r)} \right) \phi_{q\sigma}(r) \, dr, \qquad (3)$$

where the adiabatic approximation is used from the outset for the sake of simplicity. Spin density $\rho_\sigma(r)$ is related to the density matrix by

$$\rho_\sigma(r) = \sum_{pq} P_{pq\sigma} \phi_{p\sigma}(r) \phi_{q\sigma}^*(r). \qquad (4)$$

We assume that the molecule is initially in a stationary state, the electronic structure of which is suitably described by time-independent KS density functional theory and that the orthonormal basis functions $\{\phi_p(r)\}$ are the KS orbitals for this unperturbed ground state. The KS Hamiltonian and density matrices for the ground state, which are superscripted with '(0)', are simply

$$F_{pq\sigma}^{(0)} = \delta_{pq} \varepsilon_{p\sigma}, \qquad (5)$$

and

$$P_{ij\sigma}^{(0)} = \delta_{ij}, \qquad (6)$$

$$P_{ia\sigma}^{(0)} = P_{ai\sigma}^{(0)} = P_{ab\sigma}^{(0)} = 0, \qquad (7)$$

where ε are one-electron energies, and we use i,j for occupied orbitals, a,b for virtual orbitals, and p,q,r,s,t for general orbitals. These KS Hamiltonian and density matrices satisfy the time-independent KS equation

$$\sum_q \left(F_{pq\sigma}^{(0)} P_{qr\sigma}^{(0)} - P_{pq\sigma}^{(0)} F_{qr\sigma}^{(0)} \right) = 0, \qquad (8)$$

with the idem-potency condition

$$\sum_q P_{pq\sigma}^{(0)} P_{qr\sigma}^{(0)} = P_{pr\sigma}^{(0)}. \qquad (9)$$

We now apply an oscillatory perturbation, which can be described as a single Fourier component,

$$g_{pq\sigma} = \tfrac{1}{2} \left[f_{pq\sigma} \exp(-i\omega t) + f_{qp\sigma}^* \exp(i\omega t) \right], \qquad (10)$$

where the matrix f represents a one-electron operator describing the details of the perturbation. The first-order (linear) response of the density matrix P' to this applied perturbation is

$$P_{pq\sigma} = P_{pq\sigma}^{(0)} + P_{pq\sigma}', \qquad (11)$$

with

$$P_{pq\sigma}' = \tfrac{1}{2} \left[d_{pq\sigma} \exp(-i\omega t) + d_{qp\sigma}^* \exp(i\omega t) \right]. \qquad (12)$$

The first-order change in the KS Hamiltonian matrix is composed of two terms: the change in the one-electron part described by Eq. (10) and the change in the two-electron part induced by the first-order response of the density matrix, namely,

$$F_{pq\sigma} = F_{pq\sigma}^{(0)} + g_{pq\sigma} + \sum_{rs\tau} \frac{\partial F_{pq\sigma}}{\partial P_{rs\tau}} P_{rs\tau}', \qquad (13)$$

with

$$\frac{\partial F_{pq\sigma}}{\partial P_{rs\tau}} = (p_\sigma q_\sigma | s_\tau r_\tau) + (p_\sigma q_\sigma | w_{\sigma\tau} | s_\tau r_\tau), \qquad (14)$$

where the regular two-electron integrals are expressed in the Mulliken notation, and

$$
\left(p_\sigma q_\sigma | w_{\sigma\tau} | s_\tau r_\tau \right)
$$
$$
= \int \phi^*_{p\sigma}(r) \phi_{q\sigma}(r) \frac{\delta^2 E_{XC}}{\delta \rho_\sigma(r) \delta \rho_\tau(r')}
$$
$$
\times \phi^*_{s\tau}(r') \phi_{r\tau}(r') \, dr \, dr' . \tag{15}
$$

Substituting Eqs. (10) to (13) to the time-dependent KS Eq. (1) and collecting the terms which are multiplied by the $\exp(-i\omega t)$ factor, we obtain

$$
\sum_q \left[F^{(0)}_{pq\sigma} d_{qr\sigma} - d_{pq\sigma} F^{(0)}_{qr\sigma} \right.
$$
$$
+ \left(f_{pq\sigma} + \sum_{st\tau} \frac{\partial F_{pq\sigma}}{\partial P_{st\tau}} d_{st\tau} \right) P^{(0)}_{qr\sigma}
$$
$$
\left. - P^{(0)}_{pq\sigma} \left(f_{qr\sigma} + \sum_{st\tau} \frac{\partial F_{qr\sigma}}{\partial P_{st\tau}} d_{st\tau} \right) \right]
$$
$$
= \omega d_{pr\sigma} . \tag{16}
$$

The terms multiplied by the $\exp(i\omega t)$ factor lead to the conjugate complex of the above equation.

The idem-potency condition (Eq. (2)) strongly restricts the possible form of the d matrix in Eq. (12); occupied–occupied and virtual–virtual elements of the d matrix are zero. In TDDFT, all the possible non-zero elements of the d matrix, namely, virtual–occupied and occupied–virtual elements, are taken into account. Thus, writing

$$
d_{ai\sigma} = x_{ai\sigma} , \tag{17}
$$
$$
d_{ia\sigma} = y_{ai\sigma} , \tag{18}
$$

and using the diagonal nature of the unperturbed KS Hamiltonian and density matrices (Eqs. (5) and (6)), we obtain a pair of equations

$$
F^{(0)}_{aa\sigma} x_{ai\sigma} - x_{ai\sigma} F^{(0)}_{ii\sigma}
$$
$$
+ \left[f_{ai\sigma} + \sum_{bj\tau} \left(\frac{\partial F_{ai\sigma}}{\partial P_{bj\tau}} x_{bj\tau} + \frac{\partial F_{ai\sigma}}{\partial P_{jb\tau}} y_{bj\tau} \right) \right] P^{(0)}_{ii\sigma}
$$
$$
= \omega x_{ai\sigma} , \tag{19}
$$

and

$$
F^{(0)}_{ii\sigma} y_{ai\sigma} - y_{ai\sigma} F^{(0)}_{aa\sigma}
$$
$$
- P^{(0)}_{ii\sigma} \left[f_{ia\sigma} + \sum_{bj\tau} \left(\frac{\partial F_{ia\sigma}}{\partial P_{bj\tau}} x_{bj\tau} + \frac{\partial F_{ia\sigma}}{\partial P_{jb\tau}} y_{bj\tau} \right) \right]
$$
$$
= \omega y_{ai\sigma} . \tag{20}
$$

Remembering that $F^{(0)}_{pp\sigma} = \varepsilon_{p\sigma}$ (Eq. (5)) and $P^{(0)}_{ii\sigma} = 1$ (Eq. (6)) and assuming that the electronic transitions occur with an infinitesimal perturbation ($f_{ia\sigma} = f_{ai\sigma} = 0$), we obtain a non-Hermitian eigenvalue equation

$$
\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} , \tag{21}
$$

with

$$
A_{ai\sigma,bj\tau} = \delta_{ij} \delta_{ab} \delta_{\sigma\tau} (\varepsilon_{a\sigma} - \varepsilon_{i\tau})
$$
$$
+ (a_\sigma i_\sigma | j_\tau b_\tau) + (a_\sigma i_\sigma | w_{\sigma\tau} | j_\tau b_\tau) , \tag{22}
$$
$$
B_{ai\sigma,bj\tau} = (a_\sigma i_\sigma | b_\tau j_\tau) + (a_\sigma i_\sigma | w_{\sigma\tau} | b_\tau j_\tau) . \tag{23}
$$

Eqs. (21) and (23) are solved to obtain the TDDFT excitation energies ω.

In TDDFT/TDA, only the virtual–occupied elements of the d matrix are considered; in other words, the Tamm–Dancoff approximation amounts to neglecting the occupied–virtual elements of the d matrix. Writing

$$
d_{ai\sigma} = x_{ai\sigma} , \tag{24}
$$

we obtain

$$
\sum_a F^{(0)}_{aa\sigma} x_{ai\sigma} - \sum_i x_{ai\sigma} F^{(0)}_{ii\sigma}
$$
$$
+ \sum_i \left(f_{ai\sigma} + \sum_{bj\tau} \frac{\partial F_{ai\sigma}}{\partial P_{bj\tau}} x_{bj\tau} \right) P^{(0)}_{ii\sigma}
$$
$$
= \omega x_{ai\sigma} . \tag{25}
$$

Substituting Eqs. (5) and (6) and assuming $f_{ai\sigma} = 0$ leads to a Hermitian eigenvalue equation the dimension of which is one-half that of the TDDFT working equation

$$
\mathbf{AX} = \omega \mathbf{X} , \tag{26}
$$

where the definition of the $\mathbf{A}$ matrix elements are the same as before (Eq. (22)).

The TDDFT/TDA method has been implemented in a development version of Q-CHEM program package [16]. The TDDFT/TDA excitation energies are evaluated by using the Davidson's iterative subspace algorithm [17], which is widely used in the current implementation of the CIS method. In this algorithm, the solution vectors of the eigenvalue equation are expanded by a set of trial vectors and accordingly the $\mathbf{A}$ matrix is projected onto the subspace spanned by the set of trial vectors. The product formation of the $\mathbf{A}$ matrix with trial vectors, which is needed to obtain the subspace representation of $\mathbf{A}$, dominates the cpu time usage. As expected from the above equations, the TDDFT/TDA method can be incorporated into programs with minor modifications to the existing CIS or TDDFT codes. To modify the CIS codes to calculate the TDDFT/TDA excitation energies, we should simply replace the exchange-type integrals appearing in the $\mathbf{A}$ matrix elements (see, e.g., Refs. [4,15]) with appropriate exchange-correlation-type integrals (the last terms in Eqs. (22) and (23)). Explicit expression of these exchange-correlation-type integrals for general gradient-corrected functionals are given in Ref. [5] for spin-restricted case and in Ref. [10] for spin-unrestricted case.

The TDDFT excitation energies are also computed by using the Davidson-like algorithm, details of which is described in our earlier Letter [10]. In most molecular implementations including ours, the orbitals are assumed to be real, and this assumption simplifies the TDDFT working equation (21) into a Hermitian eigenvalue equation [4], the dimension of which is the same as the TDDFT/TDA working equation (26),

$$(\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2}\mathbf{Z} = \omega^2\mathbf{Z}, \qquad (27)$$

with

$$\mathbf{Z} = (\mathbf{A} - \mathbf{B})^{-1/2}(\mathbf{X} + \mathbf{Y}). \qquad (28)$$

When pure (in the sense that the HF exchange in not admixed) exchange-correlation functionals are used, the matrix $(\mathbf{A} - \mathbf{B})$ becomes diagonal (see Eqs. (22) and (23)), and one may fully exploit this to avoid the product formation of $(\mathbf{A} - \mathbf{B})$ with trial vectors. In this particular case, the Tamm–Dancoff approximation does not lead to reduction in computational costs in terms of cpu time or storage space. For general hybrid HF/DFT functionals, however, the

matrix $(\mathbf{A} - \mathbf{B})$ is no longer diagonal, and we have to form the products of the $(\mathbf{A} - \mathbf{B})$ and $(\mathbf{A} + \mathbf{B})$ matrices (or equivalently the $\mathbf{A}$ and $\mathbf{B}$ matrices) with trial vectors. We adopt this general implementation which can deal with TDDFT using pure and hybrid exchange-correlation functionals and RPA in a single scheme. Thus, when TDDFT is implemented for general functionals, the Tamm–Dancoff approximation reduces the computational costs roughly by a factor of two since it eliminates the need for the product formation involving the $\mathbf{B}$ matrix.

Apart from the reduction in the computational costs, the Tamm–Dancoff approximation significantly simplifies the algebra and the associated algorithms to obtain the excitation energies. It might be noticed from Eq. (27) that the standard algorithm of computing the TDDFT excitation energies fails when the matrix $(\mathbf{A} - \mathbf{B})$ is not positive definite. This situation takes place when the system of interest has triplet instability in the SCF wavefunctions [18]. Even when there is no such instability, the algorithm becomes unstable when the system possesses the degenerate ground-state or triplet near-instability. It is demonstrated in Section 3 that TDDFT using a hybrid HF/DFT functional and RPA yield grossly erratic excitation energies for those states with triplet near-instability and that the Tamm–Dancoff approximation remedies the situation remarkably for those pathological states.

As we shall see in Section 3, the Tamm–Dancoff approximation introduces only very small errors in the calculated excitation energies except for those states having the triplet near-instability problems. This is a consequence of the fact that the $\mathbf{B}$ matrix plays a very minor role, in fact only a negligibly small role, in the TDDFT excitation energies. By looking into the solution vectors (excited-state wavefunctions) of TDDFT, we noticed that the TDDFT solution vectors are very often dominated by a single configuration in which an electron is promoted from an occupied orbital to a virtual orbital unless the orbitals involved are degenerate. This is in contrast to the solution vectors of RPA and CIS, which are in general linear combinations of several configurations with comparable weights. This means that the off-diagonal elements of the $\mathbf{A}$ matrix and the entire $\mathbf{B}$ matrix play much less important roles in the calculated excitation energies of TDDFT than in those of

RPA and CIS. This observation further suggests that we can obtain the TDDFT excitation energies in a good approximation in a much simpler procedure. The Tamm–Dancoff approximation can be viewed as the first step in this direction, which removes some algorithmically cumbersome aspects of TDDFT and leaves the calculated excitation energies practically unchanged. Formal theoretical arguments which seem relevant to this approximation have been given by Savin et al. [19].

It should be kept in mind, however, that, while TDDFT includes exactly the response of the electron density first order to the applied perturbation, in TDDFT/TDA the response of the electron density is partitioned into two parts ($\mathbf{X}$ and $\mathbf{Y}$) with reference to the fictitious KS orbitals and the less important part is neglected. This approach reveals the Tamm–Dancoff approximation as a pragmatic truncation of the full TDDFT equations, the merit of which will be assessed numerically. Elsewhere we shall consider the question of whether an independent theoretical basis for TDDFT/TDA can be established based on parameterizing the time-dependent density matrix via exponential transformations carried through linear response.

3. Numerical applications

The TDDFT/TDA and TDDFT methods as well as the conventional HF-based single-excitation methods (CIS and RPA) are applied to calculate the vertical excitation energies of several closed- and open-shell molecules. We employ the Slater–Vosko–Wilk–Nusair (SVWN) [20,21], Becke–Lee–Yang–Parr (BLYP) [22,23], and Becke3–Lee–Yang–Parr (B3LYP) [24] functionals as representative local, gradient-corrected, and hybrid functionals. We also examine the performance of the van Leeuwen–Baerends '94 (LB94) functional [25], which, unlike the other functionals used in this study, is defined as a correction to exchange-correlation potential. The LB94 potential correction is added to the SVWN exchange-correlation potential in the self-consistent field procedure, to ensure that the electrons in the virtual orbitals should experience the qualitatively correct potential in the asymptotic region, but in the subsequent TDDFT/TDA and

TDDFT calculations the electric second derivatives of the regular SVWN functional are used. The basis set used is the 6-311(2+,2+)G** , which is sufficiently large to describe several low-lying valence and Rydberg states. The results are summarized in Table 1 for closed-shell molecules and in Table 2 for open-shell molecules. As the most important observation, the TDDFT/TDA excitation energies fall very close to the corresponding TDDFT values for the total of 56 states listed in Tables 1 and 2. The mean absolute deviations between the excitation energies obtained from these two methods are 0.04, 0.07, 0.05, and 0.07 eV, respectively, for the SVWN, LB94, BLYP, and B3LYP functional. These numbers substantiate our expectation that the performance of TDDFT/TDA is essentially the same as that of TDDFT itself and that TDDFT/TDA is regarded as an algorithmically simpler alternative to TDDFT. It should be noted that the mean absolute deviation between the CIS and RPA excitation energies (0.39 eV) is several times larger than these values.

For Rydberg excited states, the TDDFT/TDA and TDDFT excitation energies are coincident within a few hundredths of an electron volt. The mean absolute deviations of the TDDFT/TDA excitation energies from the experimental data for Rydberg states are within 0.04 eV of the corresponding values of the TDDFT results. For valence excited states, the differences in the excitation energies between these two methods tend to be slightly larger. Appreciable differences can be seen for the excited states having triplet near instability problem, namely, the $^3\Sigma_u^+$ state of nitrogen, $^3\Sigma^+$ state of carbon monoxide, $^3B_{1u}$ state of ethylene, and $^3A_1$ state of formaldehyde. For these excited states, RPA predicts seriously erratic excitation energies, which are lower than the experimental data or the corresponding CIS excitation energies by several electron volts. As has been pointed out previously [5], TDDFT is much more stable than RPA in the sense that the former provides qualitatively acceptable excitation energies for these states. Nevertheless, owing to the fraction of the RPA-type integrals in the $\mathbf{A}$ and $\mathbf{B}$ matrix elements, TDDFT employing the B3LYP functional yields the excitation energies which are significantly lower than the experimental results for these states. This contrasts with the TDDFT/TDA excitation en-

ergies obtained with the same functional which agree with the experimental data reasonably well. Overall, for the valence states, the mean absolute deviations of the TDDFT/TDA excitation energies from the

Table 1

Vertical excitation energies (in eV) for several low-lying singlet and triplet excited states of N_2, CO, water, formaldehyde, and ethylene using the 6-311(2 + ,2 +)G** basis set

Molecule [a]	State [b]	Tamm–Dancoff approximation					Time-dependent response theory					Expt. [c]
		CIS	SVWN	LB94	BLYP	B3LYP	RPA	SVWN	LB94	BLYP	B3LYP	
N_2	V $^1\Pi_g$	9.98	9.21	8.84	9.21	9.38	9.74	9.09	8.72	9.10	9.27	9.31
	V $^1\Sigma_u^-$	8.47	9.70	9.46	9.60	9.37	7.90	9.70	9.46	9.60	9.35	9.97
	V $^1\Delta_u$	9.05	10.30	10.09	9.91	9.76	8.77	10.27	10.06	9.90	9.75	10.27
	V $^3\Sigma_u^+$	6.21	8.13	7.81	7.80	7.57	3.40	7.92	7.57	7.50	7.09	7.75
	V $^3\Pi_g$	8.03	7.62	7.25	7.54	7.69	7.68	7.58	7.21	7.46	7.59	8.04
	V $^3\Delta_u$	7.32	8.93	8.65	8.43	8.26	5.90	8.88	8.60	8.30	8.02	8.88
	V $^3\Sigma_u^-$	8.47	9.70	9.46	9.60	9.37	7.90	9.70	9.46	9.60	9.35	9.67
	V $^3\Pi_u$	11.81	10.41	10.19	10.42	10.76	11.37	10.36	10.13	10.32	10.63	11.19
CO	V $^1\Pi$	9.05	8.42	8.25	8.44	8.60	8.77	8.19	7.99	8.24	8.40	8.51
	V $^1\Sigma^-$	9.71	9.89	9.92	9.78	9.74	9.35	9.89	9.92	9.79	9.72	9.88
	V $^3\Pi$	5.88	6.04	5.68	5.98	6.03	5.33	5.95	5.59	5.82	5.85	6.32
	V $^3\Sigma^+$	7.78	8.57	8.57	8.30	8.25	6.32	8.42	8.41	8.09	7.92	8.51
	V $^3\Delta$	8.74	9.25	9.26	8.81	8.83	7.91	9.21	9.22	8.72	8.66	9.36
	V $^3\Sigma^-$	9.71	9.89	9.92	9.78	9.74	9.35	9.89	9.92	9.79	9.72	9.88
H_2O	R $^1B_1$	8.64	6.51	7.84	6.19	6.84	8.59	6.50	7.82	6.18	6.83	7.4
	R $^1A_2$	10.32	7.62	9.66	7.26	8.18	10.28	7.62	9.66	7.26	8.18	9.1
	R $^1A_1$	10.88	8.40	9.85	8.05	8.85	10.86	8.39	9.81	8.04	8.84	9.7
	R $^1B_1$	11.29	7.99	11.14	7.67	8.69	11.28	7.99	11.14	7.67	8.69	10.0
	R $^1A_1$	11.55	8.62	11.37	8.35	9.13	11.51	8.58	11.33	8.31	9.08	10.17
	R $^3B_1$	7.97	6.25	7.34	5.90	6.49	7.85	6.24	7.33	5.89	6.47	7.2
C_2H_4	R $^1B_{3u}$	7.13	6.61	7.78	6.16	6.55	7.11	6.61	7.78	6.16	6.54	7.11
	V $^1B_{1u}$	7.74	7.67	8.38	7.23	7.61	7.39	7.41	7.70	7.09	7.33	7.60
	R $^1B_{1g}$	7.71	7.08	7.24	6.60	7.05	7.70	7.08	7.22	6.60	7.05	7.80
	R $^1B_{2g}$	7.86	7.06	8.47	6.55	7.04	7.85	7.05	8.46	6.55	7.03	8.01
	R ^1A_g	8.09	7.42	9.73	6.93	7.39	8.07	7.41	9.71	6.92	7.38	8.29
	R $^1B_{3u}$	8.63	7.59	9.74	7.18	7.71	8.63	7.59	9.74	7.18	7.71	8.62
	V $^3B_{1u}$	3.57	4.79	4.58	4.53	4.40	0.51	4.67	4.43	4.31	4.05	4.36
	R $^3B_{3u}$	6.91	6.57	7.62	6.10	6.48	6.88	6.56	7.61	6.10	6.47	6.98
	R $^3B_{1g}$	7.63	7.01	6.75	6.59	7.02	7.60	7.00	6.73	6.58	7.02	7.79
	R $^3B_{2g}$	7.75	7.03	8.25	6.52	6.99	7.72	7.03	8.23	6.52	6.99	7.79
	R ^3A_g	7.77	7.37	9.46	6.86	7.31	7.74	7.37	9.45	6.86	7.31	8.15
CH_2O	V $^1A_2$	4.48	3.65	3.52	3.78	3.87	4.30	3.63	3.49	3.76	3.85	4.07
	R $^1B_2$	8.63	5.90	7.45	5.63	6.44	8.62	5.89	7.43	5.63	6.43	7.11
	R $^1B_2$	9.36	6.68	8.63	6.37	7.20	9.35	6.68	8.62	6.37	7.20	7.97
	V $^1A_1$	9.45	6.54	8.76	6.21	7.16	9.07	6.54	8.73	6.20	7.15	–
	R $^1A_1$	9.66	7.22	10.09	6.98	7.94	9.58	7.22	9.58	6.98	7.94	8.14
	V $^1B_1$	9.66	8.79	8.45	8.78	8.96	9.41	8.71	8.38	8.72	8.89	–
	R $^1A_2$	9.78	6.81	9.05	6.53	7.40	9.77	6.81	9.03	6.53	7.40	8.37
	R $^1B_2$	10.61	6.90	10.04	6.64	7.66	10.60	6.90	10.01	6.64	7.66	8.88
	V $^3A_2$	3.67	3.03	2.88	3.11	3.19	3.35	3.00	2.86	3.06	3.12	3.50
	V $^3A_1$	4.65	6.16	6.01	5.82	5.62	1.24	6.02	5.86	5.59	5.20	5.86
	R $^3B_2$	8.28	5.84	7.15	5.56	6.33	8.20	5.84	7.14	5.55	6.32	6.83
	V $^3B_1$	8.37	7.65	7.35	7.60	7.78	7.94	7.62	7.32	7.55	7.69	–
	R $^3B_2$	9.04	6.65	8.44	6.33	7.13	8.99	6.65	8.43	6.33	7.12	7.79
	R $^3A_1$	9.31	6.54	8.47	6.19	7.12	9.26	6.53	8.46	6.19	7.11	7.96
Dev. [d]	Valence	0.72	0.23	0.36	0.28	0.28	1.51	0.24	0.36	0.36	0.42	
	Rydberg	0.86	1.11	0.77	1.48	0.79	0.84	1.11	0.73	1.48	0.80	

Table 2

Vertical excitation energies (in eV) for several low-lying excited states of diatomic radicals and methyl radical using the 6-311(2 + ,2 +)G$^{* *}$ basis set at the geometries given in Ref. [28]

Radical	State [a]	Tamm–Dancoff approximation					Time-dependent response theory					Expt. [d]
		UCIS [b]	SVWN	LB94	BLYP	B3LYP	URPA [b]	SVWN [c]	LB94	BLYP [c]	B3LYP [c]	
BeH	V $^2\Pi$	2.75	2.37	2.14	2.57	2.58	2.72	2.35	2.10	2.54	2.55	2.48
	R $^2\Pi$	6.53	4.86	5.71	4.69	5.18	6.42	4.86	5.65	4.69	5.18	6.32
BeF	V $^2\Pi$	4.27	4.07	3.85	4.13	4.17	4.23	4.03	3.80	4.10	4.14	4.14
	R $^2\Sigma^+$	6.36	5.33	5.61	5.11	5.52	6.35	5.32	5.60	5.10	5.52	6.16
	R $^2\Sigma^+$	6.60	5.35	6.34	5.16	5.57	6.59	5.35	6.33	5.16	5.56	6.27
CH$_3$	R $^2A'_1$	6.55	4.94	5.88	4.67	5.16	6.51	4.93	5.86	4.66	5.16	5.73
	R $^2A''_2$	7.93	5.86	8.02	5.54	6.19	7.88	5.85	7.99	5.53	6.17	7.44
CN	V $^2\Pi$	4.07	1.69	1.49	1.60	1.47	3.90	1.64	1.43	1.53	1.37	1.32
	V $^2\Sigma^+$	6.55	3.32	3.35	3.35	3.26	5.43	3.02	3.02	3.07	3.00	3.22
CO$^+$	V $^2\Pi$	7.50	3.67	2.71	3.57	3.83	6.96	3.62	2.65	3.50	3.76	3.26
	V $^2\Sigma^+$	11.32	5.13	4.30	5.22	5.90	11.22	5.03	4.14	5.11	5.79	5.82
Dev.[e]	Valence	2.70	0.29	0.50	0.24	0.16	2.37	0.32	0.55	0.24	0.15	
	Rydberg	0.41	1.12	0.39	1.35	0.86	0.37	1.12	0.39	1.36	0.87	

[a] The symmetry of the various excited states together with the qualitative description of each state as either valence (V) or Rydberg (R).

[b] Ref. [28].

[c] Ref. [10].

[d] Experimental data are taken from the compilation of Ref. [28].

[e] Mean absolute deviations from the experimental data.

experimental data are virtually the same as those of the TDDFT excitation energies, but in some cases, the TDDFT/TDA mean absolute deviations are noticeably smaller than the corresponding TDDFT values. This last point underscores the practical usefulness of this approximate method, although it may not be taken as an indication of the superiority of TDDFT/TDA to TDDFT.

Being a faithful approximation to TDDFT, TDDFT/TDA inherits the advantages and disadvantages of TDDFT over the HF-based single-excitation theories. Several groups of researchers have studied the quality of the TDDFT excitation energies for a number of molecules [5–12]. The conclusions drawn in these studies are considered to apply to the TDDFT/TDA excitation energies as well. This contrasts with a hybrid method of DFT and CIS pro-

posed previously [26], the performance of which depends not only on the exchange-correlation functionals but also on the empirical parameters used in the method. In the following, we shall give a summary of the general trend of the TDDFT/TDA excitation energies compiled in Tables 1 and 2, rather than a detailed description of the results for each molecule.

For valence excited states, the performance of TDDFT/TDA is generally significantly better than that of CIS and RPA. Typical examples are nitrogen and carbon monoxide, the low-lying excited states of which are principally of valence character. For these states, the TDDFT/TDA excitation energies agree with the experimental data reasonably well. Neither gradient correction or mixing of the HF exchange seems to give a marked improvement in the excita-

Notes to Table 1:

[a] Molecular geometries and HF energies are given as follows. N$_2$: NN = 1.0977 Å, E_{HF} = −108.971804H; CO: CO = 1.1283 Å, E_{HF} = −112.769764H; H$_2$O: OH = 0.9584 Å, HOH = 104.45°, E_{HF} = −76.052854H; C$_2$H$_4$: CC = 1.3349 Å, CH = 1.0848 Å, CCH = 121.70°, E_{HF} = −78.055617H; CH$_2$O: CO = 1.2200 Å, CH = 1.1039 Å, HCO = 122.19°, E_{HF} = −113.899919H.

[b] The symmetry of the various excited states together with the qualitative description of each state as either valence (V) or Rydberg (R).

[c] Experimental data are taken from the compilation of Ref. [5] for N$_2$, of Ref. [29] for CO, of Ref. [30] for H$_2$O, of Ref. [31] for C$_2$H$_4$, pf Ref. [32] for CH$_2$O.

[d] Mean absolute deviations from the experimental data.

tion energies. It should also be noted that the LB94 correction deteriorates the SVWN excitation energies by several tenths of an electron volt. Some of the valence excited states are known to have appreciable double-excitation character. The two lowest excited states of CN and CO^+ radicals are among this category [10,27,28]. The CIS and RPA excitation energies for these states are grossly in error, being higher than the experimental data by as much as 2–5 eV [28]. TDDFT/TDA, like TDDFT [10], remedies the situation quite remarkably, providing the qualitatively correct descriptions of these excited states. The mean absolute deviations of the TDDFT/TDA excitation energies from the experimental data for valence states are less than 0.3 eV (with the exception of the LB94 results), and are substantially smaller than the CIS and RPA mean absolute deviations.

The TDDFT/TDA excitation energies for Rydberg states obtained with the SVWN, BLYP, and B3LYP functionals are unacceptably too low as compared to the experimental data. The origin of this failure is that the exchange-correlation potentials produced by the current approximate functionals decay too rapidly with increasing distance from the center of the molecule [6,11,12]. Several groups of researchers [11,12,24] have suggested the method of correcting the potential in the asymptotic region. The LB94 correction to the SVWN potential increases the excitation energies for Rydberg states toward the direction of the experimental data. However, for closed-shell molecules, the increase in the excitation energies tends to be too large, such that the resulting excitation energies are much higher than the experimental data. As judged from the mean absolute deviations, the LB94 correction provides the excitation energies which are only slightly better than the SVWN excitation energies for closed-shell molecules. The LB94 correction appears to work better for open-shell molecules than for closed-shell molecules. For the open-shell molecules studied here, the LB94 correction improves (relative to the SVWN results) the mean absolute deviation by a factor of three.

4. Conclusion

We demonstrate that the Tamm–Dancoff approximation to TDDFT leads to a computationally simple method (TDDFT/TDA) the performance of which is essentially the same as TDDFT itself. For several closed- and open-shell molecules, TDDFT/TDA provides excitation energies which are very close to the corresponding TDDFT excitation energies. Noticeable deviations can be found between the TDDFT/TDA and TDDFT excitation energies obtained from the hybrid HF/DFT functional for the molecules having triplet near instability problem. For these states, the TDDFT excitation energies tend to be lower than the experimental data, whereas no significant degradation can be found in the TDDFT/TDA results. Overall, the mean absolute deviations of the TDDFT/TDA excitation energies from the experimental data are essentially the same as or sometimes even smaller than the TDDFT mean absolute deviations, indicating that TDDFT/TDA is a useful alternative to TDDFT.

Acknowledgements

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