

# Time-dependent density functional theory for radicals

## An improved description of excited states with substantial double excitation character

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### Abstract

Spin-unrestricted time-dependent density functional theory (TDDFT) is applied to calculate vertical excitation energies for the first several excited states of four diatomic radicals and methyl, nitromethyl, benzyl, anilino, and phenoxy radicals. While the excitation energies of Rydberg states computed by TDDFT are significantly inferior to the results of Hartree–Fock-based single excitation theories, TDDFT performs slightly better than the HF-based theories for valence states with dominant single excitation character. For valence states with substantial double excitation character, TDDFT is a striking improvement over the HF-based theories, the latter being qualitatively incorrect descriptions for these states. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Straightforward generalizations of single excitation configuration interaction (CIS) theory to open-shell molecules – unrestricted CIS (UCIS) and restricted open-shell CIS (ROCIS) theories – are less effective than CIS for closed-shell molecules [1]. Even for the commonest radicals like CN and CO<sup>+</sup>, UCIS and ROCIS overestimate the vertical excitation energies by 1–5 eV, indicating that these methods cannot describe the few lowest excited states of these radicals even in a qualitatively correct manner. The origin of this failure, as identified by the detachment–attachment density analysis [2], is that a par-

ticular class of double excitation configurations has substantial weight in the excited-state wavefunctions of many radicals, and it is neglected in these methods [1].

One possible solution to this problem is to include explicitly these double excitation configurations, which involves the simultaneous promotion of an  $\alpha$  spin electron from the singly occupied orbital and a  $\beta$  spin electron to the same orbital, among the expansion basis of the configuration interaction. This is accomplished by extended CIS (XCIS) [1], which constitutes a uniform improvement over its parent method, ROCIS, without increasing the computational complexity drastically. Although the numerical data given in Ref. [1] demonstrate that the XCIS can generally provide an appropriate zeroth-order description of low-lying electronic transitions of open-

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shell molecules, in the most difficult cases XCIS yields excitation energies which are still in error by a few electron volts, or predicts the ordering of states incorrectly. To obtain reasonable results for these cases, obviously we must take into account double or higher excitation configurations that are not included in XCIS; in other words XCIS does not include dynamical correlation effects.

In this Letter, we examine another possible solution to this problem, namely, to employ time-dependent density functional theory (TDDFT) [3–5]. Kohn–Sham density functional theory (DFT) for the ground state takes into account dynamical electron correlation within the framework of single determinant theory. TDDFT, which is a formally exact single excitation theory based on Kohn–Sham orbitals, can in principle account for the above-mentioned double excitations (from the HF determinant) and all other important excitations. TDDFT has already been implemented by several groups of researchers and has been applied to various closed-shell systems [6–12]. Although these groups inevitably employ the so-called adiabatic approximation, which amounts to approximating the exchange-correlation action functional by the time-independent exchange-correlation functional, the numerical results appear quite promising. The question is whether, in practice, existing functionals with the adiabatic approximation can properly account for excitations that have significant two-electron character.

We present the vertical excitation energies for the first several excited states of diatomic radicals and methyl, nitromethyl, benzyl, anilino, and phenoxy radicals calculated by the spin-unrestricted version of TDDFT employing local, gradient-corrected, and hybrid functionals. The calculated excitation energies are compared with those obtained from UCIS, ROCIS, XCIS, and unrestricted random-phase approximation (URPA) methods. Particular emphasis is placed on how the accuracy of TDDFT excitation energies is affected by the nature of electronic transition, in particular, by whether the transition is of dominant single excitation character or of appreciable double excitation character. Radicals are the most interesting molecular systems for this investigation since, as mentioned earlier, the UCIS and ROCIS excitation energies are grossly in error for excited states with substantial double excitation character. In

the following, we shall demonstrate that TDDFT dramatically improve the excitation energies for these excited states to the extent that the calculated excitation energies are in uniformly reasonable agreement with the experimental values for most of the low-lying valence excited states. We shall find that TDDFT performs comparably well or sometimes even better than XCIS.

## 2. Implementation

The spin-unrestricted version of TDDFT was implemented in a development version of Q-Chem program package [13]. Our implementation was primarily based on the formalism given in Refs. [6] and [8], but without invoking auxiliary fitting of electron density. To specify the algorithms implemented, we briefly review the formalism for a general hybrid HF/DFT functional, which encompasses the formalism of URPA and that of local and gradient-corrected TDDFT as special cases.

For real Kohn–Sham orbitals, excitation energies  $\omega$  within TDDFT scheme can be determined by solving the non-Hermitian eigenvalue equation of the form

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}. \quad (1)$$

Assuming that  $(\mathbf{A}-\mathbf{B})$  is positive definite, we can reduce this equation into a Hermitian eigenvalue equation with a half dimension

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

with

$$\mathbf{Z} = (\mathbf{A}-\mathbf{B})^{-1/2}(\mathbf{X}+\mathbf{Y}). \quad (3)$$

For a general hybrid HF/DFT functional, the elements of the matrices appearing in Eqs. (1)–(3) are formally written as

$$\begin{aligned} A_{ia\alpha,jb\alpha} &= \delta_{ij}\delta_{ab}(\varepsilon_{a\alpha} - \varepsilon_{i\alpha}) + (i_\alpha a_\alpha | j_\alpha b_\alpha) \\ &\quad - c_{\text{HF}}(i_\alpha j_\alpha | a_\alpha b_\alpha) + (i_\alpha a_\alpha | w_{\alpha\alpha} | j_\alpha b_\alpha), \end{aligned} \quad (4)$$

$$A_{ia\alpha,jb\beta} = (i_\alpha a_\alpha | j_\beta b_\beta) + (i_\alpha a_\alpha | w_{\alpha\beta} | j_\beta b_\beta), \quad (5)$$

and

$$B_{ia\alpha,jb\alpha} = (i_\alpha a_\alpha | b_\alpha j_\alpha) - c_{\text{HF}}(i_\alpha b_\alpha | a_\alpha j_\alpha) \\ + (i_\alpha a_\alpha | w_{\alpha\alpha} | b_\alpha j_\alpha), \quad (6)$$

$$B_{ia\alpha,jb\beta} = (i_\alpha a_\alpha | b_\beta j_\beta) + (i_\alpha a_\alpha | w_{\alpha\beta} | b_\beta j_\beta), \quad (7)$$

where we use  $i, j$  for ground-state occupied orbitals and  $a, b$  for ground-state virtual orbitals, and  $\alpha$  and  $\beta$  indicate spin. The  $\beta\beta$  and  $\beta\alpha$  block of the matrices are obtained by simply interchanging  $\alpha$  and  $\beta$  wherever they appear in Eqs. (4)–(7) and equations below. The prefactor  $c_{\text{HF}}$  on the exchange-type integrals (in the conventional Mulliken notation) is the mixing ratio of HF exchange in the hybrid functional. The last terms in Eqs. (4)–(7) originate from the exchange-correlation part of the energy, and are explicitly given by

$$(i_\alpha a_\alpha | w_{\alpha\alpha} | j_\alpha b_\alpha) \\ = 2 \int \nabla(\psi_{i\alpha} \psi_{a\alpha}) \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) \frac{\partial f}{\partial \gamma_{\alpha\alpha}} d\mathbf{r} \\ + \int \psi_{i\alpha} \psi_{a\alpha} \frac{\partial^2 f}{\partial \rho_\alpha^2} \psi_{j\alpha} \psi_{b\alpha} d\mathbf{r} \\ + 2 \int \{ \psi_{i\alpha} \psi_{a\alpha} \nabla \rho_\alpha \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) \\ + \nabla \rho_\alpha \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \psi_{j\alpha} \psi_{b\alpha} \} \frac{\partial^2 f}{\partial \rho_\alpha \partial \gamma_{\alpha\alpha}} d\mathbf{r} \\ + \int \{ \psi_{i\alpha} \psi_{a\alpha} \nabla \rho_\beta \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) \\ + \nabla \rho_\beta \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \psi_{j\alpha} \psi_{b\alpha} \} \frac{\partial^2 f}{\partial \rho_\alpha \partial \gamma_{\alpha\beta}} d\mathbf{r} \\ + 4 \int \nabla \rho_\alpha \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \\ \times \frac{\partial^2 f}{\partial \gamma_{\alpha\alpha}^2} \nabla \rho_\alpha \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) d\mathbf{r} \\ + 2 \int \nabla \rho_\alpha \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \\ \times \frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \gamma_{\alpha\beta}} \nabla \rho_\beta \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) d\mathbf{r}$$

$$+ 2 \int \nabla \rho_\beta \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \gamma_{\alpha\beta}} \\ \times \nabla \rho_\alpha \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) d\mathbf{r} \\ + \int \nabla \rho_\beta \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \\ \times \frac{\partial^2 f}{\partial \gamma_{\alpha\beta}^2} \nabla \rho_\beta \cdot \nabla(\psi_{j\alpha} \psi_{b\alpha}) d\mathbf{r}, \quad (8)$$

and

$$(i_\alpha a_\alpha | w_{\alpha\beta} | j_\beta b_\beta) \\ = \int \nabla(\psi_{i\alpha} \psi_{a\alpha}) \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) \frac{\partial f}{\partial \gamma_{\alpha\beta}} d\mathbf{r} \\ + \int \psi_{i\alpha} \psi_{a\alpha} \frac{\partial^2 f}{\partial \rho_\alpha \partial \rho_\beta} \psi_{j\beta} \psi_{b\beta} d\mathbf{r} \\ + 2 \int \psi_{i\alpha} \psi_{a\alpha} \frac{\partial^2 f}{\partial \rho_\alpha \partial \gamma_{\beta\beta}} \nabla \rho_\beta \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) d\mathbf{r} \\ + 2 \int \nabla \rho_\alpha \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \frac{\partial^2 f}{\partial \rho_\beta \partial \gamma_{\alpha\alpha}} \psi_{j\beta} \psi_{b\beta} d\mathbf{r} \\ + \int \psi_{i\alpha} \psi_{a\alpha} \frac{\partial^2 f}{\partial \rho_\alpha \partial \gamma_{\alpha\beta}} \nabla \rho_\alpha \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) d\mathbf{r} \\ + \int \nabla \rho_\beta \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \frac{\partial^2 f}{\partial \rho_\beta \partial \gamma_{\alpha\beta}} \psi_{j\beta} \psi_{b\beta} d\mathbf{r} \\ + 4 \int \nabla \rho_\alpha \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \\ \times \frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \gamma_{\beta\beta}} \nabla \rho_\beta \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) d\mathbf{r} \\ + 2 \int \nabla \rho_\alpha \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \\ \times \frac{\partial^2 f}{\partial \gamma_{\alpha\alpha} \partial \gamma_{\alpha\beta}} \nabla \rho_\alpha \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) d\mathbf{r} \\ + 2 \int \nabla \rho_\beta \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \frac{\partial^2 f}{\partial \gamma_{\beta\beta} \partial \gamma_{\alpha\beta}} \\ \times \nabla \rho_\beta \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) d\mathbf{r} \\ + \int \nabla \rho_\beta \cdot \nabla(\psi_{i\alpha} \psi_{a\alpha}) \frac{\partial^2 f}{\partial \gamma_{\alpha\beta}^2} \\ \times \nabla \rho_\alpha \cdot \nabla(\psi_{j\beta} \psi_{b\beta}) d\mathbf{r}, \quad (9)$$

where  $f$  is a sum of appropriately scaled exchange-correlation functionals of local spin densities  $\rho_\alpha, \rho_\beta$  and gradient invariants  $\gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}$ .

The Hermitian eigenvalue problem (Eq. (2)) is solved by using Davidson's iterative subspace method [8,10,14]. In this method, **A** and **B** matrices in Eq. (2) are projected onto a subspace spanned by a set of trial vectors  $\{\mathbf{t}^{[1]}, \dots, \mathbf{t}^{[n]}\}$ . Each Davidson iteration involves the formation of matrix-trial vector products

$$\bar{A}_{ia\alpha}^{[q]} = \sum_{jb} (A_{ia\alpha,jb\alpha} t_{jb\alpha}^{[q]} + A_{ia\alpha,jb\beta} t_{jb\beta}^{[q]}), \quad (10)$$

$$\bar{B}_{ia\alpha}^{[q]} = \sum_{jb} (B_{ia\alpha,jb\alpha} t_{jb\alpha}^{[q]} + B_{ia\alpha,jb\beta} t_{jb\beta}^{[q]}). \quad (11)$$

This is conveniently carried out in the direct atomic-orbital-based algorithms, which are outlined for CIS in Ref. [15], for RPA in Ref. [16], and for TDDFT in Ref. [8]. Subspace representation of **A** and **B** matrices, denoted as **A**<sup>R</sup> and **B**<sup>R</sup>, is obtained by forming the inner product of the trial vectors and the product vectors (left-hand sides of Eqs. (10) and (11)):

$$A_{pq}^R = \sum_{ia} (t_{ia\alpha}^{[p]} \bar{A}_{ia\alpha}^{[q]} + t_{ia\beta}^{[p]} \bar{A}_{ia\beta}^{[q]}), \quad (12)$$

$$B_{pq}^R = \sum_{ia} (t_{ia\alpha}^{[p]} \bar{B}_{ia\alpha}^{[q]} + t_{ia\beta}^{[p]} \bar{B}_{ia\beta}^{[q]}). \quad (13)$$

Subspace size is increased iteratively until the approximate eigenvalues  $\omega^R$  and the corresponding eigenvectors obtained by solving the eigenvalue problem with reduced dimension

$$\begin{aligned} & (\mathbf{A}^R - \mathbf{B}^R)^{1/2} (\mathbf{A}^R + \mathbf{B}^R) (\mathbf{A}^R - \mathbf{B}^R)^{1/2} \mathbf{Z}^R \\ & = (\omega^R)^2 \mathbf{Z}^R \end{aligned} \quad (14)$$

satisfies Eq. (2) within a preset tolerance. We consider the root as being converged when the norm of the residuum (left-hand side minus right-hand side of Eq. (2)) becomes smaller than  $10^{-6}$ .

### 3. Applications

In Table 1 are summarized the vertical excitation energies of BeH, BeF, CH<sub>3</sub>, CN, CO<sup>+</sup> radicals calculated by several variants of TDDFT and URPA.

We employed the Slater–Vosko–Wilk–Nusair (SVWN) [17,18], Becke–Lee–Yang–Parr (BLYP) [19,20], and Becke3–Lee–Yang–Parr (B3LYP) [21] functionals as representative local, gradient-corrected, and hybrid functionals. For these radicals, UCIS, ROCIS, and XCIS excitation energies as well as precise experimental results are available [1,22], and are listed in Table 1. XCIS character in the rightmost column is the percentage contribution of the double excitation configurations which are included in XCIS but omitted in ROCIS. This is a good index of whether the excited state is of dominant single excitation character or of partial double excitation character. The basis set used is 6-311(2 + ,2 + )G<sup>\*\*</sup>, and is sufficiently large to describe the several lowest valence and Rydberg states.

It may be immediately noticed from Table 1 that TDDFT, regardless of the functionals used, underestimates the excitation energies of Rydberg states by a few electron volts. This result is in contrast to the relatively good description of these states provided by the HF-based methods. The B3LYP excitation energies are slightly better than SVWN and BLYP values probably owing to the mixing of the HF exchange in the former functional, but they are still much lower than the experimental results. The same deficiency has already been observed for closed-shell molecules, and the sign and magnitude of deviations do not seem different from closed-shell molecules to open-shell ones of similar size [6,11,12]. Casida et al. [11] and Tozer and Handy [12] have recently carried out detailed analyses of this problem, and have identified the origin of this deficiency as the failure of the current approximate exchange-correlation functionals to correctly describe the exchange-correlation potential in the asymptotic region. Thus, we can in principle overcome this deficiency by using an improved functional that exhibits correct asymptotic behavior, but we should keep in mind that most of the functionals currently widely used would suffer from this deficiency (for exceptions, see Refs. [11,12] and van Leeuwen–Baerends '94 functional [23]).

The valence excited states may be broadly classified into two categories: excited states with dominant single excitation character and those with appreciable double excitation character. The lowest excited states of BeH and BeF are among the first category,

Table 1

Vertical excitation energies (in eV) for the several lowest excited states of small radicals calculated by UCIS, ROCIS, XCIS, URPA, and TDDFT methods with the 6-311(2 + ,2 + )G<sup>++</sup> basis set at geometries of Ref. [22]

Radical	State <sup>a</sup>	Excitation energies							XCIS character <sup>e</sup>	
		UCI <sup>b</sup>	ROCIS <sup>b,c</sup>	XCIS <sup>c</sup>	URPA	SVWN	BLYP	B3LYP	Expt <sup>d</sup>	
BeH	V <sup>2</sup> Π	2.752	2.715	2.661	2.715	2.345	2.539	2.554	2.484	1.0
	R <sup>2</sup> Π	6.525	6.544	6.468	6.423	4.862	4.689	5.179	6.318	1.6
BeF	V <sup>2</sup> Π	4.268	4.260	4.249	4.228	4.030	4.095	4.139	4.138	0.1
	R <sup>2</sup> Σ <sup>+</sup>	6.356	6.349	6.345	6.348	5.321	5.100	5.515	6.158	0.0
	R <sup>2</sup> Σ <sup>+</sup>	6.600	6.600	6.587	6.594	5.346	5.161	5.563	6.271	0.2
CH <sub>3</sub>	R <sup>2</sup> A <sub>1</sub> '	6.546	6.300	6.243	6.514	4.932	4.662	5.156	5.729	0.2
	R <sup>2</sup> A <sub>2</sub> '	7.930	7.713	7.651	7.880	5.853	5.526	6.173	7.436	0.6
CN	V <sup>2</sup> Π	4.070	2.185	1.150	3.899	1.637	1.527	1.373	1.315	4.5
	V <sup>2</sup> Σ <sup>+</sup>	6.546	6.378	4.802	5.432	3.023	3.072	2.999	3.219	14.2
CO <sup>+</sup>	V <sup>2</sup> Π	7.504	5.656	4.267	6.955	3.620	3.499	3.755	3.264	5.8
	V <sup>2</sup> Σ <sup>+</sup>	11.315	10.404	8.192	11.224	5.025	5.114	5.788	5.819	37.5

<sup>a</sup>Whether the excited states are principally of valence (V) or Rydberg (R) character is indicated.

<sup>b</sup>Ref. [22].

<sup>c</sup>Ref. [1].

<sup>d</sup>See Ref. [22] and references therein.

<sup>e</sup>Percentage contributions of the double excitation configurations accounted for by XCIS [1].

whose XCIS character is nearly zero. For these states, UCIS and ROCIS already works fairly well with errors being a few tenths of an electron volt. As expected, XCIS only slightly changes these values toward the direction of the experimental values. TDDFT excitation energies are also in reasonably good agreement with the experiments. In particular, the BLYP and B3LYP results are encouraging, which are within a few hundredths of an electron volt of the experimental values.

The two lowest excited states of CN and CO<sup>+</sup> are among the second category, whose XCIS character varies in the range of 4–38%. For these states, UCIS and ROCIS perform quite poorly with the deviations from the experiments being in the range of 1–5 eV. Thus, UCIS and ROCIS can no longer provide even zeroth-order descriptions when the XCIS character exceeds only a few percents. This is not unreasonable considering that HF theory for ground states is considered to break down under similar conditions. XCIS improves the excitation energies of its parent method ROCIS substantially, illustrating the soundness of the underlying theory, but there still remain errors on the order of a few electron volts. TDDFT excitation energies constitute remarkable improvements over these HF-based theory results. The mean absolute deviations from the experiments for these

four states are only 0.42, 0.32, and 0.20 eV for SVWN, BLYP, and B3LYP functional, respectively, and these numbers are much smaller than that of XCIS (1.28 eV). Consequently it can be said that TDDFT with current functionals yields uniformly reasonable excitation energies for valence states of small radicals with varied double excitation character.

The URPA excitation energies for these small radicals behave essentially the same way as UCIS and ROCIS excitation energies do, although quantitatively there are noticeable differences between one another. URPA, like UCIS and ROCIS, fails to provide qualitatively correct descriptions for the two lowest excited states of CN and CO<sup>+</sup> radicals. It is, therefore, not the **B** matrix in Eq. (1), which exists in URPA and TDDFT formalisms but does not exist in UCIS and ROCIS formalisms, that essentially leads to the improved valence excitation energies of TDDFT. This observation suggests that we may safely neglect the **B** matrix in the TDDFT formalism without appreciably deteriorating the calculated results. We study in a separate paper [24] the validity of this approximation, which amounts to configuration interaction from the Kohn–Sham reference.

Nitromethyl (CH<sub>2</sub>NO<sub>2</sub>) radical is another interesting test case for TDDFT, in the sense that UCIS

Table 2

Vertical excitation energies (in eV) for the lowest excited states of different symmetry of nitromethyl radical calculated by UCIS, ROCIS, XCIS, TDDFT, and G2 methods with the 6-31G<sup>\*</sup> basis set at the UMP2/6-31++G<sup>\*\*</sup> optimized geometry of Ref. [28].

State	Excitation energies							XCIS character <sup>c</sup>
	UCIS <sup>a</sup>	ROCIS <sup>a,b</sup>	XCIS <sup>b</sup>	SVWN	BLYP	B3LYP	G2 <sup>a,b</sup>	
<sup>2</sup> B <sub>2</sub>	3.379	4.557	2.607	0.982	1.242	1.856	1.990	42.6
<sup>2</sup> A <sub>1</sub>	3.676	4.688	2.928	1.551	1.765	2.033	2.473	36.4
<sup>2</sup> A <sub>2</sub>	2.179	6.183	1.512	2.040	2.098	2.312	2.476	52.7

<sup>a</sup>Ref. [22].

<sup>b</sup>Ref. [1].

<sup>c</sup>Percentage contributions of the double excitation configurations accounted for by XCIS [1].

and ROCIS yield excitation energies grossly in error and fail to reproduce the correct ordering of its three lowest states (Table 2). Here we use G2 excitation energies as reference data [22], which we believe to be within 0.1 eV of true values. As is evident from Table 2, TDDFT results are again significant improvements over UCIS and ROCIS results. All the three functionals correctly reproduce the ordering of these three states, although the excitation energies themselves are sometimes too low as compared to the G2 results. It should be noted that even XCIS

gives incorrect state ordering. In this specific case, the calculated excitation energies improve on going from SVWN to BLYP, and from BLYP to B3LYP. In fact, the B3LYP results are in reasonable agreement with G2 results, and are significantly better than XCIS excitation energies.

Many of the lowest valence excited states of benzyl, anilino, and phenoxy radicals, which are isoelectronic benzene derivatives, bear substantial double excitation character (Table 3). As expected from the above numerical data and discussions, UCIS

Table 3

Vertical excitation energies (in eV) for the valence excited states of benzyl, anilino, and phenoxy radicals calculated by UCIS, ROCIS, XCIS, and TDDFT methods with the 6-31+G<sup>\*</sup> basis set at UHF/6-31G<sup>\*</sup> optimized geometries of Ref. [1].

Radical	State <sup>a</sup>	Excitation energies							XCIS character <sup>d</sup>
		UCIS	ROCIS <sup>b</sup>	XCIS <sup>b</sup>	SVWN	BLYP	B3LYP	Expt <sup>c</sup>	
Benzyl	<sup>2</sup> A <sub>2</sub>	5.78	5.13	2.99	2.76	2.81	3.17	2.7	32.8
	<sup>2</sup> B <sub>1</sub>	5.79	5.41	2.36	3.25	3.24	3.41	2.7	42.9
	<sup>2</sup> A <sub>2</sub>	6.15	6.44	4.22	3.33	3.40	3.84	3.9	37.9
	<sup>2</sup> B <sub>1</sub>	5.91	—	4.76	4.52	4.36	4.34	—	82.8
	<sup>2</sup> B <sub>1</sub>	6.77	5.55	5.08	4.59	4.49	4.79	4.8	10.2
Anilino	<sup>2</sup> A'	3.26	2.29	2.07	1.75	1.98	2.25	—	0.9
	<sup>2</sup> A''	5.65	5.11	2.22	2.40	2.45	2.81	2.9	40.8
	<sup>2</sup> A''	5.88	5.20	2.65	3.34	3.31	3.47	2.9	31.7
	<sup>2</sup> A''	5.95	6.75	4.26	3.70	3.75	4.17	3.9	43.0
Phenoxy	<sup>2</sup> B <sub>2</sub>	1.81	0.92	0.56	0.57	0.75	1.03	—	1.7
	<sup>2</sup> A <sub>2</sub>	5.19	4.16	1.91	1.99	2.01	2.30	3.0	22.0
	<sup>2</sup> B <sub>1</sub>	5.57	3.98	2.33	3.47	3.42	3.58	3.0	23.9
	<sup>2</sup> A <sub>1</sub>	6.48	5.52	5.03	3.90	4.05	4.88	—	4.2
	<sup>2</sup> A <sub>2</sub>	6.57	6.51	4.45	4.09	4.11	4.48	4.0	27.7

<sup>a</sup>The excited states are classified under the C<sub>2v</sub> point group for benzyl and phenoxy radicals and the C<sub>s</sub> point group for anilino radical. Orientation of the molecules is taken to be the same as in Ref. [1].

<sup>b</sup>Ref. [1].

<sup>c</sup>See Ref. [1] and references therein.

<sup>d</sup>Percentage contributions of the double excitation configurations accounted for by XCIS [1].

and ROCIS provide even qualitatively incorrect descriptions for these states, and hence unacceptably too high excitation energies. XCIS remedies this situation quite remarkably; the mean absolute deviation from the experimental values is 0.5 eV, although XCIS predicts the ordering of a pair of states incorrectly (i.e., the lowest  $^2A_2$  and  $^2B_1$  states of benzyl radical). The performance of TDDFT is comparable to that of XCIS for these radicals, as can be seen in Table 3. The mean absolute deviations are 0.4, 0.4, and 0.4 eV for SVWN, BLYP, and B3LYP, respectively, and all the three functionals correctly predict the ordering of the above-mentioned states. However, for these radicals, the advantage of B3LYP over BLYP, or that of BLYP over SVWN is not apparent.

Finally, it would be interesting to note that relatively simple semiempirical methods perform remarkably well for the excited states of benzyl, anilino, and phenoxyl radicals. For example, ROCIS calculations employing CNDO parameterization predict the vertical excitation energies of these radicals within 0.2 eV of experimental results [25,26]. Considering that the excited states of these radicals have significant double excitation character and are in principle not to be described well by single excitation theory, we suppose that the orbitals generated from the self-consistent field procedure of a carefully parameterized semiempirical method should be regarded as quasi-particle states dressed with the dynamical correlation effects rather than approximations to the HF orbitals. The relatively good performance of TDDFT for the excited states with substantial double excitation character will essentially be traced back to the same mechanism which allows the semiempirical methods to yield good excitation energies for these excited states.

#### 4. Conclusion

Formally TDDFT is an exact theory of excitation energies, but in practice it may be limited by inexact functionals and the adiabatic approximation. However, with present functionals, TDDFT can reproduce the excitation energies of valence excited states of radicals typically within several tenths of an electron volt, and this numerical accuracy seems hardly

affected by the double excitation character of the excited states. This is in striking contrast with UCIS and ROCIS excitation energies, which may be acceptable when the excited states of interest are of dominant single excitation character, but unacceptably erratic when the excited states have appreciable double excitation character. Since it is usually impossible to classify the excited states according to their double excitation character from the experimental side, it is essentially important for an excited state theory to describe the excited states of different character in a well-balanced manner. TDDFT proves to be such a theory for several lowest valence excited states of radicals, and hence, is an attractive alternative to UCIS and ROCIS. We consider that TDDFT is an appropriate zeroth-order theory for valence excited states of radicals, which is potentially applicable to large systems [27].

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#### References

- [1] D. Maurice, M. Head-Gordon, *J. Phys. Chem.* 100 (1996) 6131.
- [2] M. Head-Gordon, A.M. Graña, D. Maurice, C.A. White, *J. Phys. Chem.* 99 (1995) 14261.
- [3] E. Runge, E.K.U. Gross, *Phys. Rev. Lett.* 52 (1984) 997.
- [4] M. Petersilka, U.J. Gossmann, E.K.U. Gross, *Phys. Rev. Lett.* 76 (1996) 1212.
- [5] M.E. Casida, in: D.P. Chong (Ed.), *Recent Advances in Density Functional Methods, Part I*, World Scientific, Singapore, 1995.
- [6] R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* 256 (1996) 454.
- [7] C. Jamorski, M.E. Casida, D.R. Salahub, *J. Chem. Phys.* 104 (1996) 5134.
- [8] R. Bauernschmitt, M. Häser, O. Treutler, R. Ahlrichs, *Chem. Phys. Lett.* 264 (1997) 573.

- [9] K.B. Wiberg, R.E. Stratmann, M.J. Frisch, Chem. Phys. Lett. 297 (1998) 60.
- [10] R.E. Stratmann, G.E. Scuseria, M.J. Frisch, J. Chem. Phys. 109 (1998) 8218.
- [11] M.E. Casida, C. Jamorski, K.C. Casida, D.R. Salahub, J. Chem. Phys. 108 (1998) 4439.
- [12] D.J. Tozer, N.C. Handy, J. Chem. Phys. 109 (1998) 10180.
- [13] C.A. White, J. Kong, D.R. Maurice, T.R. Adams, J. Baker, M. Challacombe, E. Schwegler, J.P. Dombroski, C. Ochsenfeld, M. Oumi, T.R. Furlani, J. Florian, R.D. Adamson, N. Nair, A.M. Lee, N. Ishikawa, R.L. Graham, A. Warshel, B.G. Johnson, P.M.W. Gill, M. Head-Gordon, Q-Chem, Version 1.2, Q-Chem, Pittsburgh, PA, 1998.
- [14] E.R. Davidson, J. Comput. Phys. 17 (1975) 87.
- [15] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, J. Phys. Chem. 96 (1992) 135.
- [16] H. Weiss, R. Ahlrichs, M. Häser, J. Chem. Phys. 99 (1993) 1262.
- [17] J.C. Slater, Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids, McGraw-Hill, New York, 1974.
- [18] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200. Parameterization 5 has been implemented.
- [19] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [20] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [21] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [22] D. Maurice, M. Head-Gordon, Int. J. Quantum Chem. Quantum Chem. Symp. 29 (1995) 361.
- [23] R. van Leeuwen, E.J. Baerends, Phys. Rev. A 49 (1994) 2421.
- [24] S. Hirata, M. Head-Gordon, unpublished.
- [25] H.M. Chang, H.H. Jaffé, Chem. Phys. Lett. 23 (1973) 146.
- [26] H.M. Chang, H.H. Jaffé, C.A. Masmanidis, J. Phys. Chem. 79 (1975) 1118.
- [27] R. Bauernschmitt, R. Ahlrichs, F.H. Hennrich, M.M. Kappes, J. Am. Chem. Soc. 120 (1998) 5052.
- [28] R.B. Metz, D.R. Cyr, D.M. Neumark, J. Phys. Chem. 95 (1991) 2900.