

On the determination of excitation energies using density functional theory†

David J. Tozer^a and Nicholas C. Handy^b

^a Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE

^b Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

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The use of time-dependent density functional theory (TDDFT) is considered for the determination of electronic excitation energies. Using beryllium and methylene as examples, we highlight (i) problems with Rydberg excitations arising from neglect of the integer discontinuity in the potential; (ii) the absence of pure double excitations in calculations using conventional exchange-correlation functionals; (iii) quantitative differences between excitation energies determined using TDDFT and the ‘delta SCF’ method; (iv) non-additivity of excitation energies calculated using TDDFT from different electronic states; (v) an apparent failure to predict single excitations to states that are lower than the reference states and (vi) the difference in quality between excitations to singlet and triplet states.

1 Introduction

Kohn–Sham density functional theory has become a powerful tool in computational chemistry, being recognised as an inexpensive and reasonably accurate method for the determination of ground state quantities. More recently it has also been used through response theory for the calculation of vertical excitation energies. In this paper we examine several issues relating to the determination of excitation energies using time-dependent density functional theory (TDDFT).

At its simplest, TDDFT is the translation of the random phase approximation (RPA) into DFT. It is best understood in terms of the response of a molecule to a time dependent electromagnetic field, for which the electric field is $E_\omega \cos \omega t$. There have been a number of active scientists in this area. In particular we highlight the work of Bauernschmitt and Ahlrichs,^{1,2} Casida and coworkers,^{3,4} Baerends and coworkers^{5,6} and Gross and coworkers.^{7,8} TDDFT is now a standard algorithm in the packages TURBOMOL,⁹ ADF,¹⁰ GAUSSIAN¹¹ and CADPAC.¹²

2 The determination of excitation energies

In the standard time-dependent perturbation theory of quantum mechanics, the linear response is measured by the change in the expectation value q_λ of a one electron operator, represented by $\hat{q}_\lambda = \sum_i \hat{f}_\lambda(\mathbf{r}_i)$, when a time-dependent electric field $E_{\omega\mu} \cos \omega t$ is applied

$$q_\lambda = q_\lambda^0 + \sigma_{\lambda\mu}(-\omega; \omega) E_{\omega\mu} \cos \omega t \quad (1)$$

The perturbation theory gives the following expression for the tensor components $\sigma_{\lambda\mu}$

$$\sigma_{\lambda\mu}(-\omega; \omega) = \sum_K \frac{[\langle 0 | \hat{f}_\lambda | K \rangle \langle K | \hat{f}_\mu | 0 \rangle + c.c.] \omega_K}{\omega_K^2 - \omega^2} \quad (2)$$

where K denotes all electronic states with energy W_K ; 0 denotes the ground state and $\omega_K = W_K - W_0$.

Let the state 0 be a singlet state. If the one-electron operator has no explicit spin dependence then excitations to singlet states will be obtained as poles of the associated tensor. For example, if the operator is the dipole operator $\hat{f}_\lambda = r_\lambda$, then singlet excitations would be obtained as the poles of the frequency dependent polarisability. Furthermore, this theory states that *all* singlet excitations are observed, because (neglecting spatial symmetry) they all have non-zero matrix elements with the state 0. Excitations to triplet states will not, however, be obtained since the numerator will vanish by spin symmetry. These excitations must be determined as the poles of a different tensor, associated with a one-electron operator whose explicit spin-dependence prevents the numerator from vanishing. An example is the spin-orbit operator $\hat{f}_\lambda = \hat{l}_\lambda \hat{s}_z$.

All excitation energies (single, double, etc.) can therefore be determined through the poles of appropriate tensor quantities, each expressed in terms of just one-electron operators. Given the one-electron nature of DFT, it would therefore appear that this method should also be able to predict all excitations, without the need to investigate any non-linear response properties. We now consider the linear response in DFT.

The basic theorem of Hohenberg and Kohn¹³ states that the electron density gives all of the required information to determine the Hamiltonian and its wavefunctions. Such an observation includes the presence of a static electric field, but not the presence of a static magnetic field, for which it is also necessary to know the electric current $\mathbf{j}(\mathbf{r})$. Furthermore knowledge of ρ and \mathbf{j} do not give information on ω (because ρ and \mathbf{j} depend upon the product of the wavefunction with its conjugate), if the electromagnetic field has a time dependence. The deduction from all of this is that to obtain excitation energy predictions from DFT, we should include an energy functional dependence on both \mathbf{j} and ω . Exchange-correlation functionals in use today do not include this dependence, because the nature of this dependence is not known. Neglect of a dependence on ω is often called the adiabatic approximation.¹ The following analysis is therefore appropriate for an exchange-correlation functional with no \mathbf{j} - or ω -dependence.

† Dedicated to Professor Reinhart Ahlrichs on the occasion of his 60th birthday.

The theory commences¹ from the time-dependent Frenkel variation of the Kohn–Sham equations

$$\left(\phi_a \left| F^{KS} - i \frac{\partial}{\partial t} \right| \phi_i \right) = 0 \quad (3)$$

where the unperturbed orbitals satisfy

$$(\phi_p | F^{KS} - \varepsilon_q | \phi_q) = 0 \quad (4)$$

We can already make an important observation of Kohn–Sham theory. In continuum DFT theory (by this we mean one where the potential varies smoothly as a function of the number of electrons, *i.e.* the functional has no orbital dependence) using in particular generalised gradient approximation (GGA) exchange-correlation functionals, all the orbitals are eigenfunctions of the same Kohn–Sham operator, which involves an $(N - 1)$ electron potential. We think that this is one reason why TDDFT in practice is often successful in contrast to TDHF theory (RPA), where the unoccupied orbitals are the eigenfunctions of an N electron potential. The matrix element of F^{KS} is given by

$$(\phi_p | F^{KS} | \phi_q) = (\phi_p | h | \phi_q) + (pq | \rho) + \int \phi_p^* v_{xc} \phi_q \, d\mathbf{r} \quad (5)$$

where v_{xc} is the exchange-correlation potential, the functional derivative of the exchange-correlation energy $E_{xc}[\rho]$.

We commence by considering singlet excitations from a closed-shell ground system, which are obtained from the poles of the frequency dependent polarisability. The orbitals are expanded as

$$\phi_p = \phi_p^0 + \frac{1}{2} E_{\omega\mu} [U_{rp}^{\mu}(\omega) e^{i\omega t} + U_{rp}^{\mu}(-\omega) e^{-i\omega t}] \phi_r^0 + \dots \quad (6)$$

where the coefficients U_{rp}^{μ} are to be found. Note that this expansion is an orbital expansion; it is not possible to introduce products of orbitals into this expansion. Orthonormality and the fact that the electron density involves a trace imply that

$$U_{pq}^{\mu}(\omega) + U_{pq}^{\mu}(-\omega) = 0 \quad (7)$$

$$U_{ij}^{\mu}(\omega) = U_{ij}^{\mu}(-\omega) = 0 \quad (8)$$

$$U_{ab}^{\mu}(\omega) = U_{ab}^{\mu}(-\omega) = 0 \quad (9)$$

The next step is to substitute this expansion into the Frenkel–Kohn–Sham equation, and equate the coefficients of $E_{\omega\mu} e^{\pm i\omega t}$ to zero. This gives

$$U_{ai}^{\mu}(\pm\omega)(\varepsilon_a - \varepsilon_i) + \left[2(ai | bj) + \int \phi_a^0 \phi_i^0 \frac{\delta v_{xc}}{\delta \rho} \phi_b^0 \phi_j^0 \, d\mathbf{r} \right] \times (U_{bf}^{\mu}(\omega) + U_{bf}^{\mu}(-\omega)) + P_{ai}^{\mu} \pm \omega U_{ai}^{\mu}(\pm\omega) = 0 \quad (10)$$

Here $P_{ai}^{\mu} = (\phi_a^0 | r_{\mu} | \phi_i^0)$. The notation $\delta/\delta\rho$ includes variations in ρ and derivatives of ρ . One then proceeds straightforwardly by defining

$$Z_{ai}^{\mu}(\omega) = U_{ai}^{\mu}(\omega) + U_{ai}^{\mu}(-\omega) \quad (11)$$

$$Y_{ai}^{\mu}(\omega) = U_{ai}^{\mu}(\omega) - U_{ai}^{\mu}(-\omega) \quad (12)$$

The coupled equations to determine Z^{μ} are

$$(\mathbf{h}_2 \mathbf{h}_1 - \omega^2 \mathbf{I}) \mathbf{Z}^{\mu} = -2\mathbf{h}_2 \mathbf{P}^{\mu} \quad (13)$$

and the frequency dependent polarisability is given by

$$\alpha_{\mu\nu}(-\omega; \omega) = -2P_{ai}^{\mu} Z_{ai}^{\nu} \quad (14)$$

The poles of $\alpha_{\mu\nu}(-\omega; \omega)$ (*i.e.* the singlet excitation energies) are therefore determined from

$$\det | \mathbf{h}_2 \mathbf{h}_1 - \omega^2 \mathbf{I} | = 0 \quad (15)$$

and so the key to the success of the theory is the evaluation of the hessian \mathbf{h}_1

$$h_{1, ai, bj} = (\varepsilon_b - \varepsilon_j) \delta_{ai, bj} + 4(ai | bj) + 2 \int \phi_a^0 \phi_i^0 \frac{\delta v_{xc}}{\delta \rho} \phi_b^0 \phi_j^0 \, d\mathbf{r} \quad (16)$$

and the diagonal (because of the omission of any j -dependence) hessian \mathbf{h}_2

$$h_{2, ai, bj} = (\varepsilon_b - \varepsilon_j) \delta_{ai, bj} \quad (17)$$

It is immediately clear from this analysis that the number of excitation energies calculated is just $N_{\text{occ}} \times N_{\text{virt}}$, where N_{occ} and N_{virt} denote the number of occupied and virtual Kohn–Sham orbitals, respectively. In other words, only single excitations are determined in this theory. Double, and higher excitations, are absent. Presumably, if an explicit dependence on ω was introduced then these additional excitations would be introduced. One must, however, be very careful in this whole discussion; although the eigenvalues may strictly be related to excitation energies, this does not follow for the eigenvectors. Only by arguments such as ‘this approach is closely related to single excitation configuration interaction’ can a meaning be attached to them. Indeed we know that local exchange terms introduce non-dynamical correlation, and it has been observed that multiconfigurational excited states are well predicted by this DFT, and so we should not be surprised in such cases that the DFT eigenvector does not look like the *ab initio* eigenvector.

The above formulae for \mathbf{h}_1 and \mathbf{h}_2 are appropriate for excitations from a closed-shell singlet ground state to excited singlet states. In order to determine excitations to excited triplet states it is necessary to repeat the theory using the appropriate spin-dependent one-electron operator. In that case, the poles are again determined from an expression of the form (15), although the hessian \mathbf{h}_1 involves a different combination of terms (in particular differences rather than sums) arising from the exchange-correlation functional and it does not involve the integral $(ai | bj)$. The accuracy of these triplet excitations will therefore more critically depend upon the accuracy of the exchange-correlation functional. Once again only single excitations will be obtained.

It is possible to formulate the linear response problem in a more general unrestricted framework, as detailed in ref. 14. In this case the zero-determinant condition for calculating the poles of the frequency dependent polarisability yields both the singlet and triplet excitation energies. This arises because the one-electron operator does not enter the expression from the poles, but is rather on the right hand side of the coupled equations.

This is the straightforward theory of TDDFT as practised today, and it is obvious that its success crucially depends upon the quality of the virtual orbitals and eigenvalues. The incorrect asymptotic behaviour of conventional continuum functionals can lead to significant errors in these quantities. In practical calculations, it is therefore necessary to asymptotically correct the potentials.

2.1 Asymptotically corrected exchange-correlation potentials

It is known that the asymptotic behaviour of the exact electron density is

$$\lim_{r \rightarrow \infty} \rho(r) \sim \exp(-2(2I)^{1/2}r) \quad (18)$$

and thus in DFT

$$\lim_{r \rightarrow \infty} \phi_{\text{HOMO}}(r) \sim \exp(-(2I)^{1/2}r) \quad (19)$$

where I is the ionisation energy. Substitution of this relation into the Kohn–Sham equation for the HOMO, evaluating in

the limit $r = \infty$, after dividing by ϕ_{HOMO} yields

$$-I + v_{xc}(\infty) = \varepsilon_{\text{HOMO}} \quad (20)$$

or

$$\lim_{r \rightarrow \infty} v_{xc} = -\frac{1}{r} + I + \varepsilon_{\text{HOMO}} \quad (21)$$

The $-1/r$ term follows from the one-electron nature of exchange. The potentials of conventional continuum functionals such as GGA give reasonably accurate HOMO eigenvalues, near $\varepsilon_{\text{HOMO}} \sim -I/2$ for open-shell systems. This is correctly shifted from $-I$, in accordance with an average over the integer discontinuity.^{15,16} However, their potentials vanish asymptotically, and so do not satisfy eqn. (21) and this leads to very poor virtual eigenvalues and orbitals. We have therefore recently presented a method for correcting GGA potentials¹⁴ in the following manner.

From the density, we determine atomic densities Q_A surrounding each atom A. If $r_A < \alpha B_A$, where B_A is the Bragg radius of atom A, for any A, then the point is in the molecular region, and we use the conventional functional derivative v_{xc} ; if $r_A > \beta B_A$, for all A, then the point is in the asymptotic region and we use the asymptotic form eqn. (21) for v_{xc} , with $r^{-1} = N^{-1} \sum_A Q_A r_A^{-1}$. If the point is in between, we linearly interpolate. α , β are parameters; we have found that $\alpha = 3.0$ and $\beta = 4.0$ work well for all systems we have studied. Clearly predictions are susceptible to having sensible values for these two parameters. We have presented evidence that this scheme obtains the orbitals of the H atom (through $n = 5$). The implementation of this correction is straightforward because the evaluation of exchange-correlation matrix elements uses numerical quadrature. I is pre-determined from separate Kohn–Sham calculations on the ground state and its cation. Note that this correction is only introduced into the Kohn–Sham equations to determine good orbitals. It plays no explicit role in the subsequent construction of the Hessians.

3 Calculations on beryllium and methylene

We demonstrate this discussion by determining excitation energies for the simple systems Be and CH_2 . We use a TDDFT code which works in spin orbitals, which therefore calculates excitations from any spin state, with M_S conserved.¹⁷ We also have a separate code for a closed shell system.^{18,19} The codes are consistent.

In our studies we have used our GGA functional HCTH,²⁰ more recently termed HCTH/93. We do not think that the points we shall make are critically dependent on this choice of GGA. We use extensive basis sets, augmented with diffuse functions to allow an accurate representation of the Rydberg orbitals. We have used a large quadrature, with no radial truncation in the solution of the Kohn–Sham equations. The methylene geometry was $|\text{CH}| = 1.078 \text{ \AA}$ and $\theta = 136^\circ$.

3.1 Discussion of results for beryllium

The DFT energy of the ground state ($1s^2 2s^2$) ^1S is $-14.6683 E_h$, and the energy of the first excited state ($1s^2 2s 2p$) ^3P is $-14.5765 E_h$. These calculations can be performed separately because the states have different symmetry ($M_S = 0, 1$ respectively). By this delta SCF method the excitation energy is 2.50 eV to be compared with an observed value of 2.73 eV. (We have obtained all our observed values from ‘*Atomic Energy Levels*’, published by the National Bureau of Standards for C. E. Moore in 1949). We would consider this prediction error of 0.23 eV to be acceptable.

In Table 1 we report excitation energies from the ground state to singlet excited states $M_S = 0$. The identification of the excited state is made by examining the dominant eigenvector

Table 1 Excitations (in eV) from $^1\text{S}(M_S = 0)(1s^2 2s^2)$ to singlet states of Be

State	HCTH	HCTH(AC)	Expt	HCTH(AC) error
$^1\text{P}(2s2p)$	4.90	5.03	5.28	−0.25
$^1\text{S}(2s3s)$	5.51	6.55	6.78	−0.23
$^1\text{P}(2s3p)$	5.65	7.19	7.46	−0.27
$^1\text{D}(2p^2)$?	?	7.00	?
$^1\text{D}(2s3d)$	5.68	7.30	7.99	−0.69
$^1\text{S}(2s4s)$	5.63	7.86	8.09	−0.23
$^1\text{P}(2s4p)$?	8.11	8.34	−0.23
$^1\text{D}(2s4d)$?	8.20	8.53	−0.33
$^1\text{S}(2s5s)$?	8.35	8.60	−0.25
$^1\text{P}(2s5p)$?	8.51	?	?
$^1\text{D}(2s5d)$?	8.55	8.80	−0.25

coefficients for the state. The table includes the excitation energies determined using HCTH; those obtained when the asymptotic correction is included (I was computed to be $0.3334 E_h$), denoted HCTH(AC); the experimental values; and the error in the HCTH(AC) values.

It is immediately clear that the non-corrected HCTH values are meaningless for Rydberg excitations; it is not possible to make the assignments. For HCTH(AC), we observe that the prediction error for the s and p Rydberg states is an acceptable 0.20–0.25 eV; these results are in line with many other published calculations to Rydberg states using asymptotically corrected potentials.^{14,18,19} The prediction for the valence $2s2p$ state is also good. It is this accuracy which has encouraged scientists to use TDDFT for excitation energy predictions for excited states.

Table 1 also clearly demonstrates that this form of TDDFT cannot describe pure double excitations—the $^1\text{D}(2p^2)$ state is absent. The ^1D state that is predicted is identified as the $2s3d$ state, and is in error by -0.69 eV. This error may reflect the presence of two states; the error from the observed average is -0.2 eV. It is interesting to note however, that although pure double excitations are absent in TDDFT, the method has previously been shown to provide an accurate representation of excitations to states with significant double excitation character. For example, in refs. 19 and 21, it is shown that excitations to states containing up to 40% double excitation character are predicted as accurately as those to singly excited states.

Table 2 gives the corresponding results for excitations from the ground state to the corresponding triplet states. Once again the non-corrected HCTH values are meaningless for Rydberg states; in the remainder of this work we shall concentrate on the HCTH(AC) values. In general the errors are larger for these triplet states (especially the lower ones) than for the singlet states. They also show a wider variation. The value of 2.19 eV for the lowest $^3\text{P}(2s2p)$ excitation is in error

Table 2 Excitations (in eV) from $^1\text{S}(M_S = 0)(1s^2 2s^2)$ to triplet states of Be

State	HCTH	HCTH(AC)	Expt	HCTH(AC) error
$^3\text{P}(2s2p)$	2.19	2.19	2.73	−0.54
$^3\text{S}(2s3s)$	5.21	6.11	6.46	−0.35
$^3\text{P}(2s3p)$	5.59	6.84	7.29	−0.45
$^3\text{P}(2p^2)$?	?	7.40	?
$^3\text{D}(2s3d)$	5.68	7.27	7.69	−0.42
$^3\text{S}(2s4s)$	5.63	7.77	8.00	−0.23
$^3\text{P}(2s4p)$	5.68	8.07	8.18	−0.11
$^3\text{D}(2s4d)$?	8.18	8.42	−0.24
$^3\text{S}(2s5s)$?	8.31	8.56	−0.25
$^3\text{P}(2s5p)$?	8.50	8.63	−0.13
$^3\text{D}(2s5d)$?	8.54	8.75	−0.21

by -0.54 eV. This excitation energy is different to—and inferior to—the value of 2.50 eV determined using the delta SCF method, which just subtracted the energy of the two Kohn–Sham calculations. Again the 3D ($2p^2$) state is absent, although this time the error of the $2s3d$ state is not out of line, although this may be explained because the two states are close together by observation.

One way to calculate the energy of the $2p^2$ state is by considering it as a single excitation from the singly excited $2s2p$ excited state. In Table 3 we consider HCTH(AC) excitations ($I_\alpha = 0.2415$, $I_\beta = 4.5136 E_h$) from the 3P ($2s2p$) ($M_S = 1$) state. Only excitations to triplet states occur, and some of the degeneracy is lost. For example, if we treat the base state as $2s2p_x$, then excitations to $2s3p_x$, $2s3p_y$ have a slightly different energy to that for $2s3p_z$; in a similar vein there are predicted excitations to the $2s2p_x$ and $2s2p_y$ states, even though these should be degenerate with the base state. The values in Table 3 are therefore average values. The predicted excitation energies have a high accuracy, with the exception once again of the $2p^2$ state, which is in error by -0.60 eV. Because of the degeneracy breaking, and the poor $2p^2$ prediction, we do not favour using TDDFT for excitation predictions from such states.

Another interesting feature of these results is the lack of additivity in TDDFT excitation energies. The sum of the HCTH(AC) excitations from the 1S ground state to the 3P ($2s2p$) state (2.19 eV); and from this state to the 3S ($2s3s$) state (3.61 eV) is 5.8 eV. This is significantly different from the value of 6.11 eV for the direct excitation from the 1S ground state to the 3S state, in Table 2. Analogous results are obtained for HCTH, and so this is not a consequence of the use of an asymptotically corrected potential.

3.2 Discussion of results for methylene

We have performed calculations on the 3B_1 ($1a_1^22a_1^21b_2^23a_11b_1$) and 1A_1 ($1a_1^22a_1^21b_2^23a_1^2$) states at the specified geometry. This geometry is appropriate for the ground triplet state. Previous experimental and theoretical studies have taken account of the significant structural difference between the singlet and triplet states and so cannot be compared with this present study of vertical excitations. The HCTH energies were -39.15897 and $-39.11393 E_h$ respectively, giving $\Delta E = 1.23$ eV. Unlike in Be, this delta SCF value cannot be compared with the TDDFT excitation from 3B_1 due to the conservation of M_S . For the triplet state $I_\alpha = 0.3872$, $I_\beta = 0.5714 E_h$, and for the singlet state $I_\alpha = I_\beta = 0.3422 E_h$. Predictions for low-lying excited states arising from these two states are given in Tables 4 and 5. Excitations to equivalent states are labelled (i)–(v).

In Table 4, it is noted that no low-lying quintet states are predicted. The eigenvectors show that the two 3B_2 states were heavily mixed. The (3s) Rydberg state 3A_1 is the lowest calculated excited state, due to M_S preservation.

Table 3 Excitations (in eV) from $^3P(M_S = 1)(1s^22s2p)$ to triplet states of Be

State	HCTH(AC)	Expt	Error
3P ($2s2p$)	0.02	0.0	0.02
3S ($2s3s$)	3.61	3.73	-0.12
3P ($2p^2$)	4.08	4.68	-0.60
3P ($2s3p$)	4.48	4.56	-0.08
3D ($2s3d$)	4.80	4.97	-0.17
3S ($2s4s$)	5.19	5.27	-0.08
3P ($2s4p$)	5.56	5.45	0.11
3D ($2s4d$)	5.66	5.70	-0.04
3S ($2s5s$)	5.78	5.83	-0.05
3P ($2s5p$)	6.00	5.91	0.09
3D ($2s5d$)	6.03	6.03	0.00

Table 4 Excitations (in eV) from the 3B_1 ($M_S = 1$)($1a_1^22a_1^21b_2^23a_11b_1$) state of CH_2

State	Excitation	HCTH(AC)	
3A_1	$1b_1 \rightarrow 3s$	6.50	(i)
3A_2	$1b_2 \rightarrow 3a_1$	6.99	(ii)
3B_1	$3a_1 \rightarrow 3s$	7.36	
3B_2	$1b_2 \rightarrow 1b_1$	7.58	
3B_2	$1b_1 \rightarrow 3p$	7.80	(iii)
3A_1	$1b_1 \rightarrow 3p$	8.05	(iv)
3B_1	$1b_1 \rightarrow 3p$	8.18	(v)
3A_2	$3a_1 \rightarrow 3p$	8.60	

In Table 5, the first observation is that the 3B_1 state is correctly predicted to exist. Although this state lies below the reference state, we would still expect a positive ω^2 and thus a real excitation energy. Instead the excitation is predicted to be imaginary. The corresponding 1B_1 state is correctly predicted above the 1A_1 state, but only by 0.31 eV. The five common triplet states in Tables 4 and 5 differ in energy by 1.31 , 1.10 , 1.41 , 1.31 and 1.54 eV, reasonably close to the delta SCF value of 1.23 eV. Note that the 1A_1 ($1a_1^22a_1^21b_2^21b_1^2$) state is not predicted because it is again a double excitation. We have every reason, based on previous experience, to believe that the vertical excitation energies predicted in Tables 4 and 5 are correct to 0.2 – 0.3 eV, with the important exceptions of the 3B_1 and 1B_1 lowest states in Table 5.

4 Conclusions

In this paper we have drawn attention to some important features of TDDFT for the prediction of excitation energies, using the simple systems Be and CH_2 as examples. These are as follows.

(i) TDDFT calculations using GGA functionals are essentially worthless for Rydberg excitations unless the exchange–correlation potential is adjusted to take the integer discontinuity effect into account. This is consistent with previous studies.^{14,19}

(ii) Pure doubly excited states are not predicted, the simplest example being the 1D ($2p^2$) state of Be, not being predicted as an excitation from 1S . Indirect methods (*i.e.* excitations from other states) to obtain such states are also associated with difficulties.

(iii) Calculating the excitation energy as the difference between two separate KS calculations is not necessarily the same as a TDDFT excitation. The former is more reliable for Be, but such a delta SCF calculation is only possible for the lowest excitation (closed-shell singlet to high-spin triplet).

(iv) Excitation energies determined using two different reference states are not additive.

Table 5 Excitations (in eV) from the 1A_1 ($M_S = 0$)($1a_1^22a_1^21b_2^23a_1^2$) state of CH_2

State	Excitation	HCTH(AC)	
3B_1	$3a_1 \rightarrow 1b_1$	0.47i	
1B_1	$3a_1 \rightarrow 1b_1$	0.31	
3A_1	$3a_1 \rightarrow 3s$	5.19	(i)
1A_1	$3a_1 \rightarrow 3s$	5.42	
3A_2	$1b_2 \rightarrow 1b_1$	5.89	(ii)
3B_2	$3a_1 \rightarrow 3p$	6.39	(iii)
1B_2	$3a_1 \rightarrow 3p$	6.52	
3B_1	$3a_1 \rightarrow 3p$	6.64	(v)
3A_1	$3a_1 \rightarrow 3p$	6.74	(iv)
1B_1	$3a_1 \rightarrow 3p$	6.83	
1A_2	$1b_2 \rightarrow 1b_1$	6.97	

(v) 'Excitations' to states that are lower in energy do not appear to be well predicted. This may be coupled to the fact that such states are often close in energy, and our experience is that TDDFT often gives poor predictions in such cases.

(vi) Excitations from the closed shell ground state to excited triplet states may not be as reliable as those to excited singlet states.

However we must conclude that our experience with TDDFT is that it is a highly successful method for the determination of excitation energies, being inexpensive but accurate. One must simply remember when it is not successful, as highlighted here. There is one other case well-known to us, namely charge transfer states, which we have not examined, but which we view as a distinct problem.¹⁸

References

- 1 R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454.
- 2 R. Bauernschmitt, M. Haser, O. Treutler and R. Ahlrichs, *Chem. Phys. Lett.*, 1997, **264**, 573.
- 3 M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439.
- 4 C. Jamorski, M. E. Casida and D. R. Salahub, *J. Chem. Phys.*, 1996, **104**, 5134.
- 5 R. van Leeuwen and E. J. Baerends, *J. Chem. Phys.*, 1994, **105**, 3142.
- 6 S. J. A. van Gisbergen, F. Kootstra, P. R. T. Schipper, O. V. Gritsenko, J. G. Snijders and E. J. Baerends, *Phys. Rev. A*, 1998, **57**, 2556.
- 7 M. Petersilka and E. K. U. Gross, *Int. J. Quantum Chem. Symp.*, 1996, **30**, 181.
- 8 M. Petersilka, U. J. Gossmann and E. K. U. Gross, *Phys. Rev. Lett.*, 1996, **76**, 1212.
- 9 R. Ahlrichs, M. Bar, H. P. Baron, R. Bauernschmitt, S. Bocker, M. Ehrig, K. Eichkorn, S. Elliot, F. Haase, M. Haser, H. Horn, C. Huber, U. Huniar, M. Kattenek, C. Kolmel, M. Kollwitz, C. Ochsenfeld, H. Om, A. Schafer, U. Schneider, O. Treutler, M. von Armin, F. Weigend, P. Weis and H. Weiss, 1997, TURBOMOL Version 4, Institut Physikalische Chemie und Elektrochemie, Universitat Karlsruhe.
- 10 Amsterdam Density Functional (ADF), Theoretical Chemistry, Vrije Universiteit, De Boelaan 1083, 1081 HV Amsterdam, The Netherlands.
- 11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrewski, J. A. Montgomery, R. E. Stratmann, J. C. Durant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, R. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Radbuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. A. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challcombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN-98, Gaussian Inc., Pittsburgh, PA, 1998.
- 12 R. D. Amos, I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, G. J. Laming, A. M. Lee, P. E. Maslen, C. W. Murray, P. Palmieri, J. E. Rice, E. D. Simandiras, A. J. Stone, M.-D. Su and D. J. Tozer, CADPAC6.5, *The Cambridge Analytic Derivatives Package*, Cambridge, UK, 1998.
- 13 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, 864.
- 14 D. J. Tozer and N. C. Handy, *J. Chem. Phys.*, 1998, **109**, 10180.
- 15 J. P. Perdew, R. G. Parr, M. Levy and J. L. Balduz, *Phys. Rev. Lett.*, 1982, **49**, 1691.
- 16 D. J. Tozer and N. C. Handy, *J. Chem. Phys.*, 1998, **108**, 2545.
- 17 A. Spielfiedel and N. C. Handy, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2401.
- 18 D. J. Tozer, R. D. Amos, N. C. Handy, B. O. Roos and L. Serrano-Andres, *Mol. Phys.*, 1999, **97**, 859.
- 19 N. C. Handy and D. J. Tozer, *J. Comput. Chem.*, 1999, **20**, 106.
- 20 F. A. Hamprecht, A. J. Cohen, D. J. Tozer and N. C. Handy, *J. Chem. Phys.*, 1998, **109**, 6264.
- 21 S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **302**, 375.