

A dressed TDDFT treatment of the 2^1A_g states of butadiene and hexatriene

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Abstract

The nature and energetics of the low-lying singlet states of polyenes have presented significant challenges for electronic structure methods. This is particularly true for conventional implementations of time-dependent density functional theory (TDDFT), which, because of their use of the adiabatic approximation, have difficulty in describing states of ‘doubly-excited character’. We show that use of our recently developed ‘Dressed TDDFT’ approach provides a compact and accurate method for treating these doubly excited states, by use of a frequency-dependent exchange-correlation kernel. We present results for the vertical absorption energy for the 2^1A_g states of butadiene and hexatriene, and the vertical fluorescence and 0–0 transitions for the 2^1A_g state of butadiene.

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1. Introduction

The determination of the character and vertical excitation energy of the low-lying excited states of the short-chain polyenes has posed a considerable challenge to theorists and experimentalists [1–11]. Hudson and Kohler [5,6] showed that for α, ω -diphenyloctatetraene the lowest singlet excited state was not the HOMO \rightarrow LUMO transition, but was instead a state of the same symmetry as the ground state (1^1A_g). Configuration interaction (CI) or MCSCF descriptions [1,2] of this state show considerable contributions of doubly excited configurations, and indicate that it is purely valence-like.

For the shortest polyenes, butadiene (C_4H_6) and hexatriene (C_6H_8), the position of the 2^1A_g state has been difficult to determine experimentally, although for *cis*-hexatriene it is known to be the lowest excited singlet state, at least in an adiabatic transition from the ground state [11]. Theoretical estimates of the vertical excitation energy are myriad and varied, but for butadiene recent CI and QDVPT results [9] support the CASPT2 value [7]

of approximately 6.3 eV, slightly above the vertical excitation energy of the 1^1B_u (HOMO \rightarrow LUMO) transition (5.92 eV) [1].

Time-dependent density functional theory (TDDFT) [12–14] in linear response is an attractive method for the treatment of electronic excitations in molecular systems. However, the adiabatic approximation used in most quantum chemical calculations (ATDDFT) cannot treat states with significant contributions from doubly excited configurations [15], since the theory is developed in a linear-response formalism to lowest order. In a recent study we have shown that the contributions of higher excitations can be recovered in a linear response formalism if the adiabatic approximation to the exchange-correlation kernel f_{XC} is abandoned – i.e. if f_{XC} is allowed to be frequency/energy dependent [15]. Here we demonstrate that including the frequency-dependence derived in [15] in the exchange-correlation kernel yields dramatically improved excitation energies for molecular states possessing significant doubly excited character.

A recent study by Hsu et al. [10] applied ATDDFT to several all-*trans* polyenes (butadiene to decapentaene). They found reasonable agreement with experiment for the vertical excitation energy to the 2^1A_g state, but only in basis sets containing Rydberg functions, using

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non-hybrid functionals. The states were largely dominated by one single excitation, in contrast to previous theoretical predictions. Our results show that diffuse functions are not needed to obtain an improved description of the 2^1A_g state, that hybrid functionals can be used, and that the state obtained from our procedure is truly multiconfigurational. In addition, our results show that the theory outlined in [15] represents a practical means of quantitatively correcting ATDDFT, leading to an improved treatment of higher excitations. We illustrate this using a simple model, outlined below, for butadiene and hexatriene.

2. Methods

To construct the model we performed a series of ATDDFT calculations to extract energetic parameters and define a model space. Using the PBE0 [16] functional with the 6-311G(d,p) basis (calculations performed using G98 [17]) ATDDFT calculations were performed in the truncated space of only two single excitations ($1b_g \rightarrow 2b_g$ and $1a_u \rightarrow 2a_u$) yielding ATDDFT excitation energies to the 2^1A_g state within 0.06 eV of full ATDDFT calculations for either butadiene or hexatriene. These two excitations form the model space for our dressed treatment. The equilibrium geometries were taken from experiment [18] for butadiene, and from a B3LYP optimization in the 6-311G(d,p) basis for hexatriene.¹

The TDDFT A and B matrices within this two state model space were then augmented by the dressing proposed in [15], based on inclusion of the double excitation $1b_g^2 \rightarrow 2a_u^2$ (defined as D below), i.e. X_{dress} was defined as:

$$\begin{bmatrix} \frac{|\langle 1b_g, 2b_g | H | D \rangle|^2}{E - E_{\text{double}}} & \frac{\langle 1b_g, 2b_g | H | D \rangle \langle D | H | 1a_u, 2a_u \rangle}{E - E_{\text{double}}} \\ \frac{\langle 1a_u, 2a_u | H | D \rangle \langle D | H | 1b_g, 2b_g \rangle}{E - E_{\text{double}}} & \frac{|\langle 1a_u, 2a_u | H | D \rangle|^2}{E - E_{\text{double}}} \end{bmatrix}, \quad (1)$$

¹ Since individual TDDFT matrix elements are not directly computed or available in G98, we used a simple method to construct them based on a series of small calculations. The diagonal and off-diagonal TDDFT matrix elements for the $1a_u \rightarrow 2a_u$ excitation can be obtained by calculating the TDDFT correction to the bare KS orbital energy difference in an orbital space allowing only this excitation. A similar procedure can be used for the $1b_g \rightarrow 2b_g$ excitation. Finally, the off-diagonal matrix elements connecting these two excitations can be obtained using the above results and the TDDFT excitation energy in the space of these two excitations. The model (based on the matrix elements obtained in this procedure) reproduced the actual two-configuration ATDDFT results for the lowest excited 1A_g symmetry, and was within 0.1 eV for the second state (since we ignored the modest differences between A and B matrix elements that result from use of a hybrid functional).

yielding a ‘Dressed’ TDDFT response matrix of the form:

$$\begin{pmatrix} A + X_{\text{dress}} & B + X_{\text{dress}} \\ B + X_{\text{dress}} & A + X_{\text{dress}} \end{pmatrix}. \quad (2)$$

The Hamiltonian matrix elements of the three relevant configurations (two single excitations and one double excitation) were calculated using RHF occupied and virtual orbitals (no significant difference is expected between the RHF and KS matrix elements in this basis for these systems) and the MELDF program [19]. The double excitation energy in the denominator was estimated as the difference of energy expectation values for the doubly excited determinant and the ground state determinant, as suggested in [15], using the RHF orbitals. We take the lowest positive eigenvalue of the dressed TDDFT equations (D-TDDFT) as the energy of the 2^1A_g state. We also dressed the Tamm-Dancoff-TDDFT method (TD-TDDFT was introduced by Hirata and Head-Gordon [20]), where only the dressed TDDFT A matrix is considered (D-TD-TDDFT).

3. Results

Results for the ground state equilibrium geometries for butadiene and hexatriene are given in Table 1. For butadiene other methods yield similar results (CASSCF: 6.63 eV [9], MRSDCI: 6.40 eV [9]) and for hexatriene the experimental vertical excitation energy is 5.21 eV [21]. The ATDDFT (PBE0) excitation energies are similar to the ATDDFT (B3LYP) results (7.22 and 6.03 eV for butadiene and hexatriene respectively).

The agreement of our D-TDDFT results with previous ab initio results is quite encouraging. Our description yields a state that is a mixture of both single and double excitations, is not dependent upon use of Rydberg basis functions to describe the 2^1A_g state, and is based on PBE0/TDDFT results.

It is known that the 2^1A_g state of butadiene is particularly sensitive to geometry variations [9]. In order to test the ability of D-TDDFT and D-TD-TDDFT to reproduce this geometry dependence, we performed calculations on butadiene analogous to those of Table 1, based on an estimate of the planar stationary point for the 2^1A_g state (central C–C bond length = 1.418 Å, end C–C bond lengths = 1.499 Å, all other lengths and angles those of the ground state) [9]. Results for the vertical excitation energy at this geometry and the 0–0 transition energy are shown in Table 2. (The CASPT2 results are based on a slightly different excited state geometry [9].)

The MRSDCI estimates (eV) (based on a slightly different excited state geometry) [9] are: Vertical: 4.41 eV, 0–0: 5.21 eV. Clearly the dressed TDDFT model captures the significant change in 2^1A_g state energy as a

Table 1
 2^1A_g state vertical excitation energies (eV) for butadiene and hexatriene

System	CASPT2	ATDDFT (B3LYP)	D-TDDFT	D-TD-TDDFT
C ₄ H ₆	6.27 [7]	7.02	5.93	6.28
C ₆ H ₈	5.20 [7]	5.83	4.85	5.16

For all but the CASPT2 results the experimental geometry was used for butadiene (central C–C bond length = 1.343 Å, end C–C bond lengths = 1.467 Å [18]) and a B3LYP/6-311G(d,p) optimized geometry was used for hexatriene.

Table 2
 2^1A_g state vertical and 0–0 excitation energies (eV) for butadiene at the estimated planar stationary point for the 2^1A_g state

ΔE	CASPT2	ATDDFT (B3LYP)	D-TDDFT	D-TD-TDDFT
Vertical	4.3 [9]	5.8	3.42	4.16
0–0	5.2 [9]	6.8	4.54	5.28

function of geometry significantly better than conventional ATDDFT, with the D-TD-TDDFT version giving somewhat better accuracy in this case. The D-TDDFT approach in fact overestimates the geometry sensitivity, compared to that obtained with other methods. It is not yet known whether the higher accuracy of the D-TD-TDDFT method is a general result or a function of this particular truncated model, and the answer likely awaits a complete implementation of the methods. However, both approaches show promise for improved qualitative and quantitative descriptions of such states, and we intend to explore them in future work.

The other possible double excitation of A_g symmetry in this space, namely the $1a_u^2 \rightarrow 2b_g^2$ double excitation, has a much higher energy than the $1b_g^2 \rightarrow 2a_u^2$ double excitation included above (nearly twice as large). We therefore expect that it will couple only weakly, and that including it in the dressing will hardly alter the ATDDFT result. To check this, we repeated the calculation reported above for butadiene at its equilibrium geometry using this double excitation, rather than the $1b_g^2 \rightarrow 2a_u^2$ double excitation to define the dressing X . In this case the results were D-TDDFT = 7.26 eV, D-TD-TDDFT = 7.37 eV. The results are extremely close to the ATDDFT result and support the neglect of this excitation in the other calculations reported here.

4. Discussion and conclusions

The above results are quite encouraging with respect to treatment of states with significant doubly excited character, but are based on a model calculation, and work is required to implement such a procedure in the context of conventional TDDFT. We next describe the path to be taken in implementing such an approach.

First, we are not advocating inclusion of all doubly excited configurations. Inclusion of the entire manifold of double excitations would lead to size-consistency problems similar to those obtained in CISD. Inclusion

of only a few important double excitations, those whose transition frequencies lie close to allowed single excitations, while not formally size-consistent, should not cause significant errors since the bulk of the correlation is treated via the XC functional. In the case where more than one double excitation is included, however, the dressing would be constructed by including a dressing term (X_{dress} , above) for each double excitation. Second, a complete implementation of such a procedure will utilize matrix elements of KS orbitals for X_{dress} , rather than the RHF orbitals used here for simplicity. Third, we expect that only a few such double excitations will be important in the description of the low-lying states of conjugated systems. As illustrated above for the second double excitation in our model space, double excitations that are far from the state of interest energetically will not contribute to the energy lowering to any significant extent. We also examined this question for the treatment of the 1^1B_u state of butadiene (HOMO \rightarrow LUMO) using the dressed TDDFT model: either of a pair of π double excitations of B_u symmetry lowers the 1^1B_u state energy by from 0.1 to 0.3 eV. The ATDDFT (PBE0) 1^1B_u excitation energy in the 6-311G(d,p) basis is 5.98 eV, thus in this case application of the correction would lead to decreased accuracy. However, these double excitations are about 9 eV higher than 1^1B_u state, and further tests of the method may suggest this is outside the range of double excitations that should be included. Furthermore, for Rydberg states the dressing numerators are expected to be small due to the diffuse character of the Rydberg orbitals, and we expect dressed TDDFT results should reduce to the TDDFT results. Overall we believe that the impact of these terms will be modest except for states of true double excitation character. Nevertheless, for true double excitations we expect that neglect of such terms will lead to states either too high in energy or seriously biased towards Rydberg character. Finally, we have used symmetry to simplify the model calculations here, but in a symmetry-broken case

we would expect similar results. One would need to scan the possible double excitations for those near in energy to the state of interest, and then compute H matrix elements between the double excitation(s) and the single excitations that were included in the TDDFT treatment. Since most off-diagonal matrix elements between a given double and the singles will be zero (i.e. in general they will be more than a double excitation apart) we expect results quite similar to those obtained here.

Note that the method proposed bears some similarity to the DFT/MRCI approach developed by Grimme and coworkers [22]. In the DFT/MRCI approach they use small CI expansions with effective Hamiltonian matrix elements based on DFT KS orbital energies and empirically fit expressions for the two-electron integral contributions. Their off-diagonal elements are exponentially scaled CI-like matrix elements based on KS orbitals. In the dressed-TDDFT approach proposed here, our diagonal elements come directly from the conventional TDDFT expressions augmented by X_{dress} , and the form of the off-diagonal matrix elements is suggested by partitioning arguments [23].

Thus multiple excitations are included in TDDFT linear response, but only by including frequency-dependent (non-adiabatic) corrections [14]. This correction is derived from first-order Görling–Levy perturbation theory [15,24], using Kohn–Sham orbitals and energies. Dressing the TDDFT response equations with contributions from low-lying double excitations leads to significant improvement in excitation energies and state characters compared to conventional TDDFT results for the 2^1A_g state of butadiene and hexatriene. Our results suggest that a simple non-empirical correction to linear-response TDDFT allows accurate treatment of doubly excited states.

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