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Calculation of excitation energies of open-shell molecules with spatially degenerate ground states. I. Transformed reference via an intermediate configuration Kohn-Sham density-functional theory and applications to d^1 and d^2 systems with octahedral and tetrahedral symmetries

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A method for calculating the UV-vis spectra of molecules with spatially degenerate ground states using time-dependent density-functional theory (TDDFT) is proposed. The new transformed reference via an intermediate configuration Kohn-Sham TDDFT (TRICKS-TDDFT) method avoids the difficulties caused by the multireference nature of spatially degenerate states by rather than utilizing the ground state instead taking a nondegenerate excited state with desirable properties as the reference for the TDDFT calculation. The scope and practical application of the method are discussed. Like all open-shell TDDFT calculations this method at times suffers from the inability to produce transitions to states that are eigenfunctions of the total spin operator. A technique for alleviating this difficulty to some extent is proposed. The applicability and accuracy of the TRICKS-TDDFT method is demonstrated through example calculations of several d^1 and d^2 transition metal complexes with tetrahedral and octahedral symmetries. For the most part, the results of these calculations are similar in quality to those obtained from standard TDDFT calculations. © 2005 American Institute of Physics. [DOI: 10.1063/1.2047553]

I. INTRODUCTION

Over the course of the last decade or so, time-dependent density-functional theory (TDDFT) has become a popular technique for the calculation of electronic excitations and frequency-dependent properties of molecules.^{1,2} While not as accurate as some alternative approaches such as multireference configuration interaction³ or equations of motion coupled cluster,⁴ it is much less computationally demanding than these high accuracy methods and is generally accurate enough (errors <0.3 eV for well behaved systems and <0.8 eV for more difficult systems) to be useful in the interpretation and prediction of experimental results. As such, it is typically the method of choice for molecules containing 10–200 atoms. In its most commonly applied form, (the adiabatic approximation to TDDFT where memory effects of the electronic density are neglected¹) TDDFT is essentially the DFT analog of the time-dependent Hartree-Fock approach and is related to a number of computational methods based on response theory such as the polarization propagator and Green's function techniques.^{5–8} TDDFT was theoretically justified for the most part by Runge and Gross.^{9–12} The form of TDDFT most commonly applied in chemical applications is the matrix formulation given by Casida¹ which is itself the DFT analog of the simplest approximation to the polarization propagator commonly known as the random phase approximation (RPA).⁷ Each of these approaches relies on evaluating the response of the reference state to a time-dependent

perturbation in order to obtain information about other states rather than calculating the wave function or electron density of the other states directly. This feature is particularly advantageous for TDDFT because the densities of only a very limited number of states can be obtained in a direct DFT calculation.

Early formulations of TDDFT considered only closed-shell molecules and were found to be capable of describing both singlet-singlet and singlet-triplet excitations dominated by single-electron excitations. The theory has been less successful in describing the transitions that are predominantly made up of two-electron excitations. This difficulty arises because of the adiabatic approximation.

More recently, TDDFT has been extended to enable the calculation of excitation energies of molecules whose ground states have unpaired electrons.^{13–15} The quality of the results obtained over a limited range of applications thus far appear to be similar to those of the closed-shell TDDFT calculations. The difficulty with transitions dominated by double excitations remains but a further problem has arisen since the limitation to single excitations often means that too few determinants can be obtained to enable all the required eigenfunctions of S^2 to be constructed (see Ref. 16 for a more detailed discussion). This problem can be alleviated somewhat through the inclusion of spin-flip transitions^{17–19} but it cannot always be eliminated completely.

Significant progress has thus been made in the application of TDDFT to molecules with nondegenerate ground states and with spin degenerate ground states but little work has been put into the third possible situation: spatially degen-

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erate ground states. Spatial degeneracy is particularly difficult to deal with within DFT because it is essentially a multiconfigurational problem while Kohn-Sham DFT is, by definition, a single determinant method. Even treating the static properties of a molecule with a degenerate ground state, e.g., a molecule with T_d symmetry and a single unpaired electron in an e orbital, is somewhat problematic. The density of such a molecule is usually generated by distributing the unpaired electron(s) evenly across the partially occupied degenerate orbital(s) ($\frac{1}{2}$ of an electron in each e component in the example given here). Such a model does not, in fact, describe a state of pure symmetry and its physical meaning is not clear. Some effort has been put into developing multireference DFT (Refs. 20 and 21) but it is not certain that these approaches can be applied to spatially degenerate systems. Indeed, in Ref. 21 the discussion was explicitly limited to spatially nondegenerate molecules though the exclusion of non-Abelian point groups. In the context of HF-based polarization propagators there has been some discussion of methods for treating spatially degenerate ground states⁶ but these approaches require either a multireference treatment or inclusion of excitations beyond singles. Casida has described some progress in including some double excitations in adiabatic TDDFT (Ref. 16) in the context of improving the treatment of spin degenerate systems. This approach could prove useful in dealing with spatially degenerate molecules but it does not yet appear that it can be applied to practical applications.

Present techniques for calculating the excitation energies of molecules with spatially degenerate ground state generally fall into two classes. The first class has been mentioned already and consists of methods based on a multiconfiguration treatment that can treat all degenerate components of the ground state on an equal footing and which often include further treatment of dynamical electron correlation. Again, as has been noted, this type of approach potentially can be very accurate but is extremely computationally demanding. The second approach is the sum method developed by Ziegler *et al.* a while ago²² and further extended and applied by Daul.²³ This method has the same computational cost as a standard DFT calculation and as a result has been applied to a wide variety of molecules. However, it suffers from the drawbacks that it is not always internally consistent and that it assumes that any given state is well described by a single symmetry determined linear combination of Slater determinants or configuration state function (CSF) which may not always be the case.

In this paper we consider first an approach for calculating excitation energies of molecules with a spatially degenerate ground state. We have avoided methods that are multireference in nature or which require excitations beyond singles as we would like to see how well we can do without recourse to the necessary increase in theoretical and computational complexities that such methods would likely entail. Rather, we would prefer a method that can be implemented within existing closed- and open-shell TDDFT codes in a straightforward manner. The method discussed in the present work, which we denote transformed reference via an intermediate configuration Kohn-Sham DFT (TRICKS-TDDFT)

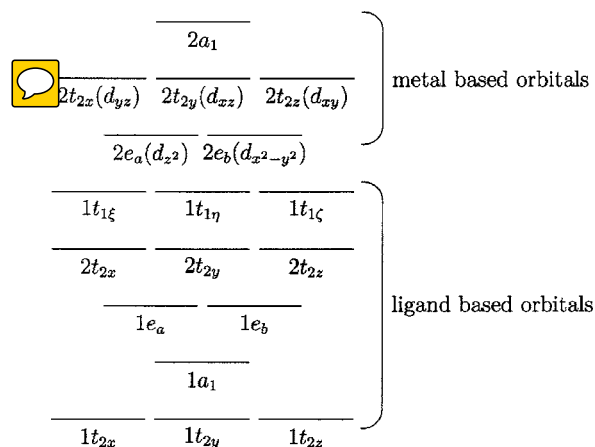
has all of the desirable features noted. The usefulness and range of applicability of this method are demonstrated through the calculation of several transition energies of a number of d^1 and d^2 systems with T_d and O_h symmetries. The emphasis in Sec. V is on demonstrating the scope of the method rather than attempting to reproduce experimental results to high accuracy. As such, the calculations presented will be relatively simple in nature and certainly could be improved upon, e.g., by exploring different choice of functional or attempting to improve the description of the molecular environment.

Before proceeding with the description of the TRICKS-TDDFT method, a few points should be clarified. In a TDDFT calculation, one starts with a reference state, necessarily described by a single Slater determinant. From the TDDFT calculation transition densities between the reference state and a number of other states are obtained. These transition densities are composed of one-electron excitations, i.e., the removal of one electron from an occupied orbital and the addition of one electron to a virtual or partially occupied orbital (these one-electron replacements will be called “excitations” as distinct from a system going from one state to another which we will call a “transition”). No state other than the reference state is explicitly constructed. However, computational chemists are usually more familiar with the description of any given state by a single Slater determinant or CSF or a linear combination of Slater determinants or CSFs. In order to make use of this familiarity we will sometimes describe a nonreference state in terms of a single configuration and the appropriate corresponding Slater determinant(s) and/or CSF. Since these functions are never actually calculated they will be referred to as auxiliary determinants and CSFs (ACSFs).

II. TRICKS-TDDFT

In an attempt to develop a simple method that is able to calculate the excitation energies of a molecule with a spatially degenerate ground state a few different approaches utilizing TDDFT were considered. Most of these methods suffered from serious drawbacks such as being unable to reproduce all of the necessary degeneracies or requiring that a lower symmetry point group be used.

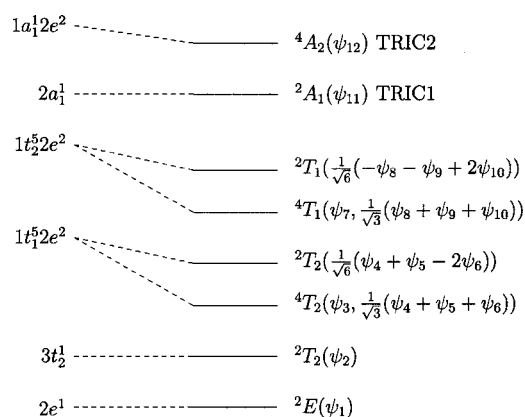
The difficulties just described arise because the reference in the TDDFT calculation is a spatially degenerate state. As was noted in the Introduction, DFT is a single determinant theory and a reasonable description of a spatially degenerate state requires multiple determinants. A solution to this problem is not to take the ground state as the reference at all but rather to use a low-lying nondegenerate excited state as the reference. This choice is allowed since propagator/RPA-type methods calculate the response of any reference state to an applied perturbation without any restriction on the nature of such a state.⁶ It is also compatible with DFT because Kohn-Sham DFT can be applied to the lowest state of each symmetry as well as the ground state.²⁴ The idea of using an excited state as reference has previously been used by us when performing spin degenerate TDDFT (Ref. 19) and even earlier by Krylov in the context of coupled cluster and single



SCHEME 1. Orbital diagram for tetrahedral transition metal complexes. The d^1 and d^2 complexes in their ground state have one and two electrons in the $2e$ levels, respectively. All ligand-based levels are fully occupied in the ground state.

reference configuration-interaction calculations^{25–27} where similar difficulties to those encountered here can arise.

The usefulness of the new procedure outlined above is perhaps best illustrated through an example. Consider a molecule of T_d symmetry with an 2E ground state corresponding to the $[\text{core}]e^1$ electron configuration where “core” represents all other orbitals that are fully occupied, see Schemes 1 and 2. This configuration would commonly occur in tetrahedral d^1 transition metal complexes. We might choose as the reference an 2A_1 state corresponding to a $[\text{core}]a_1^1$ configuration. The a_1 orbital that is now partially occupied is the lowest-energy orbital of this symmetry that was completely unoccupied in the $[\text{core}]e^1$ configuration. This new 2A_1 state could be described in a static DFT calculation through a straightforward choice of orbital occupations and a subsequent TDDFT treatment would be equally straightforward. A TDDFT calculation starting from the 2A_1 state would provide the difference in energy between this state and the ground state. To see why this is so it should be recalled that the $^2A_1 \rightarrow ^2E$ transition of interest is likely to be well described by the $a_1 \rightarrow e$ single orbital excitation, see Scheme 2. This



SCHEME 2. Low-lying electron configurations and states of a $d^1 T_d$ transition metal complex. Only the most important states arising from a given configuration are shown. Following the state label, one or two useful ACSFs corresponding to a particular electron configuration and state are given. The ψ_i are defined in Table I.

excitation is obviously included in any TDDFT treatment with our $^2A_1([\text{core}]a_1^1)$ state as reference. The calculation could also indirectly give the excitation energies from the ground state to a number of other states. An important example of this is the $^2A_1 \rightarrow ^2T_2$ transition dominated by the $a_1 \rightarrow t_2$ orbital excitation. Once the $^2A_1 \rightarrow ^2T_2$ and $^2A_1 \rightarrow ^2E$ transition energies have been calculated through a TDDFT calculation with the $^2A_1([\text{core}]a_1^1)$ state as reference, the difference of the two energies gives the rather more interesting $^2E \rightarrow ^2T_2$ crystal-field transition of d^1 tetrahedral complexes. We have thus managed to calculate a transition energy of a molecule with a degenerate ground state without breaking symmetry or being required to include any orbital excitations beyond singles.

The choice of reference just described should allow transitions to any state well described by the electron configuration $[\text{core}]x^1$ where x is any orbital that is unoccupied in the ground state to be calculated. Important transitions of this type include the $d-d$ transition already described as well as possibly metal to ligand charge-transfer (MLCT) transitions when x is a ligand orbital. A further important type of transition often observed in the spectra of $T_d d^1$ transition metal complexes is ligand to metal charge-transfer (LMCT) transitions. This type of CT transition leads to excited states assigned to an electron configuration with the general form $[\text{core}]l^{n-1}e^2$ where l is a ligand orbital that is n /two-fold degenerate, see Scheme 1 for some examples of high-lying occupied ligand orbitals. This electron configuration is doubly excited with respect to the $^2A_1([\text{core}]a_1^1)$ reference already introduced and it therefore would be expected that any TDDFT calculation starting from this reference would not include transitions to the LMCT states.

In order to treat the LMCT transitions of a $T_d d^1$ complex a second alternative reference state must be introduced. In this second reference, rather than exciting the single electron in the partially filled e orbital, an electron is excited from an occupied a_1 orbital into the valence e orbital to give a $[\text{core}]a_1^1 e^2$ configuration. The unpaired electrons in this configuration are all chosen to be spin up giving a $^4A_2(a_1^+ e_a^+ e_b^+)$ state, where “+” indicates a spin-up electron and “−” will similarly indicate a spin-down electron. The Slater determinant corresponding to this configuration will be denoted $^{++ +} |a_1 e_a e_b|$, see Table I.

A TDDFT calculation with this state as the reference will now readily give the energy difference between the 4A_2 state and any quartet LMCT states that are well described by the electron configuration $[\text{core}]a_1^2 l^{n-1}e^2$ or auxiliary determinant $^{+++} |l e_a e_b|$ through the single excitation $\bar{l} \rightarrow \bar{a}_1$. Note that for the sake of brevity, all core orbitals that are fully occupied are not included in the description of any determinants and will be neglected from electron configurations from now on.

On the other hand, spin-flip TDDFT affords the difference in energy between the 4A_2 reference and the ground state through the transition dominated by the $\bar{e} \rightarrow \bar{a}_1$ one-electron excitation. The transitions with major contributions from the $\bar{l} \rightarrow \bar{a}_1$ one-electron excitations give transition ener-

TABLE I. Auxiliary determinants corresponding to electron configurations arising from $T_d d^1$ complexes.

Config.	Auxiliary determinants ^{a,b}			
$2e^1$	$\psi_1 = e_b^+ $			
$3t_2^1$	$\psi_2 = t_{2z}^+ $			
$2t_1^5 2e^2$	$\psi_3 = t_{1\zeta}^+ e_a^+ e_b^+ $	$\psi_4 = t_{1\zeta}^+ e_a^+ e_b^- $	$\psi_5 = t_{1\zeta}^+ e_a^- e_b^+ $	$\psi_6 = t_{1\zeta}^+ e_a^- e_b^- $
$2t_2^5 2e^2$	$\psi_7 = t_{2z}^+ e_a^+ e_b^+ $	$\psi_8 = t_{2z}^+ e_a^+ e_b^- $	$\psi_9 = t_{2z}^+ e_a^- e_b^+ $	$\psi_{10} = t_{2z}^+ e_a^- e_b^- $
$2a_1^1$	$\psi_{11} = a_1^+ $			
$1a_1^1 2e^2$	$\psi_{12} = a_1^+ e_a^+ e_b^+ $			

^aFor auxiliary determinants corresponding to a given configuration that include orbitals that are fully occupied, these orbitals are omitted.

^bFor auxiliary determinants corresponding to a given configuration that include partially occupied degenerate ligand orbitals, only the appropriate half-filled component of the degenerate orbital is shown.

gies from the 4A_2 state to the state well described by the auxiliary determinant $|\bar{l}e_a^+ e_b^+|$. This determinant is not an eigenfunction of the total spin operator and the calculated transition is thus from the 4A_2 state to a state with mixed doublet and quartet spins. A procedure for dealing with this situation will be described in Sec. III.

We call the new reference introduced the “transformed reference via an intermediate configuration” or TRIC. The overall computational method we term “transformed reference via an intermediate configuration Kohn-Sham TDDFT” or “TRICKS-TDDFT” for short.

How widely applicable is TRICKS-TDDFT? For the most part, the calculations required vary from case to case depending on the ground- and excited-state electron configurations. The d^1 and d^2 examples in Sec. V will serve as an illustration. A few general statements can be made, however.

The essential requirement is to find an intermediate configuration (TRIC) that differs by a single orbital excitation from the required configuration(s). The required configurations would be those that are necessary to obtain a correct zeroth-order description of the state(s) of interest. A large number of states could therefore be examined through the TRICKS-TDDFT method. If we consider our initial example with the $^2A_1([core]a_1^1)$ TRIC again, all electron configurations of the type $[core]_x^1$ where x is any orbital that is unoccupied in the ground state can be reached from this TRIC by a single excitation.

Electron configurations that cannot be reached are limited to a set of configurations with particular occupations of several degenerate orbitals. Examples are some (but not all) cases where the electron configuration has two or more partially occupied orbitals of t symmetry or three or more partially occupied orbitals of t or e symmetry.

Molecules with lower than O_h or T_d symmetry can have only singly or doubly degenerate orbitals and therefore any possible situation can be treated except the rather unlikely case of an electron configuration with three or more partially occupied e symmetry orbitals. Octahedral and tetrahedral molecules would therefore be expected to be the more diffi-

cult subjects for the TRICKS-TDDFT approach. At the same time, molecules of O_h or T_d symmetry are more likely to have a degenerate ground state.

Another issue is that, just as was observed in normal spin degenerate TDDFT, not all possible excited states will be accessible since we are limited to single excitations. A requirement of the method is that the reference state can be well described by a single determinant. This implies that all unpaired electrons be spin up (or spin down) in the reference calculation which often can lead to high values of S and m_s . States with significantly lower values of S will be difficult to access since we are limited to $\Delta m_s = 0, \pm 1$ with respect to our chosen reference state.

Although there are a few transitions that cannot be treated, the majority of those that are of interest can be dealt with as we shall see when some example calculations are considered in the next few sections.

III. THE TD-DFT SUM METHOD

In the LMCT example described in Sec. II, a problem arises because one of the solutions obtained, that dominated by the $\bar{l} \rightarrow \bar{a}_1$ one-electron excitation corresponding to the auxiliary determinant $|\bar{l}e_a^+ e_b^+|$, does not represent a spin eigenstate. If we consider a definite example and suppose that l is an orbital with t_1 symmetry then the one-electron excitation $\bar{t}_{1\zeta} \rightarrow \bar{a}_1$ corresponds to the auxiliary determinant $|\bar{t}_{1\zeta}^+ e_a^+ e_b^+|$ which has $^4T_{2z}(m_s=3/2)$ symmetry. A calculated transition density dominated by this excitation can be reasonably associated with a transition to a $^4T_{2z}$ state. Note that we chose to always consider the z (or ζ as appropriate) component of a degenerate state. The $\bar{t}_{1\zeta}^+ \rightarrow \bar{a}_1$ excitation (corresponding to the $|\bar{t}_{1\zeta}^+ e_a^+ e_b^+|$ auxiliary determinant) leads to a state with $T_{2z}(m_s=1/2)$ symmetry but no definite total spin angular momentum.

The following discussion relies on knowledge of the form of ACSFs corresponding to a given electron configuration. In this work we will generally have the situation where an orbital with t or e symmetry corresponding to a metal d orbital is partially occupied and between zero and two other orbitals are partially occupied with either a single electron or a single hole. To construct ACSFs from these types of electron configuration we first couple the strongly interacting electrons in the d orbital. In the case of the example under consideration this gives 3A_2 symmetry with $e_a^+ e_b^+$ corresponding to $^3A_2(m_s=1)$ and $1/\sqrt{2}(e_a^+ e_b^- + e_a^- e_b^+)$ corresponding to $^3A_2(m_s=0)$. The other partially occupied orbitals are then coupled to the intermediate configuration to give the final state. For the present example the extra partially occupied orbital is a t_1 with a single hole giving the following CSFs:

$$\begin{aligned}
 & \frac{1}{\sqrt{3}}(\sqrt{2}|^3A_2(m_s=0)t_{1\zeta}^+| + |^3A_2(m_s=1)t_{1\zeta}^-|) \\
 &= \frac{1}{\sqrt{3}}(\psi_4 + \psi_5 + \psi_6)(^4T_{2z}m_s=1/2),
 \end{aligned} \tag{1}$$

$$\frac{1}{\sqrt{6}}(\sqrt{2}|^3A_2(m_s=0)t_{1\bar{z}}^+|-2|^3A_2(m_s=1)t_{1\bar{z}}^-|) \\ = \frac{1}{\sqrt{6}}(\psi_4 + \psi_5 - 2\psi_6)(^2T_{2z}m_s=1/2), \quad (2)$$

where the ψ_i represent the auxiliary determinants and are defined in Table I. The two determinants with one spin-up and one spin-down electron in the e orbital (ψ_4 and ψ_5) correspond to double excitations (the $t_{1\bar{z}}^- \rightarrow \bar{a}_1$ excitation plus the flipping of the spin of one of the electrons of the e orbital) with respect to the 4A_2 reference and as such do not appear in any TDDFT calculation starting from this reference.

To extract as much information as possible from the information available we will make use of the symmetry properties of the derived ACSFs. This procedure has several aspects in common with the sum-rule method used to derive multiplet energies from a series of DFT calculations^{22,23} and we therefore call it the TDDFT sum-rule method.

In order to obtain the transition energy to the two T_2 states with $m_s=1/2$ that we are interested in from a TDDFT calculation we would like to calculate the eigenvalues of the \mathbf{A} matrix (for the details of the TDDFT procedure, see Ref. 1)

$$\mathbf{A} = \begin{pmatrix} a_{44} & a_{45} & a_{46} \\ a_{45} & a_{55} & a_{56} \\ a_{46} & a_{56} & a_{66} \end{pmatrix}, \quad (3)$$

where we utilize the the Tamm-Dancoff approximation (TDA) and set the \mathbf{B} part of the TDDFT equations to zero. The a_{ij} are elements of the \mathbf{A} matrix corresponding to the interaction between excitations leading to auxiliary determinants i and j . In constructing the \mathbf{A} matrix we have only included the double excitations corresponding to auxiliary determinants ψ_4 and ψ_5 and the single excitation corresponding to auxiliary determinant ψ_6 . In an actual calculation the first two excitations are not available so we cannot directly calculate most of the elements but we do have access to the matrix element a_{66} . We know two of the eigenvectors of \mathbf{A} from Eq. (1) and (2). The third eigenvector can be immediately constructed through orthogonality requirements and corresponds to a 2T_2 ACSF where the two electrons in the partially occupied e orbital are coupled to give 1E rather than 3A_2 symmetry. As is usually assumed in standard sum-rule calculations²⁸ this ACSF is considered to have negligible interaction with the other 2T_2 ACSF. The matrix form of the eigenvectors is

$$\mathbf{P} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{2}{\sqrt{6}} & 0 \end{pmatrix}. \quad (4)$$

If we write the three eigenvalues of \mathbf{A} as ω_i ($i=1, 2, 3$) corresponding to the 4T_2 and 2T_2 states of interest and the

extra 2T_2 ACSF, respectively, \mathbf{A} can be rewritten as its spectral decomposition

$$\mathbf{A} = \mathbf{P} \begin{pmatrix} \omega_1 & 0 & 0 \\ 0 & \omega_2 & 0 \\ 0 & 0 & \omega_3 \end{pmatrix} \mathbf{P}^\dagger, \quad (5)$$

$$= \begin{pmatrix} \frac{2\omega_1 + \omega_2 + 3\omega_3}{6} & \frac{2\omega_1 + \omega_2 - 3\omega_3}{6} & \frac{\omega_1 - \omega_2}{3} \\ \frac{2\omega_1 + \omega_2 - 3\omega_3}{6} & \frac{2\omega_1 + \omega_2 + 3\omega_3}{6} & \frac{\omega_1 - \omega_2}{3} \\ \frac{\omega_1 - \omega_2}{3} & \frac{\omega_1 - \omega_2}{3} & \frac{\omega_1 + 2\omega_2}{3} \end{pmatrix}. \quad (6)$$

The first eigenvalue ω_1 corresponding to the transition energy to the 4T_2 state can be obtained independently through a standard TDDFT calculation as described in Sec. II. With the two pieces of information available (ω_1 and the element of \mathbf{A} ($a_{66} = \omega_1 + 2\omega_2/3$)) ω_2 can be calculated as

$$\omega_2 = \frac{3}{2} \left(a_{66} - \frac{\omega_1}{3} \right). \quad (7)$$

The relationship with the standard sum-rule method is apparent from Eq. (7). In a sum-rule calculation one might obtain the energy of the first 2T_2 state by directly calculating ψ_3 (Table I) and ψ_6 and employing

$$E(^2T_2) = \frac{3}{2} \left(E(\psi_6) - \frac{E(^4T_2(\psi_3))}{3} \right). \quad (8)$$

The similarity between the TDDFT sum-rule method and the conventional sum-rule method is a consequence of the closely related symmetry properties of the \mathbf{A} matrix and the Hamiltonian. Much like the TRICKS-TDDFT approach and the standard sum-rule procedure, the exact application of the TDDFT sum-rule method will depend on the example at hand.

In a real TDDFT calculation the \mathbf{A} matrix is far larger than that given here and the known eigenvectors only apply to a subspace corresponding to a particular set of ACSFs. We believe, however, that equations like Eq. (7) can still be used to approximate the transition energy to a pure spin state as long as a transition density is obtained that is dominated by the appropriate one-electron excitation. In the example under consideration, if a transition density dominated (coefficient >0.8 say) by the $t_{1\bar{z}}^+ \rightarrow \bar{a}_1$ excitation (auxiliary determinant ψ_6) is obtained then the eigenvalue corresponding to this transition density should be a reasonable substitute for a_{66} in Eq. (7).

IV. COMPUTATIONAL DETAILS

All calculations were performed with a modified version of the ADF (Refs. 29–35) code that is capable of performing open-shell TDDFT calculations where m_s is conserved (standard TDDFT) or where any excited electron also undergoes a spin flip.^{18,19,36} A valence triple- ζ basis set with two added polarization (TZ2P) function basis sets was applied in all

cases. The density functional chosen was the simple local-density approximation (LDA) with the parametrization of the electron gas given by Vosko *et al.*³⁷ Default frozen cores were taken for all atoms. When the subject of interest included a $4d$ or $5d$ transition metal, scalar relativistic effects on the ground and reference state densities were included through the use of the zeroth-order regularized approximation (ZORA).^{38–40} The geometry of a given molecule was taken from experimental data if available. Otherwise, an optimized geometry was obtained from the DFT calculations under the restrictions of T_d or O_h symmetry as appropriate. For the purposes of these geometry optimizations, the degenerate ground state was approximated through equal fractional occupation numbers of the degenerate orbital. The static DFT calculations that were performed as starting points for the TDDFT calculations had the orbital occupations constrained to give the desired nondegenerate reference state. The time-dependent portion of the calculations utilized the functional given by the adiabatic linear density approximation (ALDA). The overall accuracy parameter for any numerical integration was chosen to be 5.

In some cases, more than one published experimental absorption spectrum was available for a given example system. Where possible, the best resolved and most complete spectrum was chosen with particular preference for studies of single crystals (doped or otherwise) which generally provide more details about a given spectrum and which often include structural information as well.

As has been noted already, these calculations are purposely kept quite simple and as such no allowance for the environment (solvent, crystal or otherwise) has been made. This will certainly introduce errors into the calculations but the goal of this work is to give some examples of what can be done with the new approach rather than to produce the best possible numbers.

V. EXAMPLE CALCULATIONS: O_h AND $T_d d^1$ AND d^2 MOLECULES

To illustrate the possibilities of TRICKS-TDDFT we will present the results of calculations on a series of d^1 and d^2 transition metal complexes of octahedral and tetrahedral symmetries. It will be recalled that a molecule with a d^2 electron configuration and T_d symmetry will have a spatially nondegenerate 3A_2 ground state. Systems of this type were included for the sake of completeness and to provide some results for comparable systems where TRICKS-TDDFT is not necessary.

A. $d^1 T_d$ complexes

The first examples that we shall consider are a series of tetrahedral molecules and ions where the central transition metal retains a single d electron. That single d electron will occupy an e orbital (Scheme 1) giving rise to a spatially degenerate 2E ground state (see Scheme 2). The spectra of $T_d d^1$ molecules are generally quite easy to interpret. In the low-energy part of a spectrum one or more low-intensity peaks are observed corresponding to the only possible $d-d$ transition ($^2E \rightarrow ^2T_2$). At higher energies, more intense peaks

corresponding to the LMCT transitions are found. The highest-energy ligand orbitals consist of the $1t_1$, $2t_2$, $1a_1$, $1e$, and $1t_2$ (from highest to lowest in energy) orbitals made up mostly of the ligand p orbitals, Scheme 1. It is generally assumed that only excitations from the $1t_1$ and $2t_2$ orbitals are low enough in energy to be observed in the normal range of energies covered in UV-vis spectroscopy. The examples described in Sec. II outline most of the procedure required to treat the $d-d$ and LMCT transitions of $T_d d^1$ transition metal complexes using TRICKS-TDDFT. Whatever other details needed will be given in the next few paragraphs.

As well as the electron configurations of interest and the important states arising from those configurations, the useful ACSFs and auxiliary determinants corresponding to a given electron configuration and symmetry are listed in Scheme 2. The ACSFs are presented as linear combinations of auxiliary determinants denoted simply by ψ_i ($i=1, 2, \dots$, for the sake of clarity. The definitions of each of the ψ_i are given in Table I. For E states we list the E_g component, for T_1 states we list the T_{1g} component, and for T_2 states we list the T_{2z} component.

The 2A_1 TRIC required to calculate the $d-d$ transition energies is achieved by placing the electron that was formerly in the partially filled $2e$ orbital into the lowest unoccupied a_1 orbital ($2a_1$), the second highest-energy electron configuration in Scheme 2 labeled TRIC1.

The 4A_2 TRIC needed for the calculation of the LMCT transitions has electron configuration $1a_1^+ 2e_a^+ 2e_b^+$ (TRIC2 in Scheme 2).

Utilizing the TDDFT sum method described in Sec. III the transition energies from the reference to the 4T_2 and 2T_2 states of interest can be obtained.

The transition energies to the two lowest-energy LMCT states of T_1 symmetry can be calculated in a similar way to the energies of the 4T_2 and 2T_2 states just mentioned through a combination of TRICKS-TDDFT and TDDFT sum-rule calculations.

Transitions to a quartet states from the ground state are spin forbidden and would be expected to be difficult to resolve from the intense LMCT bands. Transitions to the states dominated by the $^2T_2(1t_1^5 2e^2)$ and $^2T_1(2t_2^5 2e^2)$ ACSFs given in Scheme 2 are both spin and symmetry allowed and should give rise to intense bands. The UV-vis spectrum of the manganate ion MnO_4^{2-} unlike that of most other $d^1 T_d$ complexes displays a significant amount of resolved fine structure in several bands assigned to LMCT transitions.⁴¹ From this fine structure and polarization experiments, it has been shown that the lowest-energy LMCT band indeed corresponds to a 2T_2 state.^{42–44}

The particular $T_d d^1$ molecules and ions investigated were VCl_4 , VO_4^{4-} , CrO_4^{3-} , MnO_4^{2-} , TcO_4^{2-} , and RuO_4^- . Experimental M–O bond lengths were taken to be 2.138 Å (VCl_4 (Ref. 45)), 1.760 Å (VO_4^{4-} (Ref. 46)), 1.693 Å (CrO_4^{3-} (Ref. 47)), 1.659 Å (MnO_4^{2-} (Ref. 48)), and 1.79 Å (RuO_4^- (Ref. 49)). We are unaware of any published experimental structure of TcO_4^{2-} and therefore took the Tc–O bond length to be 1.78 Å as derived from a geometry optimization calculation. This should be a good estimate of the true bond length as the

TABLE II. Experimental and calculated transition energies of tetrahedral d^1 complexes. All energies in eV.

Transition	VCl ₄		VO ₄ ⁴⁻		CrO ₄ ³⁻		MnO ₄ ²⁻		TcO ₄ ²⁻		RuO ₄ ⁻	
	Expt. ^a	Calc.	Expt. ^b	Calc.	Expt. ^c	Calc.	Expt. ^d	Calc.	Expt. ^e	Calc.	Expt. ^f	Calc.
${}^2E \rightarrow {}^2T_2$ ($1e \rightarrow 2t_2$)	1.11	0.95	1.29	1.24	1.67	1.51	1.49	1.58	1.77	1.87		1.72
${}^2E \rightarrow {}^2T_2$ ($1t_1 \rightarrow 1e$)	3.10	3.18	>4.59	5.92	3.47	3.89	2.05	2.51	2.48	4.17	4.22	2.90
${}^2E \rightarrow {}^2T_1$ ($2t_2 \rightarrow 1e$)					4.46	4.93	2.84	3.75	4.82	4.74	3.93	3.47
							4.14					

^aReferences 75 and 76.^bReference 28.^cReference 77.^dReference 78.^eReference 79.^fReference 80.

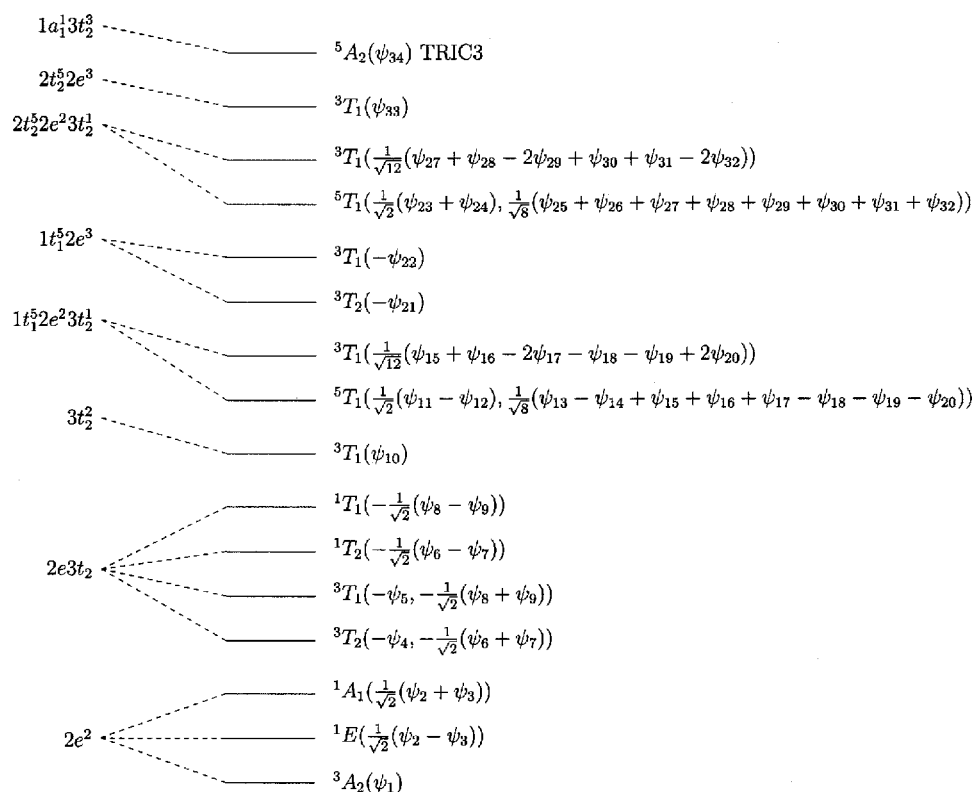
values calculated for the other molecules at the same level of theory are 2.13, 1.76, 1.66, 1.66, and 1.74 Å for VCl₄, VO₄⁴⁻, CrO₄³⁻, MnO₄²⁻, and RuO₄⁻, respectively.

The experimental transition energies of these molecules and values calculated with the TRICKS-TDDFT procedures described above are listed in Table II.

The first impression gained from Table II is that the TRICKS-TDDFT method appears to work rather well, despite the fact that TRIC1 and TRIC2 are both fairly high in energy. The $d-d$ and LMCT transitions are well separated in the calculations as is observed experimentally. The calculated ${}^2E \rightarrow {}^2T_2$ transition energies have a maximum error of 0.16 eV and a rms error of 0.12 eV. The agreement between

experiment and theory is less good for the LMCT transitions with a maximum error of 0.47 eV and a rms error of 0.34 eV. This is probably not a consequence of the approach for dealing with degenerate ground states, however, as similar errors are encountered in the TDDFT calculations of MnO₄²⁻.⁵⁰ The calculated LMCT transition energy of VCl₄ is in error by only 0.08 eV. This is the only example where the experimental spectrum is measured in the gas phase. It may well be that a very careful treatment of environment effects is necessary before the other spectra can be calculated with a similar accuracy.

The TDDFT sum-method approach used to obtain the LMCT transition energies requires that the transition density



SCHEME 3. Low-lying electron configurations and states of a $d^2 T_d$ transition metal complex. Only the most important states arising from a given configuration are shown. Following the state label, one or two useful ACSFs corresponding to a particular electron configuration and state are given. The ψ_i are defined in Table III.

TABLE III. Auxiliary determinants corresponding to electron configurations arising from $T_d d^2$ complexes.

Config.	Auxiliary determinants ^{a,b}			
$2e^2$	$\psi_1 = e_a e_b $	$\psi_2 = e_a $	$\psi_3 = e_b $	
$2e3t_2$	$\psi_4 = e_a e_{2z} $	$\psi_5 = e_b e_{2z} $	$\psi_6 = e_a e_{2x} $	$\psi_7 = e_b e_{2x} $
$3t_2^2$	$\psi_8 = e_b e_{2z} $	$\psi_9 = e_b e_{2x} $		
$1t_1^5 2e^2 3t_2^1$	$\psi_{10} = t_{2x} t_{2y} $			
	$\psi_{11} = t_{1x} e_a e_b t_{2y} $	$\psi_{12} = t_{1y} e_a e_b t_{2x} $	$\psi_{13} = t_{1x} e_a e_b t_{2y} $	$\psi_{14} = t_{1y} e_a e_b t_{2x} $
	$\psi_{15} = t_{1x} e_a e_b t_{2y} $	$\psi_{16} = t_{1y} e_a e_b t_{2x} $	$\psi_{17} = t_{1x} e_a e_b t_{2y} $	$\psi_{18} = t_{1y} e_a e_b t_{2x} $
	$\psi_{19} = t_{1x} e_a e_b t_{2y} $	$\psi_{20} = t_{1y} e_a e_b t_{2x} $		
$1t_1^5 2e^3$	$\psi_{21} = t_{1x} e_a e_b $	$\psi_{22} = t_{1y} e_a e_b $		
$2t_2^5 2e^2 3t_2^1$	$\psi_{23} = t_{2x} e_a e_b t_{2y} $	$\psi_{24} = t_{2y} e_a e_b t_{2x} $	$\psi_{25} = t_{2x} e_a e_b t_{2y} $	$\psi_{26} = t_{2y} e_a e_b t_{2x} $
	$\psi_{27} = t_{2x} e_a e_b t_{2y} $	$\psi_{28} = t_{2y} e_a e_b t_{2x} $	$\psi_{29} = t_{2x} e_a e_b t_{2y} $	$\psi_{30} = t_{2y} e_a e_b t_{2x} $
	$\psi_{31} = t_{2x} e_a e_b t_{2y} $	$\psi_{32} = t_{2y} e_a e_b t_{2x} $		
$2t_2^5 2e^3$	$\psi_{33} = t_{2x} e_a e_b $			
$1a_1^1 3t_2^3$	$\psi_{34} = a_1 t_{2x} t_{2y} t_{2z} $			

^aFor auxiliary determinants corresponding to a given configuration that include orbitals that are fully occupied, these orbitals are omitted.

^bFor auxiliary determinants corresponding to a given configuration that include partially occupied degenerate ligand orbitals, only the appropriate half-filled component of the degenerate orbital is shown.

to the state of interest be dominated by an appropriate one-electron excitation. This certainly was the case here. All the transition densities concerned have coefficient greater than 0.95 whether the excitation in question was $1\bar{t}_1 \rightarrow 1\bar{a}_1$, $2\bar{t}_2 \rightarrow 1\bar{a}_1$, $1t_1 \rightarrow 1\bar{a}_1$, or $2t_2 \rightarrow 1\bar{a}_1$.

B. $d^2 T_d$ complexes

Complexes with a d^2 electron configuration under T_d symmetry generally have a 3A_2 ground state. This state is of course not spatially degenerate and therefore no special procedure is required to treat many of the most important excitations of $d^2 T_d$ molecules within TDDFT.

As was already noted, the calculation of the excitation spectra of $T_d d^2$ systems is useful as a source of comparison with the TRICKS TDDFT calculations. Furthermore, several d^2 tetrahedral species, in particular, CrO_4^{4-} , MnO_4^{3-} , and FeO_4^{2-} species form an integral part of tunable solid-state near-infrared lasers and luminescent material.^{51–60} Their spectroscopy has been studied intensively in the last few years and also investigated theoretically by both multiconfiguration wave-function-based methods^{61,62} and DFT using ΔSCF sum rule techniques.^{63–65} This series of three molecules is also interesting from a fundamental point of view because as the oxidation state of the central metal is increased, the energy of the first charge-transfer transitions decreases to the extent that while the ligand field transitions are quite isolated in CrO_4^{4-} there could be significant overlap between the $d-d$ and CT bands in FeO_4^{2-} . Finally, the TDDFT sum method will prove useful in resolving some of the spin states of interest of the complexes. It thus seems worthwhile to investigate these species using TDDFT quite apart from any relevance to our investigation of TRICKS-TDDFT.

The ground and excited electron configurations of $T_d d^2$ complexes relevant for the present study are presented in Scheme 3. The auxiliary determinants that make up the ACSFs in Scheme 3 are given in Table III. At lowest energy is the ground-state configuration $2e^2$ and the related 3A_2 , 1E , and 1A_1 states. Above these are the $2e3t_2$ and $3t_2^2$ configurations arising from $d-d$ transitions followed by the LMCT configurations $1t_1^5 2e^2 3t_2^1$, $1t_1^5 2e^3$, $2t_2^5 2e^2 3t_2^1$, and $2t_2^5 2e^3$. All possible states are shown for the $2e^2$ and $2e3t_2$ configurations. For the others, we indicate mostly 3T_1 ACSFs and some 3T_2 and 5T_1 ACSFs. The 3T_1 ACSFs are the most important in this case since from the 3A_2 ground state the only spin and symmetry allowed transitions are to 3T_1 states.

TRICKS-TDDFT can be used to extend the range of transitions accessible through TDDFT even though the ground state is a perfectly reasonable choice as reference configuration. In experimental studies a peak is sometimes observed between those assigned to the major $d-d$ transitions and those assigned to charge-transfer bands. This peak is generally assigned to the 3T_1 state of the $3t_2^2$ configuration. As a double excitation with respect to the ground state, the $3t_2^2$ configuration is not accessible in a conventional TDDFT calculation. It is accessible from a TRIC, however. If we choose our reference state to be the 5A_2 state with electron

configuration $1a_1^+ 3t_{2x}^+ 3t_{2y}^+ 3t_{2z}^+$ (TRIC3 in Scheme 3) then the single spin-flip orbital excitation $3t_2^+ \rightarrow 1\bar{a}_1^-$ would give the desired $(1a_1^+) 3t_2^2$ configuration. The TRICKS-TDDFT calculations starting from the 5A_2 reference should provide a reasonably accurate value for the energy difference between the $^5A_2(1a_1^+ 3t_2^2)$ and the $^3T_1(3t_2^2)$ states. The value of the $^3A_2(2e^2) \rightarrow ^3T_1(3t_2^2)$ transition can then be obtained by com-

TABLE IV. Experimental and calculated transition energies of tetrahedral d^2 complexes. All energies in eV. Energies marked with an asterisk indicate transitions to mixed-spin states.

Transition	VCl_4^-		CrO_4^{4-}		MnO_4^{3-}		FeO_4^{2-}		RuO_4^{2-}	
	Expt. ^a	Calc.	Expt. ^b	Calc.	Expt. ^c	Calc.	Expt. ^d	Calc.	Expt. ^e	Calc.
$^3A_2 \rightarrow ^1E(2e^2)$		0.90	1.18	1.24	1.05	0.81	0.77	0.61	0.35	0.40
$^3A_2 \rightarrow ^1A_1(2e^2)$		1.66	1.83	1.72	1.30	1.45	1.14	1.10	0.88	0.77
$^3A_2 \rightarrow ^3T_2(2e^13t_2^1)$	0.68	0.84	1.13	1.29	1.30	1.49	1.61	1.57	1.67	1.86
$^3A_2 \rightarrow ^3T_1(2e^13t_2^1)$	1.13	1.13	1.72	1.52	1.84	1.73	2.23	1.73	2.05	2.03
$^3A_2 \rightarrow ^1T_1(2e^13t_2^1)$		1.75		2.22		2.29	>2.67	2.08		2.11
$^3A_2 \rightarrow ^1T_2(2e^13t_2^1)$		2.04		2.59	2.56	2.57	2.4	2.41		2.36
$^3A_2 \rightarrow ^3T_1(3t_2^2)$	1.88	1.12	2.54	1.94	3.31	2.65	3.72	2.91		3.51
$^3A_2 \rightarrow ^3T_1(1t_1^22e^23t_2^1)$	3.62	3.83		4.53	3.7	3.8*	3.27	3.0*		4.7*
$^3A_2 \rightarrow ^3T_2(1t_1^22e^3)$	4.61	4.56		5.01		3.37	2.48	2.23	2.91	3.32
$^3A_2 \rightarrow ^3T_1(1t_1^22e^3)$	4.61	4.56	5.33	4.88		3.39	2.48	2.38	3.22	3.52
$^3A_2 \rightarrow ^3T_1(2t_2^22e^23t_2^1)$	4.61	4.63		5.9*		5.2*		4.5*		5.4*
$^3A_2 \rightarrow ^3T_1(2t_2^22e^3)$	5.26	5.26		6.17		4.80		4.10	3.97	4.29

^aReferences 81 and 82.^bReferences 53 and 66.^cReferences 60 and 83.^dReference 51.^eReference 44.

binning the $^5A_2(1a_1^13t_2^3) \rightarrow ^3T_1(3t_2^2)$ energy difference and the difference in energy between the $^5A_2(1a_1^13t_2^3)$ and $^3A_2(2e^2)$ states derived using the total energies available from the standard DFT calculations considering these two states.

The five anions that were examined in the example calculations are VCl_4^- , the three oxygenated complexes already mentioned (CrO_4^{4-} , MnO_4^{3-} , and FeO_4^{2-}), and the 4d analog of FeO_4^{2-} , RuO_4^{2-} . The calculated V–Cl bond length was 2.20 Å while the distances for the other species were taken from experiment and were 1.76, 1.70, 1.65, and 1.76 Å for CrO_4^{4-} , MnO_4^{3-} , FeO_4^{2-} , and RuO_4^{2-} , respectively.⁴⁴

The calculated and, when available, experimental transition energies from the ground state to all the states shown in Scheme 3 are listed in Table IV.

The TDDFT sum-method approach was used to obtain pure spin symmetry $^1T_1(2e^13t_2^1)$, $^1T_2(2e^13t_2^1)$, $^3T_1(1t_1^22e^23t_2^1)$, and $^3T_1(2t_2^22e^23t_2^1)$ states when the relevant transition densities were found to be dominated by a single orbital excitation.

For the MnO_4^{3-} , FeO_4^{2-} , and RuO_4^{2-} systems with relatively strong crystal fields and more covalent metal to ligand bonding, the excited 1E and 1A_1 states are calculated to be lower in energy than the states arising from the $2e^13t_2^1$ configuration in agreement with experiment, Table IV. The $^3T_1(2e^13t_2^1)$ and $^3T_2(2e^13t_2^1)$ states are predicted to occur in the correct order and for the most part near the correct energy. The lone exception is the 3T_1 state of FeO_4^{2-} which is predicted to lie 0.5 eV lower in energy than the observed band.

VCl_4^- and CrO_4^{4-} exhibit a weaker crystal field. The $^3T_2(2e^13t_2^1)$ state is predicted to be at a similar energy to the $^1E(e^2)$ state while the $^3T_1(2e^13t_2^1)$ state is predicted to be higher in energy but still below the $^1A_1(e^2)$ state. The singlet e^2 states have not yet been observed for VCl_4^- but the calculations reproduce well what is found for CrO_4^{4-} where the $^3T_1(2e^13t_2^1)$ state is between the two e^2 singlet states⁵³ and

the $^3T_1(2e^13t_2^1)$ state can be above or below the $^1E(e^2)$ state depending on the environment the ion is in and other physical variables such as pressure.⁶⁶

Apart from the transition to the $^3T_1(2e^13t_2^1)$ state of FeO_4^{2-} and the transition to the $^1T_1(2e^13t_2^1)$ state of the same ion which is known only very approximately, the calculated $d-d$ transition energies to states arising from the e^2 and $e^1t_2^1$ configurations are in error by an average of only 0.11 eV with a maximum error of 0.24 eV. This makes it all more surprising that agreement between theory and experiment should be so poor for the $\text{FeO}_4^{2-} ^3T_1$ state. The absorption spectrum of FeO_4^{2-} (Ref. 51) consists of some weak and narrow bands assigned to the 1E and 1A_1 states, a broader, more intense band assigned to the 3T_2 state which is then followed by an even more intense broadband with significant fine structure which is attributed to the 3T_1 band overlapping with the first LMCT transition. Our calculations would place both the $^3T_2(2e^13t_2^1)$ and $^3T_1(2e^13t_2^1)$ states under the first broadband and predict that the second broadband is almost exclusively due to LMCT, as was proposed as a consequence of the MCSCF calculations.⁶¹ The TDDFT sum-rule method was applied to calculate the transition energies of all the $d-d$ transitions to singlet $2e^13t_2^1$ states. Suitable transition densities dominated (coefficient >0.8) by the appropriate $2e \rightarrow 3t_2$ or $2e \rightarrow \bar{3}t_2$ excitations were found in all cases. This approach seems to work very well in this case as the energies of the two transitions for which good experimental measurements exist, the $^3A_2 \rightarrow ^1T_2$ transitions of MnO_4^{3-} and FeO_4^{2-} , are reproduced to an accuracy of better than 0.1 eV.

The last $d-d$ transition of these systems to be discussed in that to the $^3T_1(t_2^2)$ state. For the three stronger crystal-field ions this state is predicted to be above all the e^2 and $e^1t_2^1$ states as one might expect. For the two weak field ions, it is predicted to be closer to the $^3T_1(e^1t_2^1)$ state and below the two singlet $e^1t_2^1$ states. A band has been assigned to the $^3T_1(t_2^2)$ state in four of the five examples currently under consider-

ation. In all of the four examples, the band assigned as ${}^3T_1(t_2^2)$ is considerably higher in energy (0.6–0.8 eV) than the calculated excitation energy to this state. The band corresponding to the ${}^3A_2 \rightarrow {}^3T_1(t_2^2)$ transition would be difficult to observe and assign with confidence because, as a two-electron transition, its intensity is very likely to be low.

The predicted CT bands arise from excitations out of the $1t_1$ and $2t_2$ orbitals into the $2e$ and $3t_2$ orbitals with the transitions involving the $1t_1$ always lower in energy. The difference between the $t_i \rightarrow e$ and $t_i \rightarrow t_2$ ($i=1, 2$)-based CT transitions is by no means constant. The first type of transition is favored when the spin pairing energy is less than the crystal-field splitting of the d orbitals and vice versa. Thus, the transitions to states assigned to $t_i \rightarrow e$ are lower in energy for the three ions previously described as having a stronger ligand field while the $t_i \rightarrow t_2$ transitions are lower in energy for the other two ions.

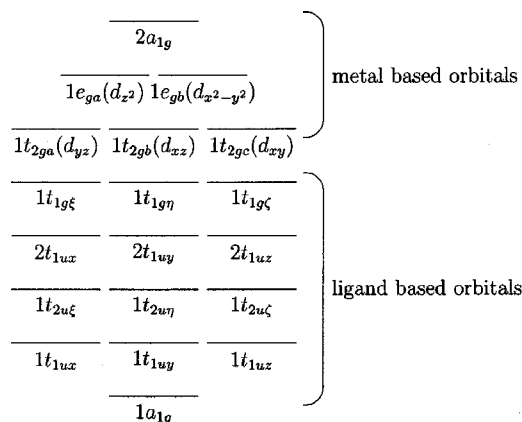
Overall, the quality of the calculated LMCT transition energies is similar to what was obtained for the d^1 systems.

Several of the transition densities at higher energies are not dominated by any single orbital excitation. In particular, several transition densities with a strong mixing of a $t_i \rightarrow 3t_2$ ($i=1, 2$) excitation also have significant contributions from a $t_i \rightarrow 2e$ ($i=1, 2$) excitation. It was therefore not possible to make use of the TDDFT sum-rule approach with these transitions to obtain transition energies to states that are spin eigenfunctions. When this occurred, the transition energy to the mixed-spin state with greatest contribution from the $t_i \rightarrow 3t_2$ ($i=1, 2$) excitation is listed in Table IV. All such mixed-spin energies are marked with an asterisk in the table. It would seem that the higher-energy LMCT transfer bands in the spectra of the $T_d d^2$ transition metal complexes cannot simply be assigned to a single one-electron excitation.

Our study represents the first extensive TDDFT study of the $T_d d^2$ systems discussed here. However, the previous Δ SCF sum-rule DFT calculations afford a qualitatively similar picture⁶⁵ that is also in line with simple qualitative molecular-orbital theory. In contrast, large MCSCF calculations afford a very complicated bonding model despite the fact that the transition energies produced by this method agree well with experiment and other calculations based on simple bonding theories. This is most likely because this model of the MO_4^{n-} electronic structure starts from a Hartree-Fock wave function that gives a description of bonding that is far too ionic.⁶⁷

C. $d^1 O_h$ complexes

Octahedral d^1 complexes have a t_{2g}^1 electron configuration and a ${}^2T_{2g}$ ground state. The orbital energy diagram of a typical O_h transition metal complex is depicted in Scheme 4. Much like the tetrahedral d^1 complexes, the UV-vis spectra of the octahedral species generally are relatively simple with a single less intense band corresponding to the only possible $d-d$ transition (${}^2T_{2g} \rightarrow {}^2E_g$) at lower energies with more intense bands at higher frequencies. The more intense bands are generally assigned to ligand to metal charge transfer



SCHEME 4. Orbital diagram for octahedral transition metal complexes. The d^1 and d^2 complexes in their ground state have one and two electrons in the $1t_{2g}$ levels, respectively. All ligand-based levels are fully occupied in the ground state.

(LMCT) though other assignments (such as metal to ligand CT) may be possible depending on the identity of the ligands attached to the transition metal.

In terms of TRICKS-TDDFT, the ${}^2T_{2g} \rightarrow {}^2E_g$ transition is straightforward to treat using essentially the same procedure that was applied to calculate the $d-d$ transition of the d^1 tetrahedral complexes. The reference is chosen to have ${}^2A_{1g}$ symmetry and this is achieved by taking the normal ground-state electron configuration and moving the $1t_{2g}$ electron to the previously unoccupied $2a_{1g}$ orbital to give TRIC4. This choice will obviously be able to treat the two states of interest through single excitations from TRIC4.

The LMCT transitions of d^1 octahedral complexes are a good example of transitions that cannot be treated by the TRICKS-TDDFT method. In this case, the excited states generally correspond to electron configurations of the type $t_{iu}^5 t_{2g}^1 e_g^1$ or perhaps $t_{iu}^5 t_{2g}^1 e_g^1$ where $i=1, 2$. With a little thought, it should be clear that no electron configuration can be found which gives a nondegenerate ground state described by a single Slater determinant and which can reach the desired electron configurations through a single excitation.

Five octahedral d^1 transition metal complexes were considered, the three Ti(III) compounds $Ti(CN)_6^{3-}$, TiF_6^{3-} , and $TiCl_6^{3-}$, the V(IV) complex VCl_6^{2-} , and the Mo(V) complex $MoCl_6^-$. Optimized geometries were used for TiF_6^{3-} ($R(Ti-F)=2.02$ Å), TiF_6^{3-} ($R(Ti-Cl)=2.49$ Å), VCl_6^{2-} ($R(V-Cl)=2.32$ Å), and $MoCl_6^-$ ($R(Mo-Cl)=2.33$ Å) while the experimental values⁶⁸ of $R(Ti-C)=2.20$ Å and $R(C-N)=1.14$ Å were taken for $Ti(CN)_6^{3-}$. The experimental and calculated values of the ${}^2T_{2g} \rightarrow {}^2E_g$ transition energy are given in Table V.

In general, the agreement between the calculated and experimental transition energies is similar to that found for the $d-d$ transitions of the tetrahedral complexes already discussed. Three of the anions have two values for the experimental transition energy. This is because the experiments were able to resolve the Jahn-Teller splitting of the excited state. Numerical comparisons will be made with the average energy of the two Jahn-Teller components. The average mag-

TABLE V. Experimental and calculated ${}^2T_{2g} \rightarrow {}^2E_g$ transition energies of octahedral d^1 complexes. All energies in eV.

TiCN $_6^{3-}$		TiF $_6^{3-}$		TiCl $_6^{3-}$		VCl $_6^{2-}$		MoCl $_6^-$	
Expt. ^a	Calc.	Expt. ^b	Calc.	Expt. ^c	Calc.	Expt. ^d	Calc.	Expt. ^e	Calc.
2.93/3.23	3.46	1.90/2.39	1.87	1.71/1.49	1.41	1.71/1.90	1.91	3.27	2.92

^aReference 68.^bReference 84.^cReference 85.^dReferences 86 and 87.^eReference 72.

nitude of the error across all the examples is 0.22 eV with two calculated values too high and three too low.

D. d^2O_h complexes

The final set of examples to be considered will be the octahedral transition metal complexes with two unpaired electrons. These electrons are expected to be found in the metal-based $1t_{2g}$ orbitals thereby giving a spatially degenerate ${}^3T_{1g}$ ground state. The UV-vis spectra of molecules of this type generally show two weaker bands corresponding to spin allowed but symmetry forbidden $d-d$ transitions to ${}^3T_{1g}(t_{2g}e_g)$ and ${}^3T_{2g}(t_{2g}e_g)$ states at lower energies and more intense bands corresponding to CT transitions (most often LMCT) at higher energies. Both of these types of transition can be handled by the TRICKS-TDDFT approach.

The LMCT transitions are the most easily dealt with. The low-energy electron configurations and related states, ACSFs, and auxiliary determinants of an $O_h d^2$ complex are given in Table VI and Scheme 5. The TRIC required to access LMCT states is given by TRIC5 in Scheme 5 and ψ_{25} in

TABLE VI. Auxiliary determinants corresponding to electron configurations arising from $O_h d^2$ complexes.

Config.	Auxiliary determinants ^{a,b}		
$1t_{2g}^2$	$\psi_1 = t_{2g}^+ t_{2g}^+ $		
$1t_{2g}^1 1e_g^1$	$\psi_2 = t_{2g}^+ e_g^+ $	$\psi_3 = t_{2g}^+ e_{gb}^+ $	
$1e_g^2$	$\psi_4 = e_{ga}^+ e_{gb}^+ $		
$1t_{1g}^1 1t_{2g}^1$	$\psi_5 = t_{1g}^+ t_{2g}^+ $	$\psi_6 = t_{1g}^+ t_{2g}^+ $	$\psi_7 = t_{1g}^+ t_{2g}^+ $
$2t_{1u}^1 1t_{2g}^1$	$\psi_8 = t_{1g}^+ t_{2g}^+ $	$\psi_9 = t_{1g}^+ t_{2g}^+ $	
$2t_{1u}^1 1t_{2g}^1$	$\psi_{10} = t_{1u}^+ t_{2g}^+ $	$\psi_{11} = t_{1u}^+ t_{2g}^+ $	$\psi_{12} = t_{1u}^+ t_{2g}^+ $
$1t_{2u}^1 1t_{2g}^1$	$\psi_{13} = t_{1u}^+ t_{2g}^+ $	$\psi_{14} = t_{1u}^+ t_{2g}^+ $	
$1t_{2u}^1 1t_{2g}^1$	$\psi_{15} = t_{2u}^+ t_{2g}^+ $	$\psi_{16} = t_{2u}^+ t_{2g}^+ $	$\psi_{17} = t_{2u}^+ t_{2g}^+ $
$1t_{1u}^1 1t_{2g}^1$	$\psi_{18} = t_{2u}^+ t_{2g}^+ $	$\psi_{19} = t_{2u}^+ t_{2g}^+ $	
$1t_{1u}^1 1t_{2g}^1$	$\psi_{20} = t_{1u}^+ t_{2g}^+ $	$\psi_{21} = t_{1u}^+ t_{2g}^+ $	$\psi_{22} = t_{1u}^+ t_{2g}^+ $
$1a_{1g}^1 1t_{2g}^1$	$\psi_{23} = t_{1u}^+ t_{2g}^+ $	$\psi_{24} = t_{1u}^+ t_{2g}^+ $	
	$\psi_{25} = a_{1g}^+ t_{2g}^+ $		

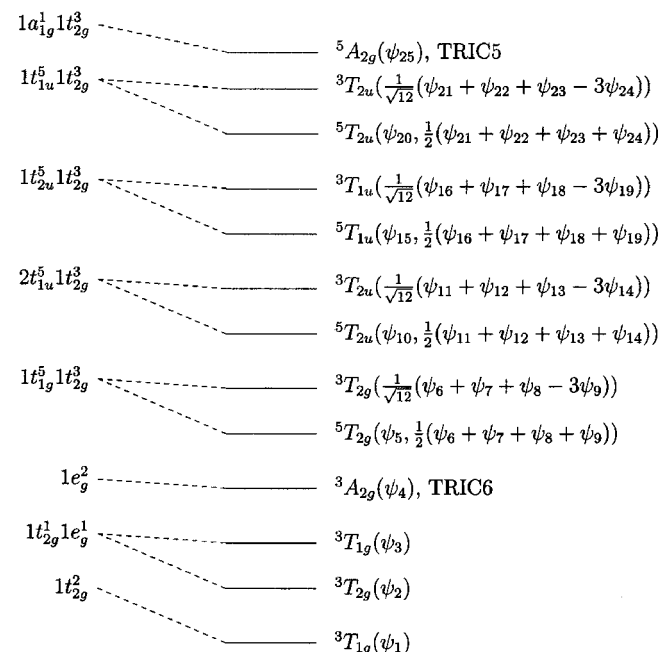
^aFor auxiliary determinants corresponding to a given configuration that include orbitals that are fully occupied, these orbitals are omitted.

^bFor auxiliary determinants corresponding to a given configuration that include partially occupied degenerate ligand orbitals, only the appropriate half-filled component of the degenerate orbital is shown.

Table VI. This reference has identical orbital occupations to the ground state except that a β electron is excited with a spin flip from the $1a_{1g}$ occupied orbital into the partially occupied $1t_{2g}$ orbital. This reference configuration has ${}^5A_{2g}$ symmetry. A spin-flip TDDFT calculation starting from this reference should include a transition to the ground state

dominated by the $1t_{2g}^+ \rightarrow 1a_{1g}^-$ orbital excitation. Transition energies to quintet LMCT states are available from a standard TDDFT calculation starting from TRIC5 through transitions dominated by orbital excitations of the type $\bar{l} \rightarrow 1a_{1g}^-$ (where l is ligand orbital) while a spin-flip TDDFT calculation gives access to mixed triplet-quintet state through transitions dominated by orbital excitations of the type $\bar{l} \rightarrow 1a_{1g}^-$. If pairs of transition densities with sufficiently large contributions from the above excitations are obtained then a TD-DFT sum-rule calculation can be used to evaluate transition energies to the triplet states.

The $d-d$ transitions of an octahedral d^2 molecule are a little trickier to obtain but can be calculated if one starts from



SCHEME 5. Low-lying electron configurations and states of a d^2O_h transition metal complex. Only the most important states arising from a given configuration are shown. Following the state label, one or two useful ACSFs corresponding to a particular electron configuration and state are given. The ψ_i are defined in Table VI.

TABLE VII. Experimental and calculated transition energies of octahedral complexes. All energies in eV.

Transition	TiCl ₆ ⁴⁻		VCl ₆ ³⁻		MoCl ₆ ²⁻		WBr ₆ ²⁻		ReCl ₆ ⁻	
	Exp. ^a	Calc.	Exp. ^b	Calc.	Exp. ^c	Calc.	Exp. ^d	Calc.	Exp. ^e	Calc.
³ T _{1g} → ³ T _{2g} (1t _{2g} ¹ e _g ¹)	1.15	1.88	1.40	1.89		2.60	2.49	2.68	3.16	3.34
³ T _{1g} → ³ T _{1g} (1t _{2g} ¹ e _g ¹)	2.00	2.18	2.41	2.13		2.74	2.49	2.79	3.43	3.44
³ T _{1g} → ³ A _{2g} (1e _g ²)	2.40	2.43	2.92	2.88		5.33		5.13		6.55
³ T _{1g} → ³ T _{2g} (1t _{2g} ⁵ 1t _{2g} ³)		6.13		2.76		2.35	2.49	2.28	1.98	1.76
³ T _{1g} → ³ T _{2u} (2t _{2g} ⁵ 1t _{2g} ³)		6.37	>3.5	3.05	3.04	2.83	3.12	2.74	2.42	2.27
³ T _{1g} → ³ T _{1u} (1t _{2g} ⁵ 1t _{2g} ³)		6.42		3.10	3.51	2.97	3.12	2.88	2.73	2.43
³ T _{1g} → ³ T _{2u} (1t _{2g} ⁵ 1t _{2g} ³)		6.81		3.82	4.07	3.86	4.09	3.99	3.69	3.65

^aReference 70.^bReferences 69 and 71.^cReference 72.^dReference 73.^eReference 74.

a doubly excited $e_g^2(^3A_{2g})$ reference (TRIC6, Scheme 5). A standard TDDFT calculation starting from this reference includes excitations leading to the configuration $t_{2g}^1e_g^1$, Scheme 5. These excitations should be the most important for describing the transition to the lowest excited $^3T_{1g}$ and $^3T_{2g}$ states. The $d-d$ transition energies from the $^3T_{1g}$ ground state to the $^3T_{1g,2g}(t_{2g}e_g)$ excited states can be obtained from a suitable combination of $E(^3A_{2g}(e^2))$, $E(^5A_{2g}(a_{1g}t_{2g}^3))$, $E(^3A_{2g}(e^2) \rightarrow ^3T_{1g,2g}(t_{2g}e_g))$, and $E(^5A_{2g}(a_{1g}t_{2g}^3) \rightarrow ^3T_{1g}(t_{2g}^2))$ all of which can be obtained from the DFT or TDDFT calculations just described.

The two TRICKS-TDDFT approaches outlined above were applied to the calculation of the absorption spectra of TiCl₆⁴⁻, VCl₆³⁻, MoCl₆²⁻, WBr₆²⁻, and ReCl₆⁻. Experimental geometries were available VCl₆³⁻ ($R(V-Cl)=2.62$ Å (Ref. 69)). In the other cases the optimized geometric parameters were $R(Ti-Cl)=2.78$ Å (TiCl₆⁴⁻), $R(Mo-Cl)=2.39$ Å (MoCl₆²⁻), $R(W-Br)=2.55$ Å (WBr₆²⁻), and $R(Re-Cl)=2.31$ Å (ReCl₆⁻). The calculated excitation energies are presented in Table VII along with the related experimental values.

The accuracy of the calculations is similar to what has been seen already. The experimental spectra of the two $3d$ complexes feature only the $d-d$ transitions.⁶⁹⁻⁷¹ The calculations predict that the most intense LMCT transitions should only be observed above 3 eV. The $d-d$ transition energies to the $^3T_{1g}$ and $^3A_{2g}$ states of these two complexes are reproduced very well but the energy to the $^3T_{2g}$ is somewhat high. The splitting of the $^3T_{1g}$ and $^3T_{2g}$ states appears to be underestimated and is predicted to be quite small in all of the examples considered here.

In contrast to the $3d$ complexes, the spectra of the $4d$ and $5d$ complexes are dominated by the CT transitions.⁷²⁻⁷⁴ The calculated values of the LMCT transition energies of these complexes are similar in accuracy to those of the LMCT transitions considered previously with errors generally of the order of 0.3–0.4 eV. The assignments of the $d-d$ transitions of WBr₆³⁻ and ReCl₆⁻ are rather tentative as these low-intensity bands are expected to be found near the CT bands and thus would be difficult to resolve.

The transition densities of the spin-flip TDDFT calculation starting from TRIC5($^5A_{2g}$) corresponding to the TRIC5 → LMCT state transitions listed in Table VII are all com-

pletely dominated (coefficient >0.99) by a single $\bar{l} \rightarrow -1a_{1g}$ orbital excitation. It therefore is reasonable to use the TD-DFT sum method in this case.

VI. CONCLUDING REMARKS

In this paper we have outlined a method for calculating the transition energies of molecules with a degenerate ground state using TDDFT. The key to this TRICKS-TDDFT method is the choice of a suitable nondegenerate excited state as the reference for the subsequent TDDFT treatment. Some ingenuity is often required to come up with a suitable choice of reference state and both standard and spin-flip TD-DFT calculations are generally needed to enable all the desired transitions to be evaluated. However, as the examples presented here illustrate, with a bit of thought and access to standard and spin-flip TDDFT calculations a large number of transitions become accessible.

Just like any other open-shell TDDFT calculation, a TRICKS-TDDFT calculation suffers from the fact that the calculated transition densities are often to states that are not spin eigenfunctions. In order to alleviate this difficulty somewhat we proposed the TDDFT sum method. Much like the standard ΔSCF sum method, the TDDFT approach takes advantage of the known form of CSFs corresponding to a given electron configuration and whatever transition energies are available to allow the calculation of transition energies that otherwise could not be obtained without somehow including the double orbital excitations in the treatment. The TDDFT sum rule does rely on appropriate transition densities dominated by a single orbital excitation being available. This was generally the case in the examples studied here but not always.

Through a combination of TRICKS-TDDFT and the TD-DFT sum rule the transition energies of a number of d^1 and d^2O_h and T_d transition metal complexes were calculated. The transition energies obtained through the TRICKS-TDDFT method were similar in quality to what we might expect from a standard open-shell TDDFT calculation such as the d^2T_d calculations presented here.

It should be recalled that in many ways O_h and T_d systems are the most difficult to treat with TRICKS-TDDFT.

Although no examples of systems with a degenerate ground state and lower symmetry were discussed, choosing a TRIC in this case is almost always trivial and we would expect that TRICKS-TDDFT should work very well with lower symmetry molecules.

The discussion in this work was devoted exclusively to transition energies. Oscillator strengths of transitions are of course also of interest and particular matrix elements between the ground and excited states may become important when certain properties are to be calculated. We are presently investigating these issues and they will form the subject of a forthcoming paper.

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