Use of Noncollinear Exchange-Correlation Potentials in Multiplet Resolutions by Time-Dependent Density Functional Theory

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ABSTRACT: The resolution of spin-multiplets in an electronic system with a spin-degenerate ground state requires a method that can deal with spin-flip excitations. We recently showed that time-dependent density functional theory (TDDFT) can treat such excitations provided that use is made of a noncollinear exchange-correlation (XC) potential. The new formulation is a generalization of conventional TDDFT. The form of the new formulation is exactly the same as that of the conventional TDDFT for transitions that do not involve spin-flips. However, the noncollinear TDDFT formulation allows in addition for spin-flip transitions. In the present account, we explain in more detail why a noncollinear formulation of the XC potential is required.   © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 2545–2550, 2006

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Introduction

Time-dependent density functional theory (TD-DFT) [1–4] has evolved as a powerful tool in the study of excited state properties over the last decade. In its original formulation [1, 2], TDDFT based on pure spin-density functionals was considered unable to treat single excitations involving spin-flips. This limitation made it difficult to fully

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resolve spin-multiplets resulting from excitations of molecules with an open-shell spin-degenerate ground state. Recently Krylov et al. [5, 6] implemented a spin-flip method in TDDFT. In their approach, the spin-flip process can only be introduced through the Hartree–Fock exchange potential mixed into the exchange-correlation (XC) potential. In fact, the lack of spin-flip transitions in ordinary TDDFT is due to the most often used representation for the XC potential, in which the XC potential only depends on the α spin and β spin densities. In recent work, Wang and Ziegler [7] demonstrated that the limitations of TDDFT based on pure spin-

density functionals can be eliminated by introducing the noncollinear representation of the XC potential [8–10]. With the noncollinear scheme for the XC potential, the spin-flip transitions can be introduced automatically without resorting to the Hartree–Fock exchange. In this account, we provide a more detailed analysis than given previously [7] of why spin-flips requires the use of a noncollinear XC representation by demonstrating that the use of the collinear representation a priori presupposes the absence of any spin-flip. The use of the noncollinear XC potential is illustrated in Ref. [10] in connection with TDDFT calculations on the excited states of CH_2 and the isoelectronic species NH_2^+, SiH_2, and PH_2^+, as well as many other systems.

Discussion

BASIC TDDFT

The fundamental equation in TDDFT reads [2, 3]

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

where the A and B matrices are defined as

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \left(\frac{\partial F_{ia}}{\partial P_{jb}}\right), \qquad B_{ia,bj} = \left(\frac{\partial F_{ia}}{\partial P_{bj}}\right), \quad (2)$$

where F_{ia} and P_{jb} are Fock and density matrix elements, respectively. Since both ω and $-\omega$ are eigenvalues of Eq. (1), the eigenvectors X, Y must satisfy [11, 12]

$$(X^+ \quad Y^+) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = 1 \quad (3)$$

to obtain the correct excitation energies.

In the above equations, $i, j, \ldots$ are indices used for occupied orbitals and $a, b, \ldots$ are indices for empty orbitals, whereas $p, q \ldots$ are indices for general orbitals. These orbitals are all unperturbed and are calculated from a Kohn–Sham equation in the absence of a frequency-dependent perturbation as

$$F^0\varphi_u = \varepsilon_u\varphi_u. \quad (4)$$

Equation (1) provides excitation energies $\{\omega_\lambda; \lambda = 1, n\}$ along with the corresponding transition densities

$$\rho_\lambda(1, 1') = \sum_i^{occ} \sum_a^{vir} [X_{ia}\varphi_i(1)\varphi_a^*(1') + Y_{ai}\varphi_a(1)\varphi_i^*(1')]. \quad (5)$$

COLLINEAR EXCHANGE CORRELATION POTENTIAL

The most often used expression for the XC energy functional and XC potential reads

$$E_{XC} \equiv E_{XC}[\rho^{\alpha\alpha}, \rho^{\beta\beta}], \qquad V_{XC}^\alpha = \frac{\delta E_{XC}[\rho^{\alpha\alpha}, \rho^{\beta\beta}]}{\delta\rho^{\alpha\alpha}},$$

$$V_{XC}^\beta = \frac{\delta E_{XC}[\rho^{\alpha\alpha}, \rho^{\beta\beta}]}{\delta\rho^{\beta\beta}}, \quad (6)$$

where $\rho^{\alpha\alpha}$ and $\rho^{\beta\beta}$ are the α and β spin electron densities, respectively. It can be seen from Eq. (1) that the XC potential only depends on the α and β spin densities. Alternatively, we might write the XC energy functional and XC potential in terms of the total density $\rho = \rho^{\alpha\alpha} + \rho^{\beta\beta}$ and the spin density $s = \rho^{\alpha\alpha} - \rho^{\beta\beta}$ as

$$E_{XC} \equiv E_{XC}[\rho, s], \quad (7a)$$

$$V_{XC}^\alpha = \frac{\delta E_{XC}[\rho, s]}{\delta\rho} + \frac{\delta E_{XC}[\rho, s]}{\delta s},$$

$$V_{XC}^\beta = \frac{\delta E_{XC}[\rho, s]}{\delta\rho} - \frac{\delta E_{XC}[\rho, s]}{\delta s}, \quad (7b)$$

where the expressions in Eq. (7) can readily be derived from Eq. (6) by observing that

$$\rho^{\alpha\alpha} = (\rho + s)/2 \qquad \text{and} \qquad \rho^{\beta\beta} = (\rho - s)/2. \quad (8)$$

We might finally introduce a two-component formalism by writing the Kohn–Sham orbitals from Eq. (4) as

$$\psi_i = \varphi_i^\alpha\alpha = \begin{pmatrix} \varphi_i^\alpha \\ 0 \end{pmatrix}; \qquad \psi_j = \varphi_j^\beta\beta = \begin{pmatrix} 0 \\ \varphi_j^\beta \end{pmatrix}. \quad (9)$$

In that case,

$$\begin{pmatrix} V_{XC}^{\alpha} & 0 \\ 0 & V_{XC}^{\beta} \end{pmatrix} = \frac{\delta E_{XC}[\rho, s]}{\delta \rho} \mathbb{1} + \frac{\delta E_{XC}[\rho, s]}{\delta s} \sigma_z, \quad (10)$$

where

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (11)$$

whereas

$$\rho = \sum_i^{occ} \psi_i^+ \psi_i; \qquad s = \sum_i^{occ} \psi_i^+ \sigma_z \psi_i \quad (12)$$

and $\mathbb{1}$ is a 2×2 unit matrix.

With spin quantization along the z-axis, the orbitals can be written on the two-component form given in Eq. (9) and the related density matrix $\hat{\rho}$ is diagonal

$$\hat{\rho} = \sum_i^{occ} \psi_i \psi_i^+ = \begin{pmatrix} \rho^{\alpha\alpha} & 0 \\ 0 & \rho^{\beta\beta} \end{pmatrix} = \frac{1}{2} \rho \mathbb{1} + \frac{1}{2} [\rho^{\alpha\alpha} - \rho^{\beta\beta}] \sigma_z,$$
$$(13)$$

where

$$\rho^{\alpha\alpha} = \sum_i^{occ} \varphi_i^{\alpha} (\varphi_i^{\alpha})^* \quad \text{and} \quad \rho^{\beta\beta} = \sum_i^{occ} \varphi_i^{\beta} (\varphi_i^{\beta})^*, \quad (14)$$

whereas σ_z is defined in Eq. (11). In the case where $\hat{\rho}$ is diagonal the spin-density can readily be defined as $s = \rho^{\alpha\alpha} - \rho^{\beta\beta}$ in line with Eq. (12).

Defined in this way, the spin density $s(\vec{r})$ is the difference in density between electrons with a positive projection of their spin-angular momentum on the direction of the spin quantization and electrons with a negative projection of their spin-angular momentum on the direction of the spin quantization at position $\vec{r}$. In the collinear representation of the XC potential given above, the direction of spin-polarization is fixed to point along the z-axis. However, it could as well have been fixed along any other direction as the orientation of the z-axis is arbitrary.

NONCOLLINEAR EXCHANGE CORRELATION POTENTIAL

In the more general case where the spin-quantization is along an arbitrary direction the orbitals in the $\{\alpha, \beta\}$ representation will have the form

$$\psi_i = \varphi_i^{\alpha} \alpha + \varphi_i^{\beta} \beta = \begin{pmatrix} \varphi_i^{\alpha} \\ \varphi_i^{\beta} \end{pmatrix}. \quad (15)$$

In this case, the density matrix reads

$$\hat{\rho} = \sum_i^{occ} \psi_i \psi_i^+ = \begin{pmatrix} \rho^{\alpha\alpha} & \rho^{\beta\alpha} \\ \rho^{\alpha\beta} & \rho^{\beta\beta} \end{pmatrix}, \quad (16)$$

where $\rho^{\alpha\alpha}$ and $\rho^{\beta\beta}$ are defined in Eq. (14) and the off-diagonal terms given by

$$\rho^{\alpha\beta} = \sum_i^{occ} (\varphi_i^{\alpha})^* \varphi_i^{\beta} \quad \text{and}$$

$$\rho^{\beta\alpha} = \sum_i^{occ} \varphi_i^{\alpha} (\varphi_i^{\beta})^* = (\rho^{\alpha\beta})^*. \quad (17)$$

The matrix in Eq. (16) is not diagonal as in Eq. (13), since $\rho^{\alpha\beta}$ and $\rho^{\beta\alpha}$ are nonzero. Thus, to define the spin density, we must first determine the direction of spin-quantization by diagonalizing $\hat{\rho}$.

To this end, we perform a unitary transformation

$$\begin{pmatrix} \alpha' \\ \beta' \end{pmatrix} = U \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (18)$$

that will diagonalize the density matrix of Eq. (16), such that

$$U^+ \begin{pmatrix} \rho^{\alpha\alpha} & \rho^{\beta\alpha} \\ \rho^{\alpha\beta} & \rho^{\beta\beta} \end{pmatrix} U = \begin{pmatrix} \rho^{\alpha'\alpha'} & 0 \\ 0 & \rho^{\beta'\beta'} \end{pmatrix}$$

$$= \frac{1}{2} \rho \mathbb{1} + \frac{1}{2} [\rho^{\alpha'\alpha'} - \rho^{\beta'\beta'}] \sigma_z, \quad (19)$$

where $\rho = \rho^{\alpha\alpha} + \rho^{\beta\beta} = \rho^{\alpha'\alpha'} + \rho^{\beta'\beta'}$. Comparing Eq. (13) with Eq. (19), we have a spin density of $s' = \rho^{\alpha'\alpha'} - \rho^{\beta'\beta'}$.

To obtain a final practical expression for s' in terms of $\rho^{\alpha\alpha}$, $\rho^{\alpha\beta}$, $\rho^{\beta\alpha}$, $\rho^{\beta\beta}$ rather than $\rho^{\alpha'\alpha'}$, $\rho^{\beta'\beta'}$, let us write the density matrix of Eq. (16) in terms of the unit matrix $\mathbb{1}$ and the three Pauli matrices $\{\sigma_i; i = x, y, z\}$, where σ_z is defined in Eq. (11) and

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \quad (20)$$

We have

$$\begin{pmatrix} \rho^{\alpha\alpha} & \rho^{\beta\alpha} \\ \rho^{\alpha\beta} & \rho^{\beta\beta} \end{pmatrix} = \frac{1}{2}[\rho^{\alpha\alpha} + \rho^{\beta\beta}]\mathbb{1} + \frac{1}{2}[\rho^{\alpha\beta} + \rho^{\beta\alpha}]\sigma_x$$

$$+ \frac{1}{2}i[\rho^{\beta\alpha} - \rho^{\alpha\beta}]\sigma_y + \frac{1}{2}[\rho^{\alpha\alpha} - \rho^{\beta\beta}]\sigma_z. \quad (21)$$

It follows from further inspection that

$$[\rho^{\alpha\beta} + \rho^{\beta\alpha}] = \sum_i^{occ} \psi_i^+ \sigma_x \psi_i = m_x \quad (22a)$$

$$i[-\rho^{\alpha\beta} + \rho^{\beta\alpha}] = \sum_i^{occ} \psi_i^+ \sigma_y \psi_i = m_y \quad (22b)$$

$$[\rho^{\alpha\alpha} - \rho^{\beta\beta}] = \sum_i^{occ} \psi_i^+ \sigma_z \psi_i = m_z. \quad (22c)$$

We can thus write

$$\hat{\rho} = \frac{1}{2}\rho\mathbb{1} + \frac{1}{2}\vec{m} \cdot \vec{\sigma}, \quad (23)$$

where $\vec{m} = m_x\vec{e}_x + m_y\vec{e}_y + m_z\vec{e}_x$ and $\vec{\sigma} = \sigma_x\vec{e}_x + \sigma_y\vec{e}_y + \sigma_z\vec{e}_x$, whereas

$$\rho = \rho^{\alpha\alpha} + \rho^{\beta\beta}.$$

Now from the unitary transformation of Eq. (19),

$$U^+\hat{\rho}U = \frac{1}{2}\rho U^+\mathbb{1}U + U^+(\vec{m}\vec{\sigma})U = \frac{1}{2}\rho\mathbb{1} + \frac{1}{2}\vec{m}' \cdot \sigma,$$

$$(24)$$

where we have used that any traceless 2×2 matrix, including $U^+(\vec{m}\vec{\sigma})U$, can be expanded in terms of the three Pauli matrices as $\vec{m}' \cdot \sigma$. However, in the present case, we know by assumption that the matrix $\vec{m}' \cdot \sigma$ must be diagonal. Thus $m_x = 0$; $m_y = 0$ and

$$U^+\hat{\rho}U = \frac{1}{2}\rho I + \frac{1}{2}m_z'\sigma_z. \quad (25)$$

A comparison with Eq. (19) indicates that m_z' is the spin density m' of Eq. (19). We can now determine m_z' by observing that

$$(m')^2 = Tr[(m'\sigma_z)(m'\sigma_z)]$$

$$= Tr[U^+(\vec{m} \cdot \sigma)UU^+(\vec{m} \cdot \sigma)U]$$

$$= Tr[(\vec{m} \cdot \sigma)(\vec{m} \cdot \sigma)]$$

$$= m^2, \quad (26)$$

where we have made use of the well-known relation [13]

$$(\vec{\sigma} \cdot \vec{C})(\vec{\sigma} \cdot \vec{D}) = \vec{C} \cdot \vec{D} + i\vec{\sigma} \cdot (\vec{C} \times \vec{D}). \quad (27)$$

We can thus write down the spin density in our original (α, β) basis, where $\hat{\rho}$ is not diagonalized as

$$|m| = \sqrt{(\rho^{\alpha\alpha} - \rho^{\beta\beta})^2 + 4\rho^{\alpha\beta}\rho^{\beta\alpha}} \quad (28)$$

using Eq. (22).

In the representation (α', β') that diagonalizes $\hat{\rho}$, we might write the exchange correlation potential as

$$\begin{pmatrix} V_{XC}^{\alpha'} & 0 \\ 0 & V_{XC}^{\beta'} \end{pmatrix} = \frac{\delta E_{XC}[\rho, s]}{\delta\rho}\mathbb{1} + \frac{\delta E_{XC}[\rho, s]}{\delta s}\sigma_z$$

$$= \frac{\delta E_{XC}[\rho, m']}{\delta\rho}\mathbb{1} + \frac{\delta E_{XC}[\rho, m']}{\delta|m'|}\frac{m'\sigma_z}{|m'|}. \quad (29)$$

In the (α, β) basis, we have for the same potential using Eqs. (18) and (26),

$$\begin{pmatrix} V_{XC}^{\alpha} & V_{XC}^{\alpha\beta} \\ V_{XC}^{\beta\alpha} & V_{XC}^{\beta} \end{pmatrix} = \frac{\delta E_{XC}[\rho, |m|]}{\delta\rho}\mathbb{1}$$

$$+ \frac{\delta E_{XC}[\rho, |m|]}{\delta|m|}\frac{U(m'\sigma_z U)^+}{|m|} = \frac{\delta E_{XC}[\rho, |m|]}{\delta\rho}\mathbb{1}$$

$$+ \frac{\delta E_{XC}[\rho, |m|]}{\delta|m|}\frac{\vec{m} \cdot \vec{\sigma}}{|m|}, \quad (30)$$

where the form of $V_{XC}^{\alpha\beta}$ and $V_{XC}^{\beta\alpha}$ can be obtained by equating to the off-diagonal terms on the right-hand side of Eq. (30).

The expression in Eq. (30) is the final form of the generalized noncollinear exchange correlation potential. It makes use of any regular exchange correlation functional $E_{XC}[\rho, s]$. However, it does not require a diagonal density matrix $\hat{\rho}$. In this formulation, the spin quantization $(\vec{m} \cdot \vec{\sigma})/|m|$ is not fixed (collinear) but allowed to change from one point in space to another (noncollinear) as the value of $\rho^{\alpha\alpha}$, $\rho^{\alpha\beta}$, $\rho^{\beta\alpha}$, $\rho^{\beta\beta}$, and thus $\vec{m}$, changes with $\vec{r}$.

The noncollinear formulation of the exchange correlation potential has already been used in non-relativistic DFT calculations on the magnetic properties of solids as well as two-component relativistic DFT calculations [9]. We refer to a recent paper by van Wüllen in Ref. [9] for further details. In the following discussion, we will apply the noncollinear formulation to TDDFT.

NONCOLLINEAR EXCHANGE CORRELATION POTENTIAL AND SPIN-FLIP EXCITATIONS

Excitation energies are calculated in TDDFT by solving Eq. (1). Such a solution requires, in turn, the evaluation of the $A_{ia,jb}$ and $B_{ia,bj}$ matrix elements that are defined in terms of derivatives of the Kohn–Sham Fock matrix element

$$F(\hat{\rho})_{ia} = F(\rho, s)_{ia} = \int \psi_i^+ \left[-\frac{1}{2}\nabla^2 + V_{Ne}(\vec{r}) + V_c(\rho) \right.$$
$$\left. + V_{XC}(\rho, s) \right] \psi_a d\tau, \quad (31)$$

with respect to the density matrix element P_{jb}. In Eq. (31), V_{Ne} is the nuclear attraction operator, V_C is the Coulomb operator, and V_{XC} is the exchange-correlation operator discussed above.

We note again that i, j are occupied orbitals and a, b are virtual orbitals determined from Eq. (4). In the nonrelativistic case considered here, we can assume without restrictions that F^0 is constructed from an exchange-correlation potential with spin polarization along the z-axis such that i, j and a, b are eigenfunctions of σ_z that can be written on the form given in Eq. (9). Thus, F^0 is constructed from a diagonal density matrix given by

$$\hat{\rho}_0 = \sum_i^{occ} \psi_i \psi_i^+ = \begin{pmatrix} \rho_o^{\alpha\alpha} & 0 \\ 0 & \rho_o^{\beta\beta} \end{pmatrix}, \quad (32)$$

where $\rho_o = \rho_o^{\alpha\alpha} + \rho_o^{\beta\beta}$ and $s_o = \rho_o^{\alpha\alpha} - \rho_o^{\beta\beta}$.

The derivative $\partial F_{ia}/P_{jb}$ is related to the change in the matrix element F_{ia} when we change the density matrix from $\hat{\rho}_o$ to $\hat{\rho}_o + P_{jb}\psi_j\psi_b^+$ as

$$\partial F_{ia}/P_{jb} = [F_{ia}(\hat{\rho}_o + P_{jb}\psi_j\psi_b^+) - F_{ia}(\hat{\rho}_o)]/P_{jb}. \quad (33)$$

If j and b are of the same spin, both $\hat{\rho}_o$ and $\hat{\rho}_o + P_{jb}\psi_j\psi_b^+$ are diagonal and the derivative can be eval-

uated by making use of the collinear XC potential. In this case, the derivative will be [7]

$$\frac{\partial F_{ia}}{\partial P_{jb}} = \int \psi_i^+(\vec{r}_1)\psi_a(\vec{r}_1)\psi_j^+(\vec{r}_2)\psi_b(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2$$
$$+ \int (\psi_j^+\psi_b)(\psi_i^+\psi_a) \frac{\delta^2 E_{XC}}{\delta\rho^2} d\tau + \int \left[(\psi_j^+\sigma_z\psi_b)(\psi_i^+\psi_a) \right.$$
$$\left. + (\psi_j^+\psi_b)(\psi_i^+\sigma_z\psi_a) \right] \frac{m_z}{s} \frac{\delta^2 E_{XC}}{\delta\rho\delta s} d\tau + \int (\psi_j^+\sigma_z\psi_b)$$
$$\times (\psi_i^+\sigma_z\psi_a) \frac{\delta^2 E_{XC}}{\delta s^2} d\tau. \quad (34)$$

We note that the above derivative only can be nonzero if i and a are of the same spin. It should also be pointed out that we would obtain the same expression if the noncollinear XC potential of Eq. (30) rather than the collinear XC potential of Eq. (10) is used to construct F, provided that i, j, a, b all are eigenfunctions of σ_z as assumed.

If j and b are of different spin, $\hat{\rho}_o + P_{jb}\psi_j\psi_b^+$ will be nondiagonal, and we must evaluate $F_{ia}(\hat{\rho}_o + P_{jb}\psi_j\psi_b^+)$ as well as the derivative $\delta F_{ia}(\hat{\rho}_o + P_{jb}\psi_j\psi_b^+)/\delta P_{jb}$ based on the noncollinear XC potential of Eq. (30) to obtain [7]:

$$\frac{\partial F_{ia}}{\partial P_{jb}} = \int (\psi_j^+\sigma_x\psi_b)(\psi_i^+\sigma_x\psi_a) \frac{1}{s} \frac{\delta E_{XC}}{\delta s} d\tau + \int (\psi_j^+\sigma_y\psi_b)$$
$$\times (\psi_i^+\sigma_y\psi_a) \frac{1}{s} \frac{\delta E_{XC}}{\delta s} d\tau. \quad (35)$$

It is clear that the above derivative only is different from zero if i has different spin from a and j has different spin from b. If we had incorrectly used the collinear XC potential to construct F_{ia}, the above derivative would have been zero as the terms containing σ_x and σ_y would have been missing [7]. The two expressions in Eqs. (34) and (35) afford the matrix elements required to construct $A_{ia,jb}$. The derivatives $\delta F_{ia}/\delta P_{bj}$ required to construct $B_{ia,bj}$ are obtained by interchanging b and j in Eqs. (34) and (35).

The indices ai and bj enumerate one-electron transitions $\psi_{i\rightarrow}\psi_a$ and $\psi_{j\rightarrow}\psi_b$ with the corresponding transition densities $\psi_i\psi_a$ and $\psi_j\psi_b$. Further $A_{ia,jb}$ and $B_{ia,bj}$ represent couplings between one-electron transitions. We note further that both $A_{ia,jb}$ and $B_{ia,bj}$

are zero if one of the pairs (i, a) or (j, b) are of the same spin and the other of different spins. Thus, spin-flip transitions $\psi_{p \to q}$, in which the two orbitals have different spins, do not mix with one-electron excitations $\psi_{t \to s}$ between orbitals of the same spin. Thus, the two types of excitation can be dealt with in separate TDDFT calculations.

The above formula do not assume a closed-shell ground state and can thus be used for spin-degenerate ground states. They are especially useful as they cover both spin-flip and spin-conserving transitions and thus can be used to resolve multiplet as we have shown in Ref. [10] where spin-flip TDDFT calculations are compared with results from ab initio wave function methods [14, 15].

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