Time-dependent density functional theory based on a noncollinear formulation of the exchange-correlation potential

Fan Wang and Tom Ziegler

Time-dependent density functional theory based on a noncollinear formulation of the exchange-correlation potential

Fan Wang and Tom Ziegler[a]
Department of Chemistry, University of Calgary, Calgary, Alberta T3A1N4, Canada

In this study we have introduced a formulation of time-dependent density functional theory (TDDFT) based on a noncollinear exchange-correlation potential. This formulation is a generalization of conventional TDDFT. The form of this formulation is exactly the same as that of the conventional TDDFT for the excitation energies of transitions that do not involve spin flips. In addition, this noncollinear TDDFT formulation allows for spin-flip transitions. This feature makes it possible to resolve more fully excited state spin multiplets, while for closed-shell systems, the spin-flip transitions will result in singlet-triplet excitations and this excitation energy calculated from this formulation of TDDFT is exactly the same as that from ordinary TDDFT. This formulation is applied to the dissociation of H_2 in its $^1\Sigma_g^+$ ground state and $^1\Sigma_u^+$ and $^3\Sigma_u^-$ excited states with $^3\Sigma_u^-$ ($M_s = +1$) as the reference state and the multiplets splitting of some atoms. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1821494]

I. INTRODUCTION

Time-dependent density functional theory (TDDFT) (Refs. 1–4) has been used extensively in studies on the properties of excited states. Ordinary TDDFT is not able to treat single excitations involving spin flips if the Hartree–Fock exchange potential is not part of the exchange-correlation (XC) potential. A spin-flip approach has already been incorporated in *ab initio* calculations by Krylov.[5,6] Recently Shao *et al.*[7] implemented a spin-flip approach in TDDFT. In their approach, the spin-flip process can only be introduced through the Hartree–Fock exchange potential mixed into the 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. This limitation makes it difficult to fully resolve spin-multiplets resulting from excitations of molecules with an open-shell ground state. In this work we will show that this limitation can be eliminated by introducing the noncollinear representation of the same XC potential.[8–10] With the noncollinear scheme for the XC potential, the spin-flip transitions can automatically be introduced without resorting to the Hartree–Fock exchange.

In this paper we will first introduce the noncollinear representation for the XC potential, then we will derive the TD-DFT formalism based on the noncollinear representation of the XC potential. We will demonstrate the potential of the noncollinear TDDFT formalism by applying it to the study of the dissociation of the ground and excited states of H_2 and the multiplets splitting of some atoms.

II. THE THEORY

A. The noncollinear representation of the XC potential

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

$$E_{XC} \equiv E_{XC}[\rho_\alpha, \rho_\beta], \quad V_{XC}^\alpha = \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha},$$
$$V_{XC}^\beta = \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta}, \tag{1}$$

where ρ_α and ρ_β are the α spin electron density and the β spin electron density, respectively. It can be seen from Eq. (1) that the XC potential only depends on the α spin and β spin densities.

In relativistic density functional calculations for open-shell systems with spin-orbital coupling, the spin is no longer a good quantum number and a noncollinear formulation for the XC potential is often used. In fact this noncollinear expression for the XC potential can also be used in nonrelativistic cases without spin-orbit coupling since the molecular orbitals may not necessarily be eigenfunctions of S_z.[11,12] In the noncollinear scheme, the XC functional and XC potential is defined as

$$E_{XC} \equiv E_{XC}[\rho, s] = E_{XC}[\rho_+, \rho_-],$$
$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho} + \frac{\delta E_{XC}}{\delta s} \frac{\vec{m} \cdot \vec{\sigma}}{s}, \tag{2}$$

where ρ is the total electron density, s is the spin density defined as the length of magnetic vector $\vec{m}$: $s = |\vec{m}|$, the magnetic vector $\vec{m}$ is defined as

$$\vec{m} = \sum_i \psi_i^+ \vec{\sigma} \psi_i, \tag{3}$$

[a]Electronic mail: ziegler@ucalgary.ca

where ψ_i is molecular spinor, $\vec{\sigma}$ in Eqs. (2) and (3) is the Pauli matrix vector, ρ_+ and ρ_- in Eq. (2) play the same role as ρ_α and ρ_β in Eq. (1) and are defined as

$$\rho_+ = \rho + s, \quad \rho_- = \rho - s. \tag{4}$$

The spin density s can be understood from the form of the density matrix $\hat{\rho}$ in S_z space,

$$\hat{\rho} = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix}. \tag{5}$$

The spin density is just the difference between the diagonal elements in the direction along which the density matrix $\hat{\rho}$ is diagonalized. The noncollinear scheme for the XC potential is in fact a generalization of the most often used form of the XC potential defined in Eq. (1). For systems without spin-orbit coupling and the orbitals associated with either α spin or β spin, the density matrix is diagonalized in S_z space and the XC potentials from these two schemes as defined in Eqs. (1) and (2) are exactly the same. The difference between these two schemes in such a case lies in the change of the XC potential with respect to the change of the electron density matrix. If a time-dependent perturbation dependent on σ_x or σ_y is acted on the ground state of the system, even if the zeroth-order density matrix is diagonalized in S_z space, such perturbation will result in a first-order change in $\rho_{\alpha\beta}$. In the ordinary definition for the XC potential in Eq. (1), the XC potential will not change with respect to the small change in $\rho_{\alpha\beta}$, while this first-order change in $\rho_{\alpha\beta}$ can result in spin-flip transitions. This is the reason why spin-flip transitions cannot be included in ordinary TDDFT with Eq. (1) as the expression for the XC potential. However, this is not

the case in the noncollinear scheme for the XC potential and spin-flip process can arise naturally in TDDFT by a change in $\rho_{\alpha\beta}$.

B. TDDFT with noncollinear XC potential

The basic equation used in TDDFT to calculate the excitation energies takes the form[2,3]

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}, \tag{6}$$

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \frac{\partial F_{ia}}{\partial P_{jb}}, \quad B_{ia,bj} = \frac{\partial F_{ia}}{\partial P_{bj}}, \tag{7}$$

where ω is the excitation energy, and F_{ia} and P_{jb} are Fock matrix and density matrix elements, respectively. Since both ω and $-\omega$ are solutions of Eq. (6), to obtain correct excitation energies the X, Y in Eq. (6) must satisfy[13,14]

$$(X^+ \quad Y^+) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = 1. \tag{8}$$

In the above equations, $i,j,\ldots$ are indices used for occupied spinors and $a,b,\ldots$ are indices for empty spinors, $p,q,\ldots$ are indices for general spinors. Equations (6)–(8) are the general equations when the orbitals are not necessarily the eigenfunctions of S_z. It can easily be seen that when the orbitals are associated with either α spin or β spin, with the definition of Eq. (1) for the XC potential, $\partial F_{pq}/\partial P_{st}$ will be zero when orbital s and orbital t have different spins. In the noncollinear scheme for the XC potential, $\partial F_{pq}/\partial P_{st}$ can be written in the following form after some derivations:

$$\frac{\partial F_{pq}}{\partial P_{st}} = \int \psi_p^+(\vec{r}_1)\psi_q(\vec{r}_1)\psi_t^+(\vec{r}_2)\psi_s(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2 + \int (\psi_t^+ \psi_s)\left[\psi_p^+\left(\frac{\delta^2 E_{XC}}{\delta\rho^2} + \frac{\delta^2 E_{XC}}{\delta\rho\delta s}\frac{\vec{m}\cdot\vec{\sigma}}{s}\right)\psi_q\right]d\tau$$

$$+ \int (\psi_t^+ \sigma_x \psi_s)\frac{m_x}{s}\left[\psi_p^+\left(\frac{\delta^2 E_{XC}}{\delta\rho\delta s} + \frac{\delta^2 E_{XC}}{\delta s^2}\frac{\vec{m}\cdot\vec{\sigma}}{s} - \frac{\delta E_{XC}}{\delta s}\frac{\vec{m}\cdot\vec{\sigma}}{s^2}\right)\psi_q\right]d\tau + \int (\psi_t^+ \sigma_y \psi_s)\frac{m_y}{s}\left[\psi_p^+\left(\frac{\delta^2 E_{XC}}{\delta\rho\delta s}\right.\right.$$

$$+ \frac{\delta^2 E_{XC}}{\delta s^2}\frac{\vec{m}\cdot\vec{\sigma}}{s} - \frac{\delta E_{XC}}{\delta s}\frac{\vec{m}\cdot\vec{\sigma}}{s^2}\right)\psi_q\Big]d\tau + \int (\psi_t^+ \sigma_z \psi_s)\frac{m_z}{s}\left[\psi_p^+\left(\frac{\delta^2 E_{XC}}{\delta\rho\delta s} + \frac{\delta^2 E_{XC}}{\delta s^2}\frac{\vec{m}\cdot\vec{\sigma}}{s} - \frac{\delta E_{XC}}{\delta s}\frac{\vec{m}\cdot\vec{\sigma}}{s^2}\right)\psi_q\right]d\tau$$

$$+ \int (\psi_t^+ \sigma_x \psi_s)(\psi_p^+ \sigma_x \psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau + \int (\psi_t^+ \sigma_y \psi_s)(\psi_p^+ \sigma_y \psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau + \int (\psi_t^+ \sigma_z \psi_s)(\psi_p^+ \sigma_z \psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau. \tag{9}$$

This is the general equation that can be used to calculate A and B matrix elements in Eq. (6) when the molecular orbitals are not eigenfunctions of S_z, for example, when spin-orbital coupling is present. Equation (9) can be further simplified in some special cases. For closed-shell systems, we will have the following additional conditions with $s \to 0$:

$$\frac{\delta E_{XC}}{\delta s} \to 0, \quad \frac{\delta^2 E_{XC}}{\delta\rho\delta s} \to 0, \quad \frac{1}{s}\frac{\delta E_{XC}}{\delta s} \to \frac{\delta^2 E_{XC}}{\delta s^2}. \tag{10}$$

Equation (9) can be simplified as follows:

$$\frac{\partial F_{pq}}{\partial P_{st}} = \int \psi_p^+(\vec{r}_1)\psi_q(\vec{r}_1)\psi_t^+(\vec{r}_2)\psi_s(\vec{r}_2)\frac{1}{|\vec{r}_1-\vec{r}_2|}d\tau_1 d\tau_2$$

$$+ \int \psi_t^+\psi_s\psi_p^+\psi_q \frac{\delta^2 E_{XC}}{\delta\rho^2}d\tau + \int (\psi_t^+\sigma_x\psi_s)$$

$$\times(\psi_p^+\sigma_x\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau + \int (\psi_t^+\sigma_y\psi_s)$$

$$\times(\psi_p^+\sigma_y\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau + \int (\psi_t^+\sigma_z\psi_s)$$

$$\times(\psi_p^+\sigma_z\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau. \tag{11}$$

Equation (11) combined with Eqs. (6)–(8) can be used to calculate the excitation energies for close-shell systems when spin-orbital coupling is present. When spin-orbital coupling is neglected and the orbitals are chosen as eigenfunctions of S_z, we have $m_x=0$, $m_y=0$, and $s=|m_z|$; Eq. (9) can be simplified as

$$\frac{\partial F_{pq}}{\partial P_{st}} = \int \psi_p^+(\vec{r}_1)\psi_q(\vec{r}_1)\psi_t^+(\vec{r}_2)\psi_s(\vec{r}_2)\frac{1}{|\vec{r}_1-\vec{r}_2|}d\tau_1 d\tau_2$$

$$+ \int (\psi_t^+\psi_s)(\psi_p^+\psi_q)\frac{\delta^2 E_{XC}}{\delta\rho^2}d\tau + \int [(\psi_t^+\sigma_z\psi_s)$$

$$\times(\psi_p^+\psi_q)+(\psi_t^+\psi_s)(\psi_p^+\sigma_z\psi_q)]\frac{m_z}{s}\frac{\delta^2 E_{XC}}{\delta\rho\delta s}d\tau$$

$$+ \int (\psi_t^+\sigma_z\psi_s)(\psi_p^+\sigma_z\psi_q)\frac{\delta^2 E_{XC}}{\delta s^2}d\tau$$

$$+ \int (\psi_t^+\sigma_x\psi_s)(\psi_p^+\sigma_x\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau$$

$$+ \int (\psi_t^+\sigma_y\psi_s)(\psi_p^+\sigma_y\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau. \tag{12}$$

From Eq. (12) it can easily be shown that when p, q have the same spin and s, t have different spins or when p, q have different spins and s, t have the same spin, the right hand side of Eq. (12) will be zero. When p, q have the same spin and s, t have the same spin, Eq. (12) can be written as

$$\frac{\partial F_{pq}}{\partial P_{st}} = \int \psi_p^+(\vec{r}_1)\psi_q(\vec{r}_1)\psi_t^+(\vec{r}_2)\psi_s(\vec{r}_2)\frac{1}{|\vec{r}_1-\vec{r}_2|}d\tau_1 d\tau_2$$

$$+ \int (\psi_t^+\psi_s)(\psi_p^+\psi_q)\frac{\delta^2 E_{XC}}{\delta\rho^2}d\tau + \int [(\psi_t^+\sigma_z\psi_s)$$

$$\times(\psi_p^+\psi_q)+(\psi_t^+\psi_s)(\psi_p^+\sigma_z\psi_q)]\frac{m_z}{s}\frac{\delta^2 E_{XC}}{\delta\rho\delta s}d\tau$$

$$+ \int (\psi_t^+\sigma_z\psi_s)(\psi_p^+\sigma_z\psi_q)\frac{\delta^2 E_{XC}}{\delta s^2}d\tau. \tag{13}$$

With the following relations:

$$\frac{\delta^2 E_{XC}}{\delta\rho^2} = \frac{1}{4}\left(\frac{\delta^2 E_{XC}}{\delta\rho_\alpha^2} + \frac{\delta^2 E_{XC}}{\delta\rho_\beta^2} + 2\frac{\delta^2 E_{XC}}{\delta\rho_\alpha\delta\rho_\beta}\right), \tag{14}$$

$$\frac{\delta^2 E_{XC}}{\delta s^2} = \frac{1}{4}\left(\frac{\delta^2 E_{XC}}{\delta\rho_\alpha^2} + \frac{\delta^2 E_{XC}}{\delta\rho_\beta^2} - 2\frac{\delta^2 E_{XC}}{\delta\rho_\alpha\delta\rho_\beta}\right), \tag{15}$$

$$\frac{m_z}{s}\frac{\delta^2 E_{XC}}{\delta\rho\delta s} = \frac{1}{4}\left(\frac{\delta^2 E_{XC}}{\delta\rho_\alpha^2} - \frac{\delta^2 E_{XC}}{\delta\rho_\beta^2}\right). \tag{16}$$

It can be seen that Eq. (13) is exactly the same as the most often used formula for $\partial F_{pq}/\partial P_{st}$ in TDDFT with the XC potential defined in Eq. (1). When p, q have different spins and s, t have different spins, Eq. (12) can be simplified as

$$\frac{\partial F_{pq}}{\partial P_{st}} = \int (\psi_t^+\sigma_x\psi_s)(\psi_p^+\sigma_x\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau$$

$$+ \int (\psi_t^+\sigma_y\psi_s)(\psi_p^+\sigma_y\psi_q)\frac{1}{s}\frac{\delta E_{XC}}{\delta s}d\tau. \tag{17}$$

It can be seen that if p, s have different spins and q, t have different spins, Eq. (17) will be zero. Due to this point, Eq. (17) can de written as

$$\frac{\partial F_{pq}}{\partial P_{st}} = \frac{1}{2}\int [(\psi_p^+\sigma_x\psi_q)(\psi_t^+\sigma_x\psi_s)+(\psi_p^+\sigma_y\psi_q)$$

$$\times(\psi_t^+\sigma_y\psi_s)]\frac{1}{(\rho_\alpha-\rho_\beta)}\left(\frac{\delta E_{XC}}{\delta\rho_\alpha} - \frac{\delta E_{XC}}{\delta\rho_\beta}\right)d\tau, \tag{18}$$

where p, s have the same spin, q, t have the same spin, and p, q have different spins. Equation (18) is the ultimate equation that is used to describe the spin-flip transitions in the noncollinear formulation of TDDFT. For closed-shell systems, the spin-flip transitions will result in singlet to triplet excitations. With Eqs. (10) and (15), it can be seen that Eq. (18) is exactly the same as the formula used to calculate the singlet-triplet excitation energies with ordinary TDDFT for closed-shell systems.

With the property of $\partial F_{pq}/\partial P_{st}$ for spin-flip transitions, the A and B matrix in Eq. (6) takes the following form:

$$A=\begin{pmatrix} A_{i^\alpha a\beta,j^\alpha b\beta} & 0 \\ 0 & A_{i\beta a\alpha,j\beta b\alpha} \end{pmatrix},$$

$$B=\begin{pmatrix} 0 & B_{i^\alpha a\beta,b^\alpha j\beta} \\ B_{i\beta a\alpha,b\beta j\alpha} & 0 \end{pmatrix}. \tag{19}$$

For this spin-flip process, the A-B matrix will no longer be diagonal as in ordinary TDDFT with pure XC potential.

From the above arguments, it can be seen that the noncollinear TDDFT is in fact a generalization of ordinary TD-DFT for systems without spin-orbit coupling and the orbitals associated with either spin α or spin β. Besides all the excitations already included in the ordinary TDDFT, the noncollinear TDDFT also includes excitations involving spin-flip transitions. The noncollinear TDDFT is exactly the same as the ordinary TDDFT theory for the excitations not involving spin-flip transitions. For closed-shell systems, the spin-flip transitions will result in singlet to triplet excitations and the excitation energies calculated from the noncollinear TDDFT for such transitions are the same as those from the ordinary TDDFT. For open-shell systems, the spin-flip process allows one to calculate excitations that are unattainable in ordinary TDDFT such as the excitations from doublet states to quartet

states. This feature makes it possible to fully resolve the spin multiplets of the excited states for systems with open-shell ground states as we will discuss in a forthcoming paper. Another interesting feature of the spin-flip TDDFT is that it makes it possible to calculate some double excitations, which will be shown below.

III. APPLICATION

In the present work, we apply this noncollinear TDDFT derived above to study the dissociation limit for the H_2 molecule and the multiplets splitting of some atoms.

A. The dissociation limit of H_2

The correct dissociation limit for the ground state of H_2 is still a problem in DFT, although the physical picture of the dissociating H_2 is very clear: to describe the dissociation of H_2 correctly the wave function of the ground state for dissociating H_2 must be expressed with a multideterminant. Theoretically DFT should be able to handle such situations with a single Slater determinant and recently Baerends and co-workers[15,16] have studied this case with a complicated XC energy functional that is a functional of both occupied and virtual Kohn-Sham orbitals. However, with the form of the current approximate XC functional, DFT can only deal with H_2 dissociation by breaking the symmetry and resort to spin unrestricted calculations. As for the study of excitation energies of dissociating H_2 with TDDFT based on Eq. (6), some recent investigations[17–19] demonstrate that the excitation energy for the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition is imaginary at large H–H bond lengths, which demonstrates that the ground state of H_2 calculated with the form of current approximate XC functionals is already unstable before dissociation. The $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ excitation energy based on Eq. (1) approaches zero at the dissociation limit with TDDFT, while it should be about 10 eV and the $^1\Sigma_u^+$ state should dissociate to H^+ and H^-. [More accurately, it should dissociate to one normal H atom and one excited H atom (Ref. 19).] With the spin-unrestricted approach, the correct dissociation limit can be obtained for the ground state of H_2, but serious spin contamination is introduced and the calculated excitation energies from such a ground state based on TDDFT cannot be used to describe the excited states of a dissociating H_2. To circumvent the above problems in TDDFT Casida et al.[18] and Gritsenko[19] et al. introduced correction terms in the XC kernel or the A matrix.

Basically, these problems are connected with the limitation of present approximate XC functionals for the states with a strong multiconfiguration character. If we can start from a state whose wave function can adequately be expressed by a single Slater determinant, the above problems may be solved to some extent. The $^3\Sigma_u^+$ ($M_S = \pm 1$) state for H_2 can to a first approximation be described by a single Slater determinant and the correct dissociation limit of this state can adequately be obtained using DFT with often used approximate XC functionals. The correct dissociation behavior of the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states may be recovered if we can calculate the transition energies from the $^3\Sigma_u^+$ ($M_S = \pm 1$) state to the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states. However, these two transitions will involve spin-flip processes and such processes can
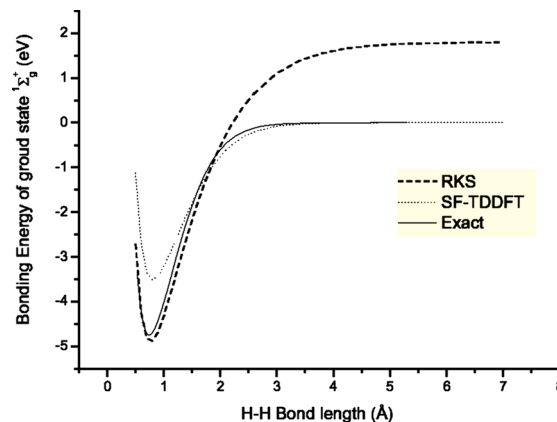

FIG. 1. The binding energy of $^1\Sigma_g^+$ state for H_2 at different H–H bond lengths with restricted Kohn-Sham method and spin-flip TDDFT.

only be studied with the noncollinear TDDFT theory introduced in the present work. It is also interesting to note that in such a case, the excitation energies of some double excitations such as $(\sigma_g)^2 \rightarrow (\sigma_u)^2$ can also be calculated with the $^3\Sigma_u^+$ ($M_S = \pm 1$) state as reference using the noncollinear TDDFT theory.

We use $^3\Sigma_u^+$ ($M_S = +1$) as the reference state to calculate the transition energies from the $^3\Sigma_u^+$ ($M_S = +1$) state to $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states for H_2 with Eqs. (18) and (19). For this $^3\Sigma_u^+$ ($M_S = +1$) state, there is no spin β electrons and Eq. (6) reduces to

$$AX = \omega X. \qquad (20)$$

This is the same as the Tamm-Dancoff approximation (TDA) (Ref. 20) for Eq. (6), and Eq. (8) can be satisfied trivially with $Y = 0$. We calculate the transition energies from $^3\Sigma_u^+$ to $^1\Sigma_g^+$ and $^1\Sigma_u^+$ at different H–H bond length with the Amsterdam Density Functional program[21] using a TZ2P basis set with the local density functional approximation (LDA) for the XC potential. The potential energy curve for $^1\Sigma_g^+$ is plotted in Fig. 1 and the excitation energies from $^3\Sigma_u^+$ to $^1\Sigma_g^+$ and $^1\Sigma_u^+$ with respect to the H–H bond length are plotted in Fig. 2 and Fig. 3, respectively. The exact potential energy curves[22,23] are also plotted for comparison. The calculated
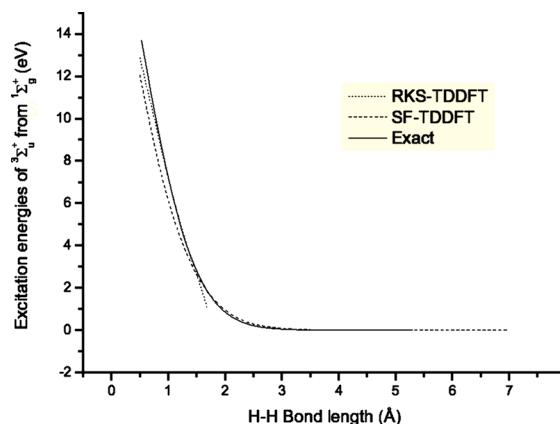

FIG. 2. The excitation energy of $^3\Sigma_u^+$ from $^1\Sigma_g^+$ state for H_2 at different H–H bond lengths with ordinary TDDFT and spin-flip TDDFT.

J. Chem. Phys., Vol. 121, No. 24, 22 December 2004

Noncollinear TDDFT   12195

FIG. 3. The excitation energy of $^1\Sigma_u^+$ from $^1\Sigma_g^+$ state for H$_2$ at different H–H bond lengths with ordinary TDDFT and spin-flip TDDFT.
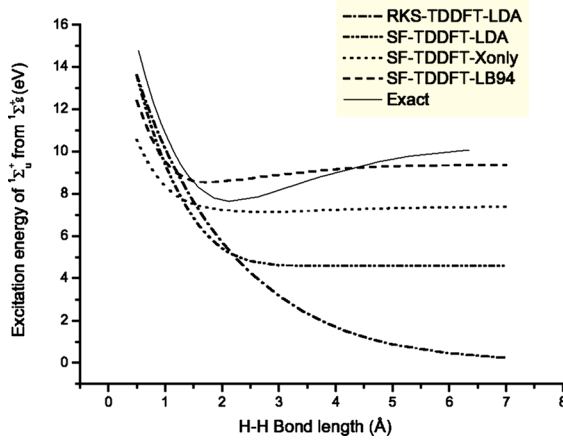
transition energies from $^3\Sigma_u^+$ ($M_S = +1$) to $^3\Sigma_u^+$ ($M_S = 0$) at different bond lengths are always <0.05 eV, which illustrates the internal consistency of this noncollinear TDDFT method for spin-flip process proposed here. From these figures it can be seen that the obtained ground state $^1\Sigma_g^+$ has a correct dissociation limit and the energy difference between $^1\Sigma_u^+$ and $^1\Sigma_g^+$ is about 4.5 eV at the dissociation limit, which is still much lower than the exact value, that is about 10 eV. Furthermore, the potential energy surface of $^1\Sigma_u^+$ does not display a weakly bound character as the exact energy surface does. The performance of this spin-flip theory for this system can be explained with a two-level model system in the dissociation limit in the following way.

Taken s_a and s_b as the $1s$ atomic orbital centered on two H atoms, the wave function of the $^3\Sigma_u^+$ ($M_S = +1$) state can be described by a Slater determinant $|\sigma_g\alpha\sigma_u\alpha|$. At the dissociation limit where s_a and s_b do not overlap with each other, σ_g and σ_u can be written as

$$\sigma_g(\vec{r}) = \frac{1}{\sqrt{2}}[s_a(\vec{r}) + s_b(\vec{r})], \tag{21}$$

$$\sigma_u(\vec{r}) = \frac{1}{\sqrt{2}}[s_a(\vec{r}) - s_b(\vec{r})]. \tag{22}$$

It can easily be shown that the orbital energies of σ_g and σ_u and the $\partial F_{ia}/\partial P_{jb}$ in Eq. (7) satisfies

$$\varepsilon_g^\alpha = \varepsilon_u^\alpha = \varepsilon_H^\alpha, \quad \varepsilon_g^\beta = \varepsilon_u^\beta = \varepsilon_H^\beta, \tag{23}$$

$$\frac{\partial F_{\sigma_g^\beta\sigma_g^\alpha}}{\partial P_{\sigma_g^\beta\sigma_g^\alpha}} = \frac{\partial F_{\sigma_u^\beta\sigma_u^\alpha}}{\partial P_{\sigma_u^\beta\sigma_u^\alpha}} = \frac{\partial F_{\sigma_g^\beta\sigma_u^\alpha}}{\partial P_{\sigma_g^\beta\sigma_u^\alpha}}$$

$$= \frac{\partial F_{\sigma_u^\beta\sigma_g^\alpha}}{\partial P_{\sigma_u^\beta\sigma_g^\alpha}}$$

$$= \frac{\partial F_{\sigma_u^\beta\sigma_u^\alpha}}{\partial P_{\sigma_g^\beta\sigma_g^\alpha}} = \frac{\partial F_{\sigma_g^\beta\sigma_u^\alpha}}{\partial P_{\sigma_u^\beta\sigma_g^\alpha}}$$

$$= \frac{1}{2}(\varepsilon_H^\alpha - \varepsilon_H^\beta), \tag{24}$$

TABLE I. The multiplet splitting of some atoms (unit eV).

Atom (Ground sate)	State	SF-TDA	SF	Expt.[a]
Carbon (^3P)	^1D	1.358	1.318	1.264
Nitrogen (^4S)	^2D	2.417	2.375	2.384
	^2P	4.025	4.025	3.576
Oxygen (^3P)	^1D	1.933	1.892	1.967
Silicon (^3P)	^1D	0.732	0.699	0.781
Phosphorus (^4S)	^2D	1.253	1.213	1.409
	^2P	2.172	2.172	2.323
Sulfur (^3P)	^1D	0.970	0.920	1.145

[a]Reference 25.

where ε_H^α and ε_H^β are α spin and β spin orbital energies of an isolated H atom. The transition energies from $^3\Sigma_u^+$ to $^1\Sigma_g^+$ and $^1\Sigma_u^+$ are calculated to be zero and $\varepsilon_H^\beta - \varepsilon_H^\alpha$, respectively with Eqs. (18) and (19) at the dissociation limit. The correct dissociation limit of $^3\Sigma_u^+$ results in the correct dissociation limit of $^1\Sigma_g^+$. The orbital energy difference $\varepsilon_H^\beta - \varepsilon_H^\alpha$ can be written as

$$\varepsilon_H^\beta - \varepsilon_H^\alpha = \int (V_{XC}^\beta - V_{XC}^\alpha)s_a^2 d\tau. \tag{25}$$

The underestimation of the dissociation limit energy with the LDA for $^1\Sigma_u^+$ can be understood from Eq. (25). For the one-electron H atom system, V_{XC}^β should be zero and V_{XC}^α should be equal to minus the Coulomb potential of this electron. In the LDA potential, V_{XC}^β does not equal to zero due to the contribution of the correlation part and V_{XC}^α could not cancel the Coulomb potential because of the self-interaction error embedded in the approximate XC potential. We calculate the transition energy with exchange only potential as well as the LB94 potential[24] which has a correct long-range asymptotic behavior to cancel the Coulomb potential partially at large interelectron distance. The results are plotted in Fig. 3. It can be seen that the results are improved dramatically for $^1\Sigma_u^+$. Both results show a weakly bound character and the dissociating limit with the LB94 potential agrees much better with the accurate value.

B. The multiplet splitting of the lowest energy configurations for some atoms

We calculated the multiplets splitting of C, N, O, Si, P, and S with LDA approximation for XC potential and TZ2P basis set. The multiplet splitting of atoms can only be resolved with spin-flip TDDFT. The calculated multiplet splitting of these atoms are listed in Table I. For N and P, the ground states are spatially nondegenerate with the term ^4S and it is relatively easy to resolve the multiplets ^2D and ^2P. This is not the case for the other atoms, all of which have two unpaired p orbitals. In our calculations, we make use of D_{7d} symmetry and situate the two unpaired p electrons in the two e_{1u} orbitals of α spin for the ground state configuration. This ground state corresponding to the configuration $(e_{1u})^2$ gives rise to the ^3P state with M_S equal to one and M_l equal to zero. The calculated excited states can be assigned according to the irreducible representation of the D_{7d} group. With the current implementation of spin-flip TDDFT, we can only

calculate the ^3P and ^1D splitting of these atoms. From the results in Table I, it can be seen that the multiplet splitting calculated even with the simple LDA XC potential agrees very well with the experimental data, except for the ^4S $-^2P$ splitting of C. The error for the splittings is always <0.2 eV.

IV. CONCLUSION

In the present work, we have introduced a TDDFT formulation based on the noncollinear XC potential. This noncollinear TDDFT is a generalization of ordinary TDDFT. Besides the excitations that can be treated in ordinary TDDFT, the noncollinear TDDFT can also deal with spin-flip transitions. This makes it possible to resolve more fully the spin multiples of excited states from an open-shell ground state, while for closed-shell systems, the spin-flip transitions will result in singlet-triplet excitations and the excitation energies calculated from the noncollinear TDDFT for spin-flip transitions are the same as those from the ordinary TDDFT. We have applied this theory to a study of the dissociation limit for H_2 using ordinary XC potential and the multiplets splitting of some atoms. It is shown that the correct dissociation limit for the ground and excited states for H_2 can be recovered with noncollinear TDDFT for the spin-flip transitions from the reference state $^3\Sigma_u^-$ ($M_S=+1$). As for the multiplets splitting, the results agree very well with experimental data with an error mostly <0.2 eV.

ACKNOWLEDGMENTS

[1] E. K. U. Gross and W. Kohn, Adv. Quantum Chem. **21**, 255 (1990).
[2] M. E. Casida, in *Recent Advances in Density Functional Methods*, edited by D. P. Chong (World Scientific, Singapore, 1995), Vol. I, p. 155.
[3] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).
[4] J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, Comput. Phys. Commun. **118**, 119 (1999).
[5] A. I. Krylov, Chem. Phys. Lett. **338**, 375 (2001).
[6] A. I. Krylov, Chem. Phys. Lett. **350**, 522 (2001).
[7] Y. Shao, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **118**, 4807 (2003).
[8] H. Eshrig and V. D. P. Servedio, J. Comput. Chem. **20**, 23 (1999).
[9] C. van Wüllen, J. Comput. Chem. **23**, 779 (2002).
[10] F. Wang and W. Liu, J. Chin. Chem. Soc. (Taipei) **50**, 597 (2003).
[11] S. Yamanaka, D. Yamaki, Y. Shigeta, H. Nagao, Y. Yoshioka, N. Suzuki, and K. Yamaguchi, Int. J. Quantum Chem. **80**, 664 (2000).
[12] S. Yamanaka, D. Yamaki, Y. Shigeta, H. Nagao, and K. Yamaguchi, Int. J. Quantum Chem. **84**, 670 (2001).
[13] P. Jørgensen and J. Simons, *Second Quantization Based Methods in Quantum Chemistry* (Academic, New York, 1981).
[14] F. Furche, J. Chem. Phys. **114**, 5982 (2001).
[15] E. J. Baerends, Phys. Rev. Lett. **87**, 133004 (2001).
[16] M. Grüning, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **118**, 7183 (2003).
[17] Z. Cai and J. R. Reimers, J. Chem. Phys. **112**, 527 (2000).
[18] M. E. Casida, F. Gutierrez, J. Guan, F. Gadea, D. Salahub, and J. Daudey, J. Chem. Phys. **113**, 7062 (2000).
[19] O. V. Gritsenko, S. J. A. van Gisbergen, A. Görling, and E. J. Baerends, J. Chem. Phys. **113**, 8478 (2000).
[20] S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **314**, 291 (1999).
[21] G. te Velde, F. M. Bickelhaupt, E. J. Baerend, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001).
[22] W. Kolost and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).
[23] W. Kolost and L. Wolniewicz, J. Chem. Phys. **45**, 509 (1966).
[24] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[25] C. E. Moore, *Atomic Energy Levels*, Nat. Bur. Stand. (U. S.) Circ. No. 467, (U. S. GPO, Washington, D.C., 1949), Vol. 1.