

High-order-harmonic generation and ionization from H₂ by time-dependent density-functional theory

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Abstract. The ionization and high-order harmonic generation (HHG) of a hydrogen molecule in an ultra-short intense laser are investigated by using the time-dependent density functional theory (TDDFT). Our numerical results show, the higher ionization probability and lower cutoff energy of harmonic emission compared with those from the time-dependent Schrödinger equation (TDSE), which is caused by the smaller ionization energy from TDDFT. The disparities of the HHG transient behavior and the attosecond pulse are also discussed.

Key words: time-dependent density functional, high-order harmonic generation, attosecond

1. Introduction

When atoms and molecules are irradiated by intense laser pulses, many novel nonlinear phenomena are observed, such as the above threshold ionization, higher-order harmonic generation (HHG), and non-sequential double ionization, etc.[1-4]. Recently, experiment development provided novel light source with shorter duration (up to a attosecond scale) and higher frequency (through a HHG process or a free electron laser technique)[5-17]. When atoms and molecules interact with the novel light source, many interesting phenomena are observed, such as the ionization and HHG from the inner shell, the ionization delay from the different shell and the charge transfer in the different atoms of the molecules etc. [18-21]. In these process, the electron correlation play an important role and the single active electron approximation is invalid [22-25].

In the interaction of strong laser pulses with molecules, the time-dependent Schrödinger equation including many electrons should be considered, many approaches have been developed, however the accurate solution of TDSE is restricted only the two electron system because of (due to) the limitation of computational ability[26]. When the laser field is linear polarized, one can investigate the multi-electron system by using the scheme of reduction of the computational dimension [27, 28]. Based on the expansion of the basis functions, the multi-configuration time-dependent method and the time-dependent multi-configuration self-consistent field scheme can obtain an accurate result [29-31]. Using this scheme, the multi-photon excitation and ionization process were investigated. However, this scheme meets huge computation difficulty when the laser intensity is strong. In this situation, the electron after tunnel can reach the state with high energy, thus the necessary number of the basis functions is very large [32, 33].

Recently, the time-dependent density functional theory (TDDFT) is used in the strong field physics due to the more efficiency dealing with the multi-electron problem. Using this

scheme, Russakoff et al. investigated the ionization and dissociation process the molecules, and analyzed the effect of molecular the alignment and ionization from inner shell [34-35]. Using the scheme, one (to) investigate the attosecond absorb spectrum to analyze the instant variation of the excited energy level in the femtosecond laser pulse [36-38]. In addition, the HHG processes were (was) also studied by using TDDFT [39-41].

By adopting an accurate correlation function, the TDDFT can be regard as the exact method [42, 43]. The adiabatic local density functional approximation (LDA) or Generalized Gradient Approximation (GGA) potential function are usually adopted. However, in the process of molecules interact with the strong laser field, the potential function shows a steep behavior due to the rapid ionization [44, 45]. Therefore, the adequacy of the TDDFT on the strong field study should be examined. In this work, by using TDDFT, we systematically investigate the HHG and ionization process of one-dimensional hydrogen molecule irradiated by a linearly polarized laser pulse. In the interaction of the linearly polarized laser, the one-dimensional model can well describe the physical process. The model molecule can also be studied by directly integrating the corresponding Schrödinger equation, which provides a reliable test standard. Using TDDFT and TDSE schemes, the ionization and HHG of the hydrogen molecule irradiated by the strong laser pulse are compared. It is found that, the results from TDDFT qualitatively agree with those from TDSE, which provide a obvious proof that the TDDFT can be used to study the interaction between strong laser pulses with complex many electron molecules.

Atomic units are used throughout this paper unless otherwise stated.

2. Theoretical methods

Under the dipole approximation and length gauge, the TDSE for a hydrogen molecule interacting with an intense laser pulse can be described:

$$\hat{H} = \sum_{i=1}^2 \left[-\frac{1}{2} \frac{\partial^2}{\partial r_i^2} - \frac{1}{\sqrt{(r_i \pm R/2)^2 + c}} \right] + \frac{1}{\sqrt{(r_1 - r_2)^2 + d}} + (r_1 + r_2) E_0 \varepsilon(t) \cos(\omega t), \quad (1)$$

Where r_1 , r_2 are the coordinates of the two electrons respectively, the distance between the two nuclei $R=1.68a.u.$, c and d are the soft-core parameters for avoiding the singularity problem. $\varepsilon(t)$ is the

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envelope function of the laser pulse, E_0 and ω is the peak amplitude and frequency of the incident laser pulse, t_0 is the middle time of the electric field, τ_0 is full width at half maximum, $\phi = \pi$ is the initial phase. The electric field chosen in this paper is the *cos* form:

$$f(x) = \begin{cases} E_0 \cos\left(\frac{\pi t - 2\tau_0 - t_0}{2\tau_0}\right) \cos(\omega t + \phi), \\ 0 & |t - t_0| > \tau_0, |t - t_0| > 0. \end{cases} \quad (2)$$

Using the symmetric splitting operator method to solve the equation (1), we obtain the time-dependent wave function of the system at any time. The initial state is produced by the imaginary time evolution scheme [46,47]. This equation also can be calculated by TDDFT, the above TDSE is transformed into the time-dependent Kohn-Sham equations of single particle[48-50]:

$$i \frac{\partial}{\partial t} \Psi_i(\mathbf{r}, t) = \left[-\frac{\nabla^2}{2} + V_{\text{eff}}(\mathbf{r}, t) \right] \Psi_i(\mathbf{r}, t) \quad i = 1, \dots, N, \quad (3)$$

N is the number of Kohn-Sham(KS) orbitals $\Psi_i(\mathbf{r}, t)$, and $V_{\text{eff}}(\mathbf{r}, t)$ is the KS potential defined as:

$$V_{\text{eff}}(\mathbf{r}, t) = \int \frac{n(\mathbf{r}', t)}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + V_{\text{ext}}(\mathbf{r}, t) + V_{\text{xc}}(\mathbf{r}, t), \quad (4)$$

Where $n(\mathbf{r}', t)$ represents the time-dependent density of the multi-electron interacting system given by $n(\mathbf{r}', t) = \sum_{i=1}^N |\Psi_i(\mathbf{r}, t)|^2$. $V_{\text{ext}}(\mathbf{r}, t)$ represents the interaction energy the electrons and the laser field. $V_{\text{xc}}(\mathbf{r}, t)$ is the exchange correlation potentials:

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}, \quad (5)$$

In this paper, the exchange correlation energy E_{xc} are chosen as the LDA:

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3 \mathbf{r} e_{\text{xc}}^{\text{unif}}(n(\mathbf{r})), \quad (6)$$

and the GGA scheme:

$$E_{\text{xc}}^{\text{GGA}}[n] = \int d^3 \mathbf{r} e_{\text{xc}}(n(\mathbf{r}), |\nabla n|), \quad (7)$$

By using the Fourier transform of the time-dependent dipole, the harmonic spectrum of hydrogen molecule under strong laser field can be obtained:

$$P(\omega) = \left| \frac{1}{t_f - t_i} \int_{t_i}^{t_f} d(t) e^{-i\omega t} \right|^2, \quad (8)$$

In order to compare the results of TDDFT and TDSE in detail, the time and frequency behavior of harmonic emission is studied by the wavelet transform:

$$A(t_0, \omega) = \int_{t_i}^{t_f} d(t) \kappa_{t_0, \omega}(t) dt, \quad (9)$$

Here, the core of the wavelet is chosen as:

$$\kappa_{t_0, \omega}(t) = \frac{1}{\sqrt{\tau}} e^{i\omega t} e^{-\omega^2(t-t_0)^2/(2\tau^2)}, \quad (10)$$

3. Results and discussion

In order to study the ionization and HHG of H_2 molecule under an intense laser pulse, we first calculate the initial wave function and energy of the system. The soft-core parameters $c=0.7$ and $d=1.2375$, respectively. The initial energy of the system is -2.31 a.u. by calculating TDSE. The initial energies from TDDFT by using LDA and GGA are -2.25 a.u. and -2.28 a.u., respectively. The corresponding initial state electron densities are shown in Figure 1. It can be seen that, the two electron density distributions are almost the same, and the density from TDSE is more local because of the lower energy of the ground state.

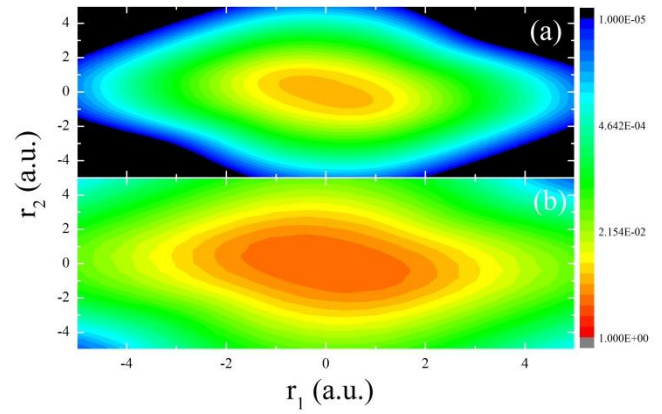


Figure 1: Spatial distributions of the ground state electron density calculated from (a) the TDSE and (b) the TDDFT schemes.

The wave function of H_2 molecule in the strong laser field can be achieved from the initial state by the time-dependent evolution. Figure 2 presents the ionization probabilities of the hydrogen molecule under the ultra-short laser pulses from TDSE and TDDFT. Here, the frequency and duration of the incident laser are 0.057 a.u. and 3 cycles, respectively, and the peak electric field amplitude is increased from 0.01 a.u. to 0.15 a.u.. It can be seen from the figure, the ionization behaviors from TDSE and TDDFT are qualitatively consistent: the ionization yields are gradually enhanced with the increase of the laser intensities.

The ionization probability of LDA is larger than that of GGA, and the calculated ionization probability of GGA is larger than that of TDSE. The difference can be attributed to the ground state energy is different, with the same laser intensity in the three calculated systems and the ground state binds to a larger corresponding ionization.

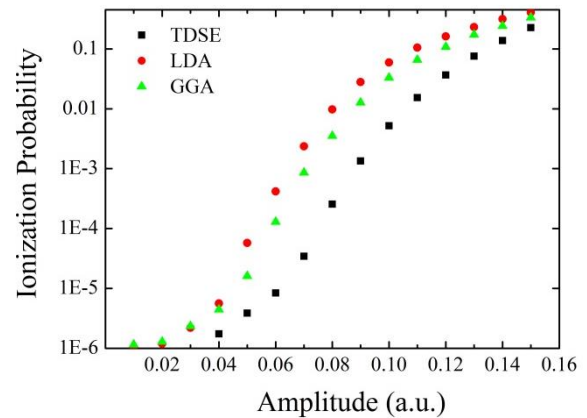


Figure 2: Variation of ionization probability with the laser electric field amplitude calculated from TDSE and TDDFT.

In addition to the ionization of the system, TDDFT can be used to study the HHG of complex molecular systems. Figure 3 shows the high-order harmonic spectrum from the hydrogen molecule in the strong ultra-short laser pulse. It can be noticed that, with the increase of the harmonic order, the harmonic intensity begins to decrease rapidly, then a platform structure appears, and the harmonic efficiency is quickly declined when the harmonic order is larger than the 53rd. According to the semi-classical three-step model[51], the cutoff of the harmonic spectrum by solving the