

# High-order-harmonic generation and ionization from H<sub>2</sub> 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  $\omega$  is the peak amplitude and frequency of the incident laser pulse,  $t_0$  is the middle time of the electric field,  $\tau_0$  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]:

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

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

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

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

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

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

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

and the GGA scheme:

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

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

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

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.

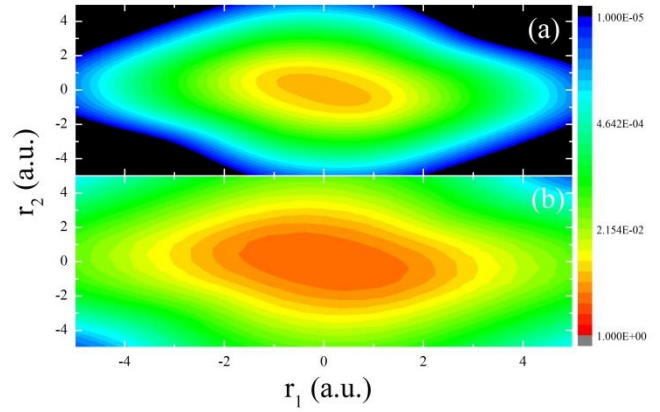


Figure 1: Spatial distributions of the ground state electron density calculated from (a) the TDSE and (b) the TDDFT schemes.

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.

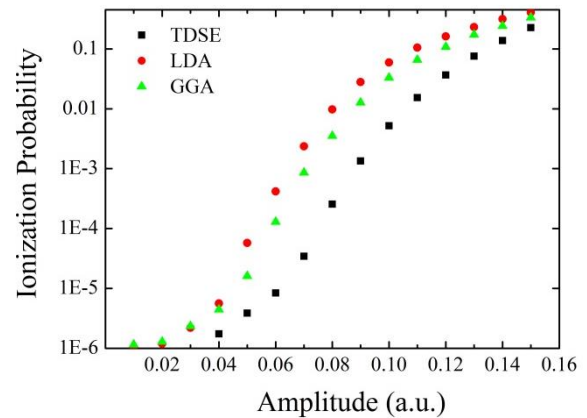
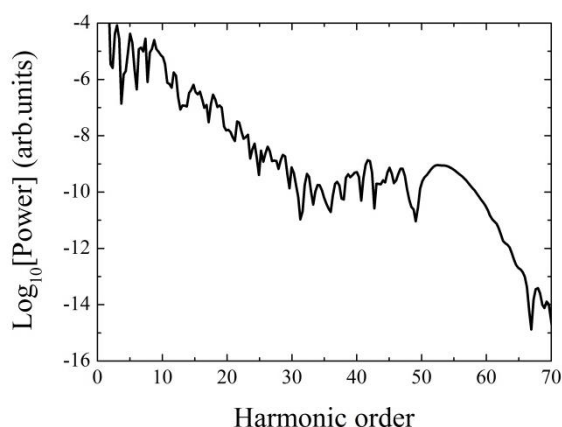


Figure 2: Variation of ionization probability with the laser electric field amplitude calculated from TDSE and TDDFT.

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

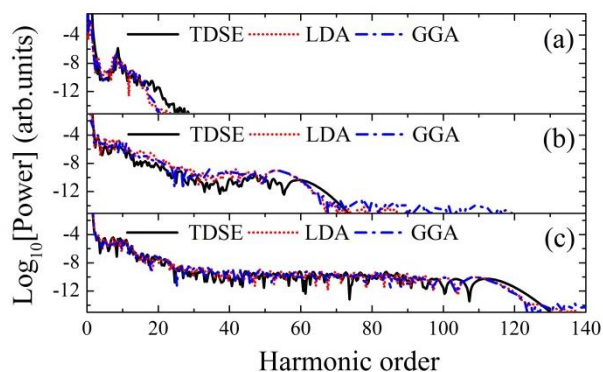
Newton equation is also the 53rd, which is the same with that from TDDFT. Furthermore, there exists a minimum near the 35th.

harmonic spectra, and the dip in the case of TDSE becomes more clearly.



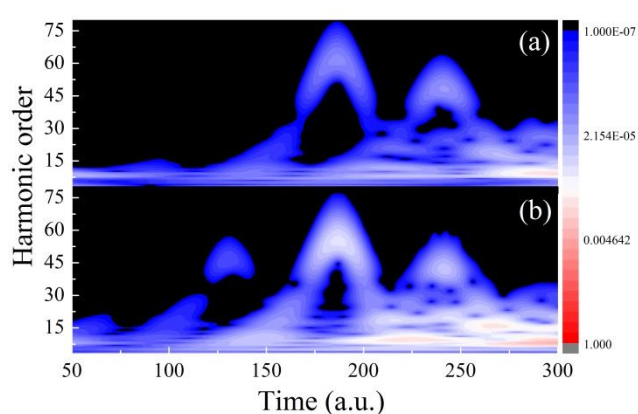
**Figure 3:** Harmonic spectrum from TDDFT. The peak amplitude of the laser field is 0.1 a.u..

Figure 4 shows the harmonic spectra in the strong laser pulse from TDSE and TDDFT, and the laser peak electric field amplitude is 0.05 a.u., 0.1 a.u., and 0.15 a.u.. It can be found that, the cutoff frequencies of the HHG spectra are increased with the enhancement of the laser intensity. Furthermore, the cutoff positions from quantum calculations agree well with those from the three-step model. The harmonic photon is equal to the electronic kinetic energy from the laser field plus the ionization energy of the molecule. Due to the higher ground state energy of TDDFT, the cutoff from TDDFT is less than that from TDSE. From Figure 4, it can also be seen that, the harmonic efficiency from TDDFT is higher than that from TDSE. Because the HHG process is a stimulated recombination one, the harmonic efficiency is related with the populations of the ground state and the continuum states, the less ionization rate from TDSE leads to the lower harmonic intensity.



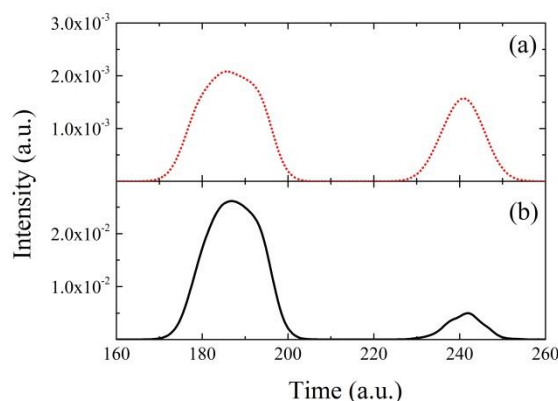
**Figure 4:** High-order harmonic spectra from TDSE and TDDFT in the laser pulse whose peak electric field amplitude are: (a) 0.05a.u., (b) 0.10a.u. and (c) 0.15a.u.

In order to analyze the difference between the harmonic spectra from TDSE and TDDFT, we use wavelet analysis to observe the time and frequency behaviour of the harmonic emission, as shown in Figure 5. It can be observed that, the time-frequency distribution in the two harmonic spectra from TDSE and TDDFT are very similar, there exists a major emission peak in every half cycle of the laser field, which has a negative slope branch (the long quantum path) and positive slope one (the short quantum path). In addition, a large difference appears near the dips in the two



**Figure 5:** Time-frequency distribution of HHG calculated by TDSE (a) and TDDFT (b)

An important application of HHG is the generation of the attosecond pulse. In the following, we calculate the attosecond pulse generation supported by the continuum spectra in Figure 4 (b). In figure 6, we calculated attosecond pulses by the use of the TDDFT and TDSE. Due to the difference in the ionization potential in both cases of TDSE and TDDFT, we choose 40th-70th and 46th-76th harmonics to obtain attosecond pulses. From Figure 6, it is clear that two attosecond pulses are generated by superposing the above harmonics, and the corresponding duration are 18 and 10, respectively.



**Figure 6:** Temporal profiles of the attosecond pulses calculated from the scheme TDSE (a) and LDA (b)

## 4. Conclusions

In conclusion, we systematically investigate the ionization probability and HHG from TDDFT. To compare with the result from TDSE, the ionization probability and the harmonic yield is higher. The cutoff energy of the harmonic spectra from TDDFT is consistent with that predicted by the three-step model. The time-frequency distribution and the attosecond pulse generation from TDDFT agree well with those from TDSE. The consistency with the TDSE calculation provides an important opportunity on the study of attosecond pulse generation from molecules by using TDDFT. Due to the initial energy difference in the two calculation, there exists a clear disparity for the harmonic spectra near the cutoff. To obtain a more accurate result, one needs to optimize the pseudopotential of the molecule.

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