Revisiting the tunnelling site of electrons in strong field enhanced ionization of molecules

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We investigated electron emissions in strong field enhanced ionization of asymmetric diatomic molecules by quantum calculations. It is demonstrated that the widely-used intuitive physical picture, i.e., electron wave packet direct ionization from the up-field site (DIU), is incomplete. Besides DIU, we find another two new ionization channels, the field-induced excitation with subsequent ionization from the down-field site (ESID), and the up-field site (ESIU). The contributions from these channels depend on the molecular asymmetry and internuclear distance. Our work provides a more comprehensive physical picture for the long-standing issue about enhanced ionization of diatomic molecules.

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Tunnnelling ionization is one of the most fundamental quantum effects when atoms and molecules are exposed to strong laser field. As the doorway step of various strong-field processes, such as, high-order harmonic and attosecond pulse generation [1, 2], double ionization [3, 4] and high-order above-threshold ionization [5, 6], understanding the ionization dynamics is of essential importance for controlling the electron dynamics in these processes. Moreover, molecular ionization signal itself also preserves some information of the molecular structure, and thus can be used to image molecular structure [7, 8]. Therefore, the ionization has attracted significant interests over the past several decades. Theories, including PPT [9], ADK [10], have been well established for atoms. Lots of efforts have also been made to extend these theories to molecules [11]. Nevertheless, because the molecules have more degrees of freedom and more complicated structure, the underlying physics becomes richer and the ionization dynamics is still not completely clear yet. It has been demonstrated that when the molecule is stretched to a critical internuclear distance $R_c$, the ionization probability sharply increases, which is called enhanced ionization (EI) [12–14]. An intuitive physical picture [12–14] based on the quasi-static tunneling theory [20] have been proposed to explain the behavior of molecular EI. When the molecule is stretched to the critical distance $R_c$, an inner potential barrier between the two cores emerges and localizes the electron population at each of cores. Then, the up-field population only needs to tunnel through the inner barrier directly to the continuum, which is considerably easier than tunnelling through the outer barrier between the down-field core and the continuum. Thus a remarkable enhancement of the ionization probability happens around the critical distance $R_c$. According to the intuitive physical picture, electron wave packet direct ionization from the up-field site (DIU) is considered responsible for molecular EI.

Although such a DIU physical picture has been commonly used to analyze and explain the experiments of molecular ionization and related processes [21], the physical picture of molecular EI is still unclear and confusing. For instance, in Ref. [22], Betsch et al. measured the ejection direction of multiply charged ion fragments from a variety of molecules (N$_2$, O$_2$, CO, CO$_2$, and HBr) driven by a two-color laser field. The observed forward-backward dissociation asymmetries imply that the electron is preferentially emitted from the down-field site, in contradiction with the DIU physical picture. Recently, a single-color elliptically polarized laser pulse is used to probe the tunnelling site of electrons from the dimer ArXe by angular streaking technique [23, 24]. Wu et al. reported that the ionization more easily happens at the up-field site, supporting the DIU physical picture. Because the intuitive physical picture is based on the quasi-static theory, lacking a perspective on the dynamics of ionization processes, controversy still exists in these experiments.

To understand the long-standing issues about EI [22, 23, 24, 25, 27], in this Letter, we investigate the electron dynamics and the tunnelling site by carefully examining time evolution of the electron density and ionization rate with numerically solving time-dependent Schrödinger equation (TDSE). A more comprehensive physical picture is established for EI dynamics of diatomic molecules. Besides the DIU ionization channel, we find another two new ionization channels. The contributions from these channels depend on the asymmetry and internuclear distance of the molecules.

This work is intended to explore a general effect, rather than to model a special experiment, so we consider a generic model diatomic molecule aligned along the electric field vector of the linearly polarized light. The two-dimensional TDSE can be written as [atomic units (a.u.)] are used throughout this paper unless stated otherwise:

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distinct difference between these two molecules. For the try [see Fig. 1(b)], respectively. However, one can see a large asymmetry [see Fig. 1(a)] and small asymmetry in the molecular motion.

The molecule with large asymmetry (e.g., HeH$^+$) and the molecule with small asymmetry (e.g., ArXe$^+$) will have different ionization behaviors. The red and blue curves show the ionization probabilities from the molecule with large asymmetry and the molecule with small asymmetry, respectively. The red curve reads as $H(x, y, t)\psi(x, y, t)$, where $x$, $y$ denote the electron coordinates. $H(x, y, t)$ is the Hamiltonian and reads

$$H(x, y, t) = \left[-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{Z_1}{\sqrt{x+R/2+y^2+a}} - \frac{Z_2}{\sqrt{x-R/2+y^2+b}} + xE(t)\right]_R$$

where $a$, $b$ are the screening parameters of left and right nuclei. $E(t) = E_0\sin(\pi\tau/\tau_p)^2\cos(\omega t)$ is the electric field of the laser pulse, with the angular frequency $\omega = 0.057$ a.u. (corresponding to the wavelength 800 nm) and the full duration $\tau_p = 10T$ (T is the laser cycle). In order to investigate the role of molecular asymmetry, we chose a set of parameters $Z_1 = 2$, $Z_2 = 1$, $a = 0.5$ and $b = 0.5$ to represent a model molecule with large asymmetry (e.g., HeH$^+$). The asymmetry is defined by the parameter $A = I_{pl}/I_{pr}^z$, where $I_{pl}$ and $I_{pr}$ denote the ionization energies of the left and right cores when the neighboring core is removed, respectively. According to this definition, the asymmetry parameter is $A = 1.38/0.54 = 2.6$. The other set of parameters $Z_1 = 1$, $Z_2 = 1$, $a = 0.39$ and $b = 0.92$ is used to represent a model molecule with small asymmetry (e.g., ArXe$^+$). Its asymmetry parameter is $A = 0.58/0.45 = 1.3$. In our work the laser intensity of $1 \times 10^{15}$ W/cm$^2$ is used for the former molecule, and $9 \times 10^{13}$ W/cm$^2$ for the latter molecule. The split-operator spectral method [28] is used to numerically solve the TDSE.

Figure 1(a) and (b) show the ionization probabilities as a function of internuclear distance $R$ for the molecules with large and small asymmetries, respectively. The red and blue curves show the ionization probabilities from the left ($x < 0$) and right ($x > 0$) sides, which are obtained by integrating the probability flux at $x = -R/2 - 9$ and $x = R/2 + 9$ from the beginning to end of the laser pulse. The green curve represents the total ionization probability. With the increase of $R$, the total ionization probabilities for these two molecules both firstly increase and then gradually decrease. A remarkable enhancement happens around $R = 4$ a.u. and 6 a.u. for the molecule with large asymmetry [see Fig. 1(a)] and small asymmetry [see Fig. 1(b)], respectively. However, one can see a distinct difference between these two molecules. For the molecule with large asymmetry, the probability of electrons escaping from the left side is much larger than that from the right side around the critical distance. Whereas for the molecule with small asymmetry, the ionization probability from the left side is slightly smaller than that from the right side around the critical distance. At large internuclear distance ($R > 8$), both molecules show slightly more electrons emitted from the right side.

In order to explore if the electron is emitted from the up-field site or down-field site, we carefully examine the time evolution of the electron density along the polarization direction. We first discuss the EI at large internuclear distance. Figure 2(b) and 2(c) show the electron density as a function of time for the molecule with large asymmetry at $R = 8$ a.u. and for the molecule with small asymmetry at $R = 10$ a.u. respectively. Recall that the electron is preferentially emitted from the right side at these internuclear distances as shown in Fig. 1. From Fig. 2(b) and 2(c) one can see that the ionization mainly occurs at the two instants around $t = 4.5T$ and $t = 5.5T$. At those times, the electric field is negative and thus the left core is up-field. The result indicates that electron wave packet located at the left (i.e., up-field) core directly tunnels through the inner potential barrier to the continuum. This ionization channel, so-called direct ionization from the up-field site (DIU), is consistent with the intuitive physical picture of molecular EI. Therefore, for asymmetric diatomic molecules DIU is the dominant ionization channel at the large internuclear distance.

Next, we discuss the ionization dynamics at the relatively small internuclear distance. Figure 3(b) shows the ionization rate from the left (red curve) and right (blue curve) sides as a function of time for the molecule with large asymmetry at $R = 4$ a.u. One can see that the dominant ionization burst is from the left side around $t = 5.0T$,...
when the electric field is positive. There are also some electron wave packets escaping away from the right side with low probabilities around $t=4.65T$ and $t=5.65T$, and from the left side around $t=6.0T$. In order to more clearly reveal the dynamics of electron emissions, the time evolution of the electron density is examined. As shown in Fig. 3(c), the molecule is initially at the ground state and the electron wave packet is dominantly localized at the left core. At the instant of $t=4.45T$, some electron population is firstly excited to the right core [15], as indicated by the black arrow. A short time later, at the instant of $t=4.6T$ a small part of the excited population leaves from the right core [see the red arrow]. When this electron wave packet arrives at $x=11$ a.u. [the white dashed curve], it is considered that ionization occurs. At this time the electric field is still negative and thus the right core is down-filed. That is to say, the electron escapes away from the down-field site by this process. Furthermore, more excited population remains localized at the right core. When the electric field becomes positive and the right core is promoted to the up-field site, the excited population quickly tunnels through the inner potential barrier to the continuum around $t=5.0T$ [see the green arrow], which corresponds to the highest ionization peak in Fig. 3(b). In this channel the electron is emitted from the up-field site. Different from DIU channel at large $R$, the ionization channel at small $R$ mentioned above is a two-step process. The only difference is that those excited electron population emitted from the down-field site stays at the right core for a longer time. The emitted electrons from the left and right sides correspond to the ionization of the up-field and down-field sites, respectively. Further, we integrate the ionization rate from the left and the right sides shown in Fig. 4(b) over the time. The result reveals that the ionization probability from the right side is slightly larger than that from the left side. That is to say, the excited electron population is more likely ionized from the up-field site. Moreover, for large asymmetric molecules, there is more excited electron population ionized from the up-field site.

Furthermore, we analyze the ionization dynamics for small asymmetric molecules. Figure 4 shows the ionization rate from the left (red curve) and right (blue curve) sides and the electron density along the polarization direction as a function of the time for the molecule with small asymmetry at $R=6$ a.u. Due to the periodicity of ionization signal, we only need to analyze the region of $4.6T$-$5.7T$. One can see that a part of electron population is excited to the right core at $t=4.6T$ [see the black arrow]. Then the electric field turns positive at $t=4.75T$ and within the subsequent positive half-cycle [4.75T, 5.25T] a part of excited electron population tunnels through the inner barrier to ionize from the left side [see the green arrow]. After the electric field reverses again at $t=5.25T$, the right core is lowered to the down-field site. The residual excited population localized at the right core tunnels through the right outer barrier to the continuum around $t=5.5T$ [see the red arrow]. Similar to the molecule with large asymmetry, these two ionization channels are also a two-step process. The only difference is that those excited electron population emitted from the down-field site stays at the right core for a longer time. The emitted electrons from the left and right sides correspond to the ionization of the up-field and down-field sites, respectively. Further, we integrate the ionization rate from the left and the right sides shown in Fig. 4(b) over the time. The result reveals that the ionization probability from the right side is slightly larger than that from the left side. That is to say, the excited electron population is more likely ionized from the up-field site. Moreover, for large asymmetric molecules, there is more excited electron population ionized from the up-field site.
FIG. 5: (color online) Sketches of the three different ionization channels.

As the internuclear distance decreases the contribution from the DIU channel quickly decreases. At the small internuclear distance, the other two ionization channels dominate. Both of the two channels are a two-step process, and their first step is the same. The first step is that the electron population located at the left core is excited to the right core when the electric field is negative [see Fig. 5(b)]. Then the excited electron wave packet can be emitted by two paths. One path is that the excited electron wave packet around the right core tunnels through the right outer barrier to the continuum when the electric field is negative. In this case the right core is down-field [see Fig. 5(c)]. So this ionization channel can be called field-induced excitation with subsequent ionization from the down-field site (ESID). The other path is that the excited electron wave packet stays until the electric field turns positive. Then the excited electron wave packet tunnels through the inner potential barrier directly to the continuum. This ionization channel is referred to as field-induced excitation with subsequent ionization from the up-field site (ESIU), as shown in Fig. 5(b) and 5(d).

In conclusion, we have investigated the dynamics of electron emissions in strong field EI of diatomic molecules by numerically solving TDSE. It is found that there are three ionization channels leading to ionization enhancement. Their relative contributions are related to the molecular asymmetry and internuclear distance. At the large internuclear distance the dominant contribution is from DIU ionization channel regardless of molecular asymmetry, which is consistent with the intuitive physical picture of EI. However, at small internuclear distance the other two new ionization channels dominate and their relative contributions depend on the molecular asymmetry. For the molecule with large asymmetry the electron is preferentially ionized from the up-field site by the ESIU channel. Whereas for the molecule with small asymmetry the electron is more likely ionized from the down-field site by the ESID channel. Our work provides a more comprehensive physical picture for EI of diatomic molecules. It can promote the understanding of the dissociation dynamics of molecules.

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