Non-sequential double ionization of $\text{CO}_2$ molecule and Kr atom in linearly polarized laser fields

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Abstract. Using two-dimensional classical ensemble method, a theoretical study of non-sequential double ionization (NSDI) with Krypton (Kr) and carbon dioxide ($\text{CO}_2$) is presented at different laser intensities. The numerical results show that the probability for NSDI of Kr atom is higher than that of $\text{CO}_2$ molecule. Moreover, for the same laser intensity, the momentum correlation spectrum of $\text{CO}_2$ molecule is drastically different from Kr atom. For example, for the laser intensities $I = 0.065$ PW/cm$^2$ and $I = 0.15$ PW/cm$^2$, the correlation spectrum of $\text{CO}_2$ molecule tends to distribute in the first and third quadrants, and presents a “finger-like” structure. However, for Kr atom at $I = 0.065$ PW/cm$^2$, the emitted electrons pairs tend to distribute in the second and fourth quadrants; When the laser intensity increases to 0.15PW/cm$^2$, the two electrons mainly distribute in the first and third quadrants and along two distinct lines being parallelled to the diagonal. In addition, our numerical calculations reveal that this different phenomenon is closely related to the Coulomb focusing effect: Coulomb potential will attract the returning electron more dramatically when it moves near the atomic or molecular core. For $\text{CO}_2$ molecule, the returning electron is dramatically attracted by three cores, so the returned electron of $\text{CO}_2$ molecule possesses higher energy than Kr atom does.

1 Introduction

Double ionization (DI) is the fundamental and important process when atoms and molecules are exposed to ultra short laser pulses, which has been attracting much attention during the past ten years, because it provides a particularly clear manner to study the electron-electron correlation [1–3]. Recently, the recollision model [4] is widely accepted to describe the ionization events that one electron ionizes first and revisits the core to let the second electron free by collision. According to the recollision mechanism, atomic and molecular NSDI process in strong laser fields can occur either by directly ionizing of the second electron up on collision with turning first electron (recollision impact ionization, RII), or by excitation of the second electron to an excited state to be ionized in the laser field at a later time (recollision excitation with subsequent ionization, RESI) [5]. Comparing to atoms, due to diverse molecular structure and additional nuclear degree of freedom, molecules exhibit much more complicated processes in strong-field ionization [6]. Fortunately, previous studies have shown that many aspects of strong-field ionization of molecules are similar with those in atoms. For example, the “knee” structure has been observed in simple diatomic [7–10] and linearly triatomic molecules [11–13], and even more complicated polyatomic molecules [14]. Moreover, the presence of revisiting electrons, which are at the basis of atomic NSDI, was reported for molecules [13, 15, 16]. Thus, electron correlation in a rescattering event is also at the basis of molecular NSDI in general. Furthermore, the investigations [17–20] have shown that electronic structure plays a key role in influencing nonsequential processes. For example, a closed-shell molecule will behave like a rare gas atom [17].

In this paper, we investigate the double ionization mechanism of $\text{CO}_2$ molecule and Kr atom in linearly polarized laser fields by the classical ensemble method, and make a comparative study. The numerical results show that the rate for NSDI of Kr atom is higher than that of $\text{CO}_2$ molecule. The momentum distribution illustrates this phenomenon. In addition, our numerical calculations of angular and energy distributions reveal that this different phenomenon is closely related to the Coulomb focusing effect: Coulomb potential will attract the returning electron more dramatically when it moves near the atomic or molecular core.

2 Theoretical Method

In this paper, we use the classical ensemble method proposed by Haan and Eberly et al [21, 22] which has previously been used successully [8–10, 13] to explore the ionization dynamics of $\text{CO}_2$ molecule and Kr atom in intense laser fields. In our calculation, the $\text{CO}_2$ molecule axis is along the x axis. The classical Hamiltonian of $\text{CO}_2$ molecule and Kr atom in an intense laser field can be given by:

$$H(r_1, r_2; P_1, P_2; t) = T(p) + V(q, t), \quad (1)$$

where the $\text{CO}_2$ molecular and Kr atomic kinetic energy $T$ are given by:

$$T_{\text{CO}_2}(P) = \frac{p_1^2}{2} + \frac{p_2^2}{2},$$

$$T_{\text{Kr}}(P) = \frac{p_1^2}{2} + \frac{p_2^2}{2}. \quad (2)$$

respectively.

The $\text{CO}_2$ molecular and Kr atomic potential energy $V$ are given:

$$V_{\text{CO}_2}(q, t) = -\sum_{i=1}^{3} \frac{Z_c}{\sqrt{x_i^2 + y_i^2}} - \sum_{i=1}^{3} \frac{Z_0}{\sqrt{(x_i - R)^2 + y_i^2}} - \sum_{i=1}^{3} \frac{Z_0}{\sqrt{(x_i - R)^2 + y_i^2}} + \frac{1}{|r_1 - r_2|} + (r_1 + r_2)E(t), \quad (3)$$

$$V_{\text{Kr}}(q, t) = -\sum_{i=1}^{3} \frac{Z_c}{\sqrt{x_i^2 + y_i^2}} - \sum_{i=1}^{3} \frac{Z_0}{\sqrt{(x_i - R)^2 + y_i^2}} - \sum_{i=1}^{3} \frac{Z_0}{\sqrt{(x_i - R)^2 + y_i^2}} + \frac{1}{|r_1 - r_2|} + (r_1 + r_2)E(t), \quad (4)$$

where $Z_c$, $R$, and $Z_0$ are the atomic number of carbon, the radius of proximate core, and the atomic number of the core, respectively. $r_1$ and $r_2$ are the positions of the first and second electrons, respectively.
The symplectic method is different and preserves the symplectic structure especially suitable for the long-time many-step calculations. We choose a set of initial stable states \( r_i(0), P_i(0) \) = 1,2 and solved the above canonical equations numerically in order to obtain the time evolution of the electron positions and the corresponding momenta \( r_i(t), P_i(t) \) = 1,2. Since the Hamiltonian system (1) is a separable Hamiltonian system in the sense that \( q \) and \( p \) are contained separately in \( V(q, t) \) and \( T(p) \).

\[
\begin{align*}
\dot{q}_i &= \frac{\partial V(q, t)}{\partial p_i}, \\
\dot{p}_i &= -\frac{\partial T(p)}{\partial q_i},
\end{align*}
\]

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**3 Results and discussion**

Figure 1 shows the double ionization probability of \( \text{CO}_2 \) molecule and Kr atom as a function of the laser intensity for 800 nm field. For both gases, the characteristic "knee" structure of NSDI can be clearly seen. Besides, the double ionization probability of Kr atom is higher than that of \( \text{CO}_2 \) molecule. For triatomic molecule, the electronic structures play a key role in NSDI [17, 18], thus we first take into account the valence electron orbits of \( \text{CO}_2 \) molecule (\( 4\sigma_2, 2(3\sigma_2), 2(1\pi_2), 4(1\pi_1) ) \) [23]. It should be noticed that \( \text{CO}_2 \) molecule are closed-shell structure with the outermost \( 1\pi_2 \) orbital fully occupied with 4 electrons, like the rare gas atom. The closed-shell molecule will behave like a rare-gas atom (e.g. N\(_2\) and Ar) [17]. However, why the rate for NSDI of Kr and \( \text{CO}_2 \) show a different behavior? Due to \( \text{CO}_2 \) molecule, the removal of \( 1\pi_2 \) electrons has two chances: (i) the two electrons can be both removed from one of the pairs of degenerate orbits; (ii) the two electrons can each be removed from a separate \( 1\pi_2 \) orbital [18, 23]. The rate for NSDI is higher when two electrons are removed from the same orbital but lower when two electrons are removed from different orbitals [18, 23]. That is to say, in theory, when the two electrons are each removed from a different \( 1\pi_2 \) orbital, the doubly ionized \( \text{CO}_2^{2+} \) is in either the \( ^1\Sigma_g^+ \) or \( ^3\Sigma_g^- \) state. When the two electrons are both removed from a same \( 1\pi_2 \) orbital, the doubly ionized \( \text{CO}_2^{2+} \) is in the \( ^1\Sigma_g^+ \) state, and this state is about 2.0 eV above the \( ^1\Sigma_g^+ \) state and 0.8 eV above the \( ^3\Sigma_g^- \) state [20]. Thus, the different behavior of NSDI of Kr and \( \text{CO}_2 \) may be due to the different second ionization energy of Kr and \( \text{CO}_2 \).
Figure 2 shows the end-of-pulse momentum correlation between the two emitted electrons of CO₂ molecule [Fig.2(a)] and Kr atom [Fig.2(b)] along the laser polarization direction (x direction), where the laser intensities are 0.065 PW/cm² and 0.15 PW/cm², respectively. We can see from the Fig.2 that for the same laser intensity, the momentum correlation spectrum of CO₂ molecule is drastically different from Kr atom. When the laser intensity is I = 0.065PW/cm², for CO₂ molecule [Fig.2 (a1)], the two emitted electrons tend to distribute in the first and third quadrants, and present a "finger-like" structure [24], meaning that RII is predominant; for Kr atom [Fig.2 (b1)], the emitted electrons pairs tend to distribute in the second and fourth quadrants, which is a strong indication of the RESI double ionization channel. When the laser intensity increases to 0.15PW/cm², for CO₂ molecule [Fig.2 (a2)], the two emitted electrons still distribute in the first and third quadrants, and presents a "finger-like" structure; for Kr atom [Fig.2 (b2)], the two electrons mainly distribute in the first and third quadrant sand along two distinct lines being parallelled to the diagonal, indicating that there is a momentum difference between two electrons from NSDI. This is a RESI double ionization channel [25]. The detailed mechanism leading to this kind of structure has been analyzed theoretically and experimentally by N. Camus in [26].

In our calculation E(t)=E_0(1+q_0), q_0 is all CEP average. Under this condition, the correlated electron momentum distributions should be symmetric. Thus, for NSDI of CO₂ molecule it should be symmetric about the diagonal px1+px₂=0, because in CO₂ molecule, RII is predominant and \( \mathbf{\bar{p}} = \mathbf{E}(t)/\omega \). For Kr, the momentum distribution is also symmetric about the diagonal px₁(px₂=0).However, under low laser intensity, due to the smaller returning energy, a part of the return electrons are recaptured and form a doubly excited state, and then the two electrons are ionized by the laser field from the doubly excited state and emitted indiscriminately, thus the distributions are asymmetric about the diagonal px₁(px₂=0). There are three interactions in the whole dynamic process of strong field double ionization: e-e interaction; e-laser field interaction; e-core interaction. Therefore, by comparing the correlation spectra of the two models under the same laser intensity [Fig.2 (a1) (b1); (a2) (b2)], we find the difference stems mainly from e-core interaction. Physically speaking, the shielding of nuclear potential would widely diminish the Coulomb focusing effect, but Coulomb potential will attract the returning electron more dramatically when it moves near the atomic or molecular core. For CO₂ molecule, the returning electron is dramatically attracted by three cores, so the attraction of CO₂ molecule is higher than Kr atom. Such strong attraction may bring the returning electrons to share more kinetic energy with the bound one. Thus, under low laser intensity, for CO₂ molecule, the RII double ionization channel is predominant, while for Kr atom, the RESI double ionization channel is predominant.

Figure 3 shows the angular distribution of the electron emission (θ is the angle between two electrons at the end of laser pulse) for all double ionization events, obtained from the CO₂ molecule [Fig.3 (a)] and Kr atom [Fig.3 (b)], where the laser intensities are 0.065 PW/cm² and 0.15 PW/cm², respectively. When the laser intensity equals 0.05PW/cm², for CO₂ molecule [Fig.3 (a1)], the angle θ is mostly distributed about 10°~56° and 304°~320°, which means that the two electrons tend to be emitted to the same direction; on the contrary, for Kr atom, the angle θ is mostly centered at 156°~203°, which means the two electrons are more likely to be emitted to the opposite direction. When the laser intensity increases to 0.15 PW/cm², for CO₂ molecule, the angle θ is mostly centered at 43°~53° and 307°~317°, which means the two electrons tend to be emitted the same direction; for Kr atom, the angle θ is mostly centered at 22° and 338° which means the two electrons are mainly emitted to the same hemisphere. The main differences between CO₂ molecular and Kr atomic DI can be clearly seen by analyzing typical trajectories.

Figure 4 shows the typical energy of double ionized electrons of CO₂ molecule [Fig.4(a)] and Kr atom [Fig.4(b)] are as function of time, where the laser intensities are 0.065 PW/cm² and 0.15 PW/cm², respectively. The arrows denote the recollision. The \( E_1 \) and \( E_2 \) represent the energies of two electrons, respectively. When the laser intensity equals 0.065 PW/cm², for CO₂ molecule [Fig.4(a1)], the first electron is driven back by the laser field at about 2.3 O.C. to collide the bound electron, and then the bound electron is ionized quickly, which means the RII mechanism. However, for Kr atom [Fig.4 (b1)], the returning energy is insufficient to directly ionize the bound electron. After the recollision, the second electron undergoes a time-delay field-assisted ionization of the excited state. However, the first electron is bound by nucleus. After the second recollision, the first electron is ionized. When the laser intensity equals 0.15 PW/cm², for CO₂ molecule [Fig.4 (a2)], the return electron possesses sufficient energy to "kick out" the bound electron through a single recollision. However, for Kr atom [Fig.4 (b2)], the bound electrons excited after the collision, after the second recollision, the bound electron is ionized. Moreover, it is interesting to note that under the same laser intensity, the returned electron of CO₂ molecule possesses higher energy than Kr atom does. This is why the RII mechanism is predominated for CO₂ molecule, and the RESI is predominated for Kr atom under the same laser intensity.
4 Conclusions

In summary, we investigate the double ionization mechanism of CO₂ molecule and Kr atom in linearly polarized laser fields by the classical ensemble method and compared them together. The numerical results show that the probability for NSDI of Kr atom is higher than that of CO₂ molecule. For the laser intensities $I = 0.05\text{ PW/cm}^2$ and $I = 0.15\text{ PW/cm}^2$, the correlation spectra of CO₂ molecule tends to distribute in the first and third quadrants; whereas for Kr atom at $I = 0.065\text{ PW/cm}^2$, the emitted electrons pairs tend to distribute in the second and fourth quadrants. When the laser intensity increases to $0.15\text{ PW/cm}^2$, the two electrons mainly distribute in the first and third quadrants. In conclusion, our numerical calculations reveal that this different phenomenon is closely related to the Coulomb focusing effect: Coulomb potential will attract the returning electron more dramatically when it moves near the atomic or molecular core. For CO₂ molecule, the returning electron is dramatically attracted by three cores, so the returned electron of CO₂ molecule possesses higher energy than Kr atom does.

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References