

Alignment-Dependent Ionization of CO₂ in the Intense Laser Fields: Single-Active-Electron Approach *

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(Received 8 July 2013)

We perform Hartree–Fock calculations to obtain occupied orbitals for triatomic molecule CO₂, based on one-center method and B-splines to deal with cusps and speed up convergence. Both the orbital energies and charge distribution are in good accordance with the reference data. The valence orbital is propagated with single-active-electron approximation, and the alignment-dependent ionization yield peaks about 40°. However, there are discrepancies between our results and the experimental data, and many-electron effects may need to be exploited further to describe them.

PACS: 31.15.A–, 33.80.–b, 33.80.Wz

DOI: 10.1088/0256-307X/30/10/103103

Single ionization is the first step of the three-step model, so it is crucial to understand nonsequential double ionization, high-order harmonic generation and tomographic imaging.^[1,2] Theoretically, the commonly used approaches for calculating ionization are the Ammosov–Delone–Krainov (ADK) theory,^[3–5] the strong field approximation (SFA) theory^[6] and the time-dependent Schrödinger equation (TDSE). For the ADK theory, the ionization rate is determined by the strength of the laser field and the structure parameters of atoms or molecules, and is independent of wavelength and pulse length. For the SFA theory, the initial state of the electron is ground state, while the final state of the electron is described by Volkov states. In addition, the Coulomb potential is negligible when atoms or molecules interact with the laser field. For the TDSE, though it is time-consuming, it could account for the role of excited states in contrast to the ADK and SFA theories. Furthermore, it could take into account the variation of carrier-envelope phase for an ultrashort laser pulse.

In experiments, molecular ionization has attracted great attention, since there are various types of peculiar character, such as ionization suppression,^[7,8] charge resonant enhanced ionization^[9] and alignment-dependent ionization.^[10,11] For alignment-dependent ionization yields $P(\eta)$ (η is the angle between the polarization vector of the laser field and the molecular axis), the ionization from the highest occupied molecular orbital (HOMO) of N₂, O₂ and CO₂ has been measured and drawn great interest recently,^[12] because the experimental results and molecular tunneling the-

ory (MO-ADK) are in good accordance for N₂ and O₂, while much difference exists for CO₂.

Shortly afterward, a number of theoretical efforts were devoted to the investigation of the alignment-dependent ionization for CO₂. It is well known that the structure parameters of molecular orbital are usually obtained from software like Gaussian, in which the molecular orbitals are expanded by Gaussian bases. However, the radial wave function decays in an exponential way in the asymptotic regime, while linear combination of the Gaussian basis could not describe the long-range wave function properly. Consequently, Zhao *et al.* modify the radial wave function applying B-splines instead of Gaussian bases, and the peak ionization probability is located at 34°.^[13,14] In addition, the asymptotic behavior of wave function is also corrected in Ref. [15], and the peak ionization yield is positioned at 33° compared with 24° obtained from GAMESS. A semiclassical complex-time method is advanced for tunneling ionization, and the peak ionization yield is at 28° for CO₂.^[16] Zhang *et al.* show SFA in length gauge is suitable for investigation on the strong-field ionization for CO₂,^[17] and find the behavior of the wavefunction around the core has an important effect on the ionization. By solving TDSE with the single-active-electron (SAE) model, the results show that the ionization yields maximum at about 42° and the intermediate resonant states have an important impact on the ionization behavior.^[18] Meanwhile, the results obtained from time-dependent density-functional theory (TDDFT) demonstrate that the peak ionization yields are predicted at 40°.^[19] Re-

*Supported by the National Natural Science Foundation of China under Grant No 11274348, the National Basic Research Program of China under Grant Nos 2010CB832803 and 2013CB922203, and the Major Research Plan of the National Natural Science Foundation of China under Grant No 91121017.

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cently, Murray *et al.* found that the interplay of coordinate and momentum space also affects the location of the maximum ionization.^[20]

In this Letter, we generalize our previous work^[21] to triatomic molecule CO₂, and develop an SAE approach to study the alignment-dependent ionization probabilities (atomic units are employed throughout this study).

Assuming the position of the carbon nucleus to be the origin of the spherical coordinates, the field-free Schrödinger equation for HOMO with fixed nuclear approximation could be written as

$$[H_0(\mathbf{r}) + 2\hat{J}(\mathbf{r}) - \hat{K}(\mathbf{r})]\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}). \quad (1)$$

$$H_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 - \frac{Z_a}{|\mathbf{r} - \mathbf{R}/2|} - \frac{Z_a}{|\mathbf{r} + \mathbf{R}/2|} - \frac{Z_b}{r}, \quad (2)$$

$$\frac{1}{|\mathbf{r} \pm \mathbf{R}/2|} = \sum_{\lambda=0}^{\infty} (\pm)^{\lambda} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} P_{\lambda}(\xi), \quad (3)$$

where $r_{>}$ ($r_{<}$) corresponds to the larger (smaller) one of $(r, \frac{R}{2})$, and $\xi = \cos\theta$. $P_{\lambda}(\xi)$ represents the Legendre polynomials. In this work, the maximum value of λ is 200. $Z_a = 8$ and $Z_b = 6$ denote the charges of the oxygen nucleus and carbon nucleus, respectively. R is the equilibrium distance of the two O nuclei, which equals to 4.39 a.u. The coordinates of CO₂ could be found in Fig. 1.

$$\hat{J}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \sum_{\mu \neq i}^N \int \frac{|\psi_{\mu}(\mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_2 \psi_i(\mathbf{r}_1) + \frac{1}{2} \int \frac{|\psi_i(\mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_2 \psi_i(\mathbf{r}_1), \quad (4)$$

$$\hat{K}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \sum_{\mu \neq i}^N \int \frac{\psi_{\mu}(\mathbf{r}_2)^* \psi_i(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \psi_u(\mathbf{r}_1), \quad (5)$$

where the two-electron interaction operator could be written as

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{r_{>}} \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^l} P_l(\cos\theta_{12}) \\ &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{(l-|m|)!}{(l+|m|)!} \frac{r_{<}^l}{r_{>}^{l+1}} P_l^{|m|}(\xi_1) P_l^{|m|}(\xi_2) \\ &\quad \cdot e^{im(\phi_1 - \phi_2)}, \end{aligned} \quad (6)$$

where $r_{>}$ ($r_{<}$) is \max (\min) (r_1, r_2), and $P_l^{|m|}(\xi_1)$ are associated with Legendre polynomials. In our calculation, we let the maximum value of $l = 30$. Equation (4) denotes the electron-electron Coulomb interaction, and Eq. (5) indicates the electron-electron exchange interaction. Here $\psi_{\mu}(\mathbf{r}_2)$ is the molecular orbital obtained from Hartree-Fock calculations, which has been described in detail in Ref. [21]. For a given

magnetic quantum number, the molecular orbital is expressed in the form

$$\psi_i(r, \xi, \varphi) = \frac{1}{\sqrt{2\pi}} \sum C_{\mu\nu}^i \frac{B_{\mu}^k(r)}{r} B_{\nu}^k(\xi) (1-\xi^2)^{\frac{|m|}{2}} e^{im\varphi}. \quad (7)$$

The order of the radial B-spline $B_{\mu}^k(r)$ and the angular B-spline $B_{\nu}^k(\xi)$ is $k = 7$. The knots of radial B-spline and angular B-spline are distributed in exponential and sine-like sequence, respectively.^[22]

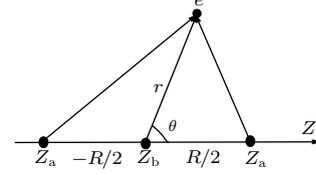


Fig. 1. The coordinates of CO₂.

After the molecular orbits are obtained, the TDSE for the HOMO of CO₂ in an intense laser field is written as

$$i \frac{\partial}{\partial t} \Phi(r, \xi, \varphi, t) = [H_0 + 2\hat{J}(\mathbf{r}) - \hat{K}(\mathbf{r}) - r\xi E(t)] \Phi(r, \xi, \varphi, t), \quad (8)$$

where $E(t) = E_0 \sin^2(\pi t/t_{\max}) \sin(\omega t)$. E_0 is the amplitude of the electric field, and $\omega = 0.057$ a.u.; t_{\max} is the pulse duration and is 10 optical cycles. The time-dependent wave function could be expressed with the field-free eigenstates as follows:

$$\Phi(r, \xi, \varphi, t) = \sum_i C_i(t) \psi_i(r, \xi, \varphi). \quad (9)$$

We employ the Crank-Nicolson method^[22] to propagate wave function, and the ionization probability at the end of the pulse is defined as

$$P_{\text{ion}}(t_{\max}) = 1 - \sum_{i=1}^{n(E_i < 0)} |\langle \psi_i(r, \xi, \varphi) | \Phi(r, \xi, \varphi, t_{\max}) \rangle|^2. \quad (10)$$

In this study, the radial box is truncated at $r_{\max} = 70$ a.u., and 70 radial B-splines and 20 angular B-splines are employed. A $\cos^{1/8}$ mask function is used in the range [40,70] to avoid spurious reflection from the boundary. The time step is $\Delta t = 0.12$ a.u.

In Table 1, the orbital energies of CO₂ are presented to compare with the results obtained by Gaussian software at the Hartree-Fock level, and the Gaussian basis set is cc-pVQZ.^[23] The inner orbitals $1\sigma_g$ and $1\sigma_u$ are degenerated, and the relative errors of orbital energies are within 0.008 compared with those in Ref. [23]. The probability distributions of the $1\pi_u$ and $1\pi_g$ orbitals are shown in Fig. 2. For the $1\pi_u$ orbital, it distributes mostly near O nuclei, and no electron cloud locates along the molecular axis. For the $1\pi_g$ orbital,

the picture reveals that most of the electron cloud distributes symmetrically near O nuclei, and less electron cloud distributes near the C nucleus compared with the $1\pi_u$ orbital. The maximum charge density is located about $\theta = 20^\circ$ and $\theta = 160^\circ$ for HOMO, which is in a good agreement with the results in Ref. [18].

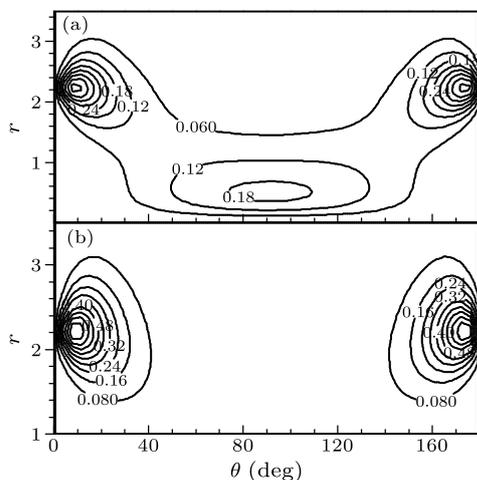


Fig. 2. The charge distribution for (a) the $1\pi_u$ orbital and (b) the $1\pi_g$ orbital.

Table 1. Comparison of orbital binding energies of CO_2 with those obtained by Gaussian software.

Orbitals	Present	Ref. [23]
$1\sigma_u$	20.5022	20.6494
$1\sigma_g$	20.5022	20.6494
$2\sigma_g$	11.4614	11.4591
$3\sigma_g$	1.5261	1.5299
$2\sigma_u$	1.4718	1.4767
$4\sigma_g$	0.8005	0.8003
$3\sigma_u$	0.7451	0.7429
$1\pi_u$	0.7161	0.7149
$1\pi_g$	0.5456	0.5442

In Fig. 3(a), we compare the ionization yields obtained from our TDSE method with those from other TDSE approaches and the experimental results for laser intensity $I = 1.1 \times 10^{14} \text{ W/cm}^2$ with fixed laser wavelength 800 nm. Abu-samha *et al.* adopted the LB94 potential to construct a single-active-electron model to study alignment-dependent ionization probabilities, and the peak ionization yield is about 42° . [18] In Ref. [19], TDDFT was applied to calculating the alignment-dependent ionization yields, and the maximum ionization yield is located around 40° . The present method predicts the maximum ionization yield at about 40° . There are discrepancies between our results and those in Ref. [18], and the possible reason is that the excited states for the two approaches are different. To illustrate, the energy levels of the first excited state in Ref. [18] and the present study are -0.21 a.u. and -0.12 a.u. , respectively. However, the peak ionization from the experimental measurement is about 46° , and the width of the angular ionization distribution is much narrower. In Ref. [24], Petretti

et al. also find that the SAE model fails to describe the narrow ionization distribution and attribute it to field-induced coupling between the HOMO orbital and the HOMO-1 orbital. Figure 3(b) shows the ionization probabilities for $I = 0.3 \times 10^{14} \text{ W/cm}^2$ except those in Refs. [18,19]. The maximum ionization probability is located at around 43° and 40° for the experiment and the present work, respectively. Moreover, the experimental values have a broad angular distribution, which is in reasonable agreement with the theoretical data.

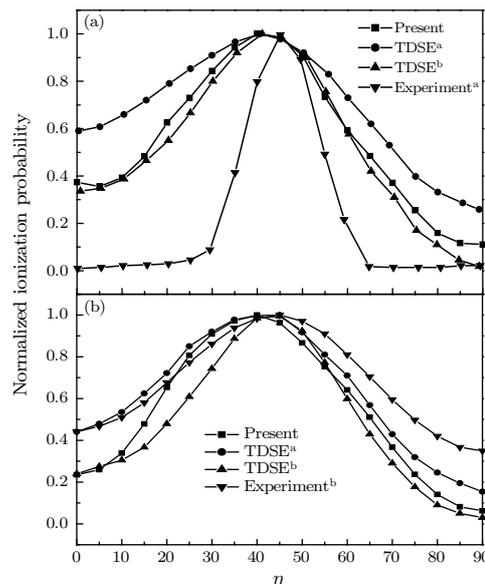


Fig. 3. The normalized alignment-dependent ionization probabilities of CO_2 . (a) Laser intensity is $1.1 \times 10^{14} \text{ W/cm}^2$; (b) Laser intensity is $0.3 \times 10^{14} \text{ W/cm}^2$. Note that $0.5 \times 10^{14} \text{ W/cm}^2$ and $0.56 \times 10^{14} \text{ W/cm}^2$ were adopted in Refs. [18,19], respectively. TDSE^a from Ref. [19], TDSE^b from Ref. [18], Experiment^a from Ref. [12], and Experiment^b from Ref. [25].

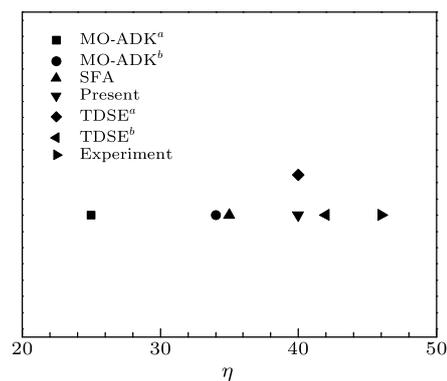


Fig. 4. The locations of peak ionization yield for different theories and the experiment. MO-ADK^a from Ref. [12], MO-ADK^b from Ref. [13], SFA from Ref. [5], TDSE^a from Ref. [19], TDSE^b from Ref. [18], and the experiment from Ref. [12].

Figure 4 compares the locations of peak ionization yield obtained by the experiment and various theories for laser intensity $I = 1.1 \times 10^{14} \text{ W/cm}^2$. The peak

ionization yield is located at 25° or 34° by the MO-ADK theory,^[12,13] and the ADK coefficients are improved in Ref. [13]. The maximum ionization yield is positioned at 35° calculated by LG-SFA, which is better than that of the improved MO-ADK model, since the wave function near the core could not be taken into account in the MO-ADK theory. Note that 42° and 40° have been obtained by SAE in Ref. [18] and in the present work, respectively, which are much better than those of the MO-ADK and SFA theories, since the SAE model could take account of excited states. However, there is still difference between the SAE results and the experimental data, and many-electron effects may play an important role,^[26] since the energy gaps are not large for HOMO, HOMO-1, and HOMO-2 in Table 1. In Ref. [19], the maximum ionization peaks at 40° calculated by TDDFT, and there is discrepancy if it is not an experimental uncertainty.^[13] Consequently, multi-electron effects may be instigated in depth to account for the difference between the theoretical results and the experimental data.

In conclusion, an SAE approach has been developed for triatomic molecule CO_2 in spherical coordinates, in which the occupied molecular orbitals are obtained by Hartree–Fock calculations associated with B-splines and one-center method. The orbital energies are in good agreement with those evaluated by Gaussian software. The present approach is applied to studying the alignment-dependent ionization of CO_2 , and the results show that the maximum ionization yield is located about 40° and the ionization distribution is much broader than the experimental results for $I = 1.1 \times 10^{14} \text{ W/cm}^2$. There is still deviation between the experimental results and the theoretical values, and many-electron dynamics may need to be explored further to explain the experimental phenom-

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References

- [1] Krausz F and Ivanov M 2009 *Rev. Mod. Phys.* **81** 163
- [2] Itatani J et al 2004 *Nature* **432** 867
- [3] Ammosov M V, Delone N B and Krainov V P 1986 *Zh. Eksp. Teor. Fiz.* **91** 2008
- [4] Tong X M, Zhao Z X and Lin C D 2002 *Phys. Rev. A* **66** 033402
- [5] Zhang B and Zhao Z X 2010 *Chin. Phys. Lett.* **27** 043301
- [6] Keldysh L V 1965 *Sov. Phys. JETP* **20** 1307
- [7] DeWitt M J, Wells E and Jones R R 2001 *Phys. Rev. Lett.* **87** 153001
- [8] Lin Z Y et al 2012 *Phys. Rev. Lett.* **108** 223001
- [9] Bocharova I et al 2011 *Phys. Rev. Lett.* **107** 063201
- [10] Litvinyuk I V et al 2003 *Phys. Rev. Lett.* **90** 233003
- [11] Zhang S, Xia Y Q, Wang Y Q, Lu Z Z and Chen D Y 2009 *Chin. Phys. Lett.* **26** 083202
- [12] Pavičić D et al 2007 *Phys. Rev. Lett.* **98** 243001
- [13] Zhao S F, Jin C, Le A T, Jiang T F and Lin C D 2009 *Phys. Rev. A* **80** 051402(R)
- [14] Zhao S F, Jin C, Le A T, Jiang T F and Lin C D 2010 *Phys. Rev. A* **81** 033423
- [15] Abu-samha M and Madsen L B 2010 *Phys. Rev. A* **81** 033416
- [16] Gallup G A and Fabrikant I I 2010 *Phys. Rev. A* **81** 033417
- [17] Zhang B and Zhao Z X 2010 *Phys. Rev. A* **82** 035401
- [18] Abu-samha M and Madsen L B 2009 *Phys. Rev. A* **80** 023401
- [19] Son S K and Chu S I 2009 *Phys. Rev. A* **80** 011403
- [20] Murray R, Spanner M, Patchkovskii S and Ivanov M Y 2011 *Phys. Rev. Lett.* **106** 173001
- [21] Hu S L, Zhao Z X and Shi T Y 2013 *arXiv:1308.6408v1*
- [22] Bachau H, Cormier E, Decleva P, Hansen J E and Martín F 2001 *Rep. Prog. Phys.* **64** 1815
- [23] Frisch M J et al 2003 *Gaussian 03* (Gaussian Inc. Pittsburgh PA)
- [24] Petretti S, Vanne Y V, Saenz A, Castro A and Decleva P 2010 *Phys. Rev. Lett.* **104** 223001
- [25] Thomann I et al 2008 *J. Phys. Chem. A* **112** 9382
- [26] Wu C Y, Zhang H, Yang H and Gong Q H 2011 *Phys. Rev. A* **83** 033410