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## Theoretical study of $(\gamma, 2e)$ photo-double ionization of CO<sub>2</sub> in the equal energy sharing regime using Dyson orbitals and the parameterized three center continuum wave function

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#### Abstract

The theoretical procedure for the determination of the multiply differential cross sections (MDCS) applied recently [1, 2] to the vertical photo-double ionization of a diatomic N<sub>2</sub> molecule is extended to the three center  $CO_2$  molecule producing dissociative  $CO_2^{2+}$  dication. Dyson orbitals for the bound active electrons are introduced, and the parameterized three-center continuum wave function in its correlated form is used to describe the two ejected electrons. The variation of the MDCS for the coincidence detection of the two ejected electrons, for a randomly orientated internuclear axis is studied. The comparison of our results to those obtained by the Gaussian parametrization formula shows the similarities and the differences between the behavior of an atomic target and  $CO_2$ .

Keywords: photo-double ionization, three center continuum, electron–electron correlation, Dyson orbitals

#### 1. Introduction

The  $(\gamma, 2e)$  photo-double ionization (PDI) is a complete experiment, which measures the multiply differential cross section (MDCS) of the double ionization by a polarized photon of atomic or molecular targets by detecting, in coincidence, the two ejected electrons emerging simultaneously from the collision for given energy values [3–8]. The theoretical interpretation of this complex quantum phenomenon [9–11] requires the study of the electronic structure of the target, the modeling of the ionization mechanisms and the introduction of the electron correlation between the two ejected electrons without which the double ionization cannot take place [12–19].

In spite of the fact that diatomic or other molecular gases exist naturally and are thus easily available, and that ( $\gamma$ , 2e) experiments on these types of targets bring no supplementary difficulties compared to atomic targets, these experiments are less often performed mainly because of the lack of appropriate theoretical treatments due to the supplementary degrees of freedom and the difficulty in describing the two ejected electrons in the field of many centers. In the past, Le Rouzo [20, 21] first extended the wave function approach of Byron and Jochain [22] to the PDI of H<sub>2</sub>. Later, Feagen [23] and Wightman *et al* [24] observed the similarities of the electron pair distribution between the variations of the MDCS of D<sub>2</sub> and helium. To establish the PDI of H<sub>2</sub>, Walter and Briggs [25] applied a correlated two-center continuum wave function



**Figure 1.** The variation, in polar representation, of the TDCS in the atomic units equation (19) of the PDI of CO<sub>2</sub>, for different values of the energy of the ejected electrons. The polar angle represents the ejection angle  $\theta_2$  and  $\theta_1 = 90^\circ$ . The results are obtained for  $Z_a = 0.2$  and  $Z_c = 2(1 - Z_a) = 1.6$  for the final state (see text for details).

with LCAO-Slater type orbitals for the determination of the MDCS. Kheifets [26] applied one-center wave function in a convergent close-coupling procedure. We can also mention two numerical approaches using prolate spheroidal solutions in an external complex scaling (ESC) procedure [27, 28]. The PDI of other simple molecules is less often studied.

The PDI of N2 for an equal energy sharing regime has recently been determined theoretically [1] and experimentally [2]. The theoretical procedure applied succeeded quite well in reproducing the corresponding experimental results. The aim of the present work is to extend this procedure to the PDI of CO<sub>2</sub>. We will consider the ionization of the  $1\pi_g$  orbital of CO<sub>2</sub> resulting in  $CO_2^{2+}$  dication in its fundamental  ${}^{3}\Sigma_{g}^{-}$  state. The  $1\pi_g$  bound electrons of CO<sub>2</sub> will be described by the Dyson orbitals used in [29]. The vibrational and rotational levels of the residual ion cannot be resolved by the present experiments, so we have simplified the transition matrix element, as in our preceding paper [1], by applying the closure relation over these levels (see the paper of Iijima, Bonham and Ando [30] for a clear explanation). To describe the two ejected electrons, we use a three-center correlated (ThCC) model, which is an approximate solution of the Shrödinger equation, for specific waves vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . It has lately been applied to the simple ionization of CO<sub>2</sub> for the description of the free ejected electron in the field of three attractive centers in [31].

#### 2. Theory

The theoretical procedure that we apply in the determination of the MDCS of the ( $\gamma$ , 2e) PDI of CO<sub>2</sub> is quite similar to that described in [1] for the N<sub>2</sub> molecule. The main difference here is that in the final state, the residual CO<sub>2</sub><sup>2+</sup> dication, whose electronic configuration is given by

$$1\sigma_{g}^{2}1\sigma_{u}^{2}2\sigma_{g}^{2}3\sigma_{g}^{2}2\sigma_{u}^{2}4\sigma_{g}^{2}3\sigma_{u}^{2}1\pi_{u}^{4}1\pi_{g}^{2}$$
(1)

is in a  ${}^{3}\Sigma_{g}^{-}$  state, in contrast to  $N_{2}^{2+}$ , whose fundamental state is a singlet state. Now as the photon-electron interaction has no spin operator, the total spin should be conserved. As we will see below, this will impose given combinations for the spin values of the ejected electrons.

We start, as in [1], with the expression of the MDCS of the PDI of the three-center collinear molecule  $CO_2$  for the fixed orientation of the internuclear distance  $\rho$  given in atomic units

$$\sigma^{(4)}(\rho) = \frac{d^4\sigma}{d\Omega_{\rho}d\Omega_1 d\Omega_2 d\left(k_1^2/2\right)} = \frac{4\pi^2}{\omega} \alpha k_1 k_2 \frac{1}{3} \sum_{q=1}^3 |T_{fi}^q|^2.$$
(2)

Here  $d\Omega_1$ ,  $d\Omega_2$  and  $d\Omega_\rho$ , represent the elements of the solid angles for the orientations of the ejected electrons and the internuclear axis respectively.  $k_1$  and  $k_2$  give the modula of the wave vectors of the two ejected electrons.  $\alpha = 1/c = 7.29735 \times 10^{-3}$  a.u. is the fine-structure constant and  $\omega$  is the photon frequency. We admit the energy conservation equation

$$E_1 + E_2 = E_i + \omega, \tag{3}$$

where  $E_1 = k_1^2/2$ ,  $E_2 = k_2^2/2$  represent the energy values of the two ejected electrons respectively, and  $E_i$  the energy necessary for the double ionization.

The summation index q runs over three possible spin combinations of the ejected electrons and the residual ion, satisfying the conservation of the total spin. Let  $M_{s_{ion}}$  represent the total z component of the spin of the residual ion  $CO_2^{2+}$ , which is in the lowest  ${}^{3}\Sigma_{g}^{-}$  state. It can take the values 1,0 and -1. Furthermore, let  $M_{s_{ej}}$  represent the total z component of the two ejected electrons. It can also take the values 1,0 and -1. To satisfy the conservation of the total spin, we must consider the three cases, which give the sum  $M_{s_{ion}}+M_{s_{ej}}=0$ . These are (+1, -1), (0, 0) and (-1, +1). Let us represent the final state wave function by the possible Slater determinants. For simplicity, we exclude the inner orbitals in the expression of the determinants and keep only the electrons of the  $1\pi_{g}$ level and the ejected electrons. We have the following three possibilities:

For the case  $M_{s_{ion}} = 1$ ,  $M_{s_{ej}} = -1$  we have one possible determinant:

$$|M_{s_{ion}} = 1, M_{s_{ej}} = -1\rangle = |1\pi_g^1 1\pi_g^{-1} \bar{\chi}_1 \bar{\chi}_2|.$$
 (4)

Here  $\chi_1, \chi_2$  represent the ejected electrons with the bar indicating individual negative spin -1/2.

For the case  $M_{s_{ion}} = 0$  and  $M_{s_{ej}} = 0$  we have a combination of four determinants:

$$|M_{s_{ion}} = 0, M_{s_{ej}} = 0 \rangle = \frac{1}{\sqrt{4}} \left( \left[ \left| 1 \bar{\pi}_{g}^{1} 1 \pi_{g}^{-1} \bar{\chi}_{1} \chi_{2} \right| \right. \right] \\ \left. - \left| 1 \pi_{g}^{1} 1 \bar{\pi}_{g}^{-1} \bar{\chi}_{1} \chi_{2} \right| \right] \\ \left. - \left[ \left| 1 \bar{\pi}_{g}^{1} 1 \pi_{g}^{-1} \chi_{1} \bar{\chi}_{2} \right| \right] \\ \left. + \left| 1 \pi_{g}^{1} 1 \bar{\pi}_{g}^{-1} \chi_{1} \bar{\chi}_{2} \right| \right] \right).$$
(5)

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**Figure 2.** Gray scale representations (in color scale online) of the variation of the TDCS in the atomic units equation (19) of the PDI of the  $1\pi_g$  level of CO<sub>2</sub> obtained by the velocity gauge, in terms of the two ejection angles  $\theta_1$  and  $\theta_2$ . (a) The results obtained by the gaussian parametrization formula [33] and [1] (b) the results for the case  $Z_a = 0.2$  and (c) that of  $Z_a = 0.8$ . Here  $E_1 = E_2 = 10$  eV, and the vectors  $\mathbf{k}_1$ ,  $\mathbf{k}_2$  and  $\epsilon$  are coplanar.

For the case  $M_{s_{ion}} = -1$  and  $M_{s_{ej}} = +1$  we have one possible determinant:

$$|M_{s_{ion}} = -1, M_{s_{ej}} = +1 \rangle = \left| 1 \bar{\pi}_g^1 1 \bar{\pi}_g^{-1} \chi_1 \chi_2 \right|.$$
 (6)

Let us now define the three transition matrices:

$$T_{fi}^{q=1} = \left\langle \left| 1\pi_g^1 1\pi_g^{-1} \bar{\chi}_1 \bar{\chi}_2 \right| |V| \left| 1\pi_g^1 1\pi_g^{-1} 1\bar{\pi}_g^{-1} 1\bar{\pi}_g^{-1} \right| \right\rangle, \quad (7)$$

$$T_{fi}^{q=2} = \left\langle \frac{1}{\sqrt{4}} \left( \left[ \left| 1\bar{\pi}_{g}^{-1}1\pi_{g}^{-1}\bar{\chi}_{1}\chi_{2} \right| - \left| 1\pi_{g}^{1}1\bar{\pi}_{g}^{-1}\bar{\chi}_{1}\chi_{2} \right| \right] - \left[ \left| 1\bar{\pi}_{g}^{1}1\pi_{g}^{-1}\chi_{1}\bar{\chi}_{2} \right| + \left| 1\pi_{g}^{1}1\bar{\pi}_{g}^{-1}\chi_{1}\bar{\chi}_{2} \right| \right] \right) \times |V| \left| 1\pi_{g}^{1}1\pi_{g}^{-1}1\bar{\pi}_{g}^{1}1\bar{\pi}_{g}^{-1} \right| \right\rangle,$$
(8)

$$T_{fi}^{q=3} = \left\langle \left| 1\bar{\pi}_{g}^{1} 1\bar{\pi}_{g}^{-1} \chi_{1} \chi_{2} \right| |V| \left| 1\pi_{g}^{1} 1\pi_{g}^{-1} 1\bar{\pi}_{g}^{1} 1\bar{\pi}_{g}^{-1} \right| \right\rangle.$$
(9)



**Figure 3.** The variation in polar representation of the TDCS in the atomic units equation (19) of the PDI of CO<sub>2</sub>, for  $E_1 = E_2 = 10 \text{ eV}$  and for the different values of  $Z_a$ . As in figure 1, the polar angle represents the ejection angle  $\theta_2$  and  $\theta_1 = 2\pi - \theta_2$ .

These expressions

$$V = \epsilon \left( \boldsymbol{\nabla}_{r_1} + \boldsymbol{\nabla}_{r_2} \right) \tag{10}$$

represent the photon-electron interaction taken in the velocity gauge, which is less sensitive to the approximations made in the wave functions than the dipole length gauge [22].

After eliminating the spin part in these expressions, we obtain the following expression

$$\sigma^{(4)}(\rho) \propto \frac{1}{3} \sum_{q=1}^{3} |T_{f\bar{t}}^{q}|^{2}$$

$$= \frac{1}{3} \left| \left\langle \chi_{1}\chi_{2} \right| |V| \left| 1\pi_{g}^{1}1\pi_{g}^{-1} \right\rangle + \left\langle \chi_{1}\chi_{2} \right| |V| \left| 1\pi_{g}^{-1}1\pi_{g}^{1} \right\rangle \right|^{2}$$

$$+ \frac{2}{3} \left| \left\langle \chi_{1}\chi_{2} \right| |V| \left| 1\pi_{g}^{1}1\pi_{g}^{-1} \right\rangle - \left\langle \chi_{1}\chi_{2} \right| |V| \left| 1\pi_{g}^{-1}1\pi_{g}^{1} \right\rangle \right|^{2}.$$
(11)

Here the  $1\pi_g$  orbitals in the initial state will be given by the corresponding Dyson orbitals of CO<sub>2</sub> [29]. We think that this is a good compromise between the use of simple Hartree–



Fock orbitals and an all electron treatment of  $CO_2$  taking into account all the inactive electrons, which would result in very cumbersome calculations.

The two ejected electrons represented symbolically by  $\chi_1\chi_2$  in the transition matrix elements will be described by a correlated product of the three-center continuum (ThCC) wave function as applied in [1, 2, 25] for the two-center case,

$$\phi_f(\mathbf{k}_1, \mathbf{r}_1, \mathbf{k}_2, \mathbf{r}_2) = v(k_{12})_1 F_1(\imath \alpha_{12}, 1, -\imath(k_{12}r_{12} + \mathbf{k}_{12}\mathbf{r}_{12})) T(\mathbf{k}_1, \mathbf{r}_1) T(\mathbf{k}_2, \mathbf{r}_2), \quad (12)$$

in which we have introduced, as in the case of atoms [32], the electron-electron correlation. Here  $k_1$  and  $\mathbf{k}_2$  represent the respective wave vectors of the two electrons and  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$  their relative position.

$$v(k_{12}) = \exp\left(-\frac{\pi\alpha_{12}}{2}\right)\Gamma(1-i\alpha_{12}), \quad (13)$$

represents the Gamow factor with

$$\alpha_{12} = \frac{1}{2k_{12}}, \quad \mathbf{k}_{12} = \frac{1}{2} (\mathbf{k}_1 - \mathbf{k}_2).$$
 (14)

The final state wave function satisfies the ortho-normality condition in the sense

$$\left\langle \phi_f \left( \mathbf{k}_1, \, \mathbf{r}_1, \, \mathbf{k}_2, \, \mathbf{r}_2 \right) \middle| \phi_f \left( \mathbf{k}_1', \, \mathbf{r}_1, \, \mathbf{k}_2', \, \mathbf{r}_2 \right) \right\rangle$$
  
=  $\delta \left( \mathbf{k}_1 - \mathbf{k}_1' \right) \delta \left( \mathbf{k}_2 - \mathbf{k}_2' \right).$  (15)

In equation (12), the one electron (ThCC) wave function describing the state of a slow electron in the field of three fixed coulomb centers [31] is given by

$$T(\mathbf{k}_{i}, \mathbf{r}_{i}) = \frac{\exp(\imath \mathbf{k}_{i} \mathbf{r}_{i})}{(2\pi)^{3/2}} M_{a} {}_{1}F_{1}(\imath \alpha_{ia}, 1, -\imath [k_{i}r_{ia} + \mathbf{k}_{i}\mathbf{r}_{ia}])$$

$$\times M_{b} {}_{1}F_{1}(\imath \alpha_{ib}, 1, -\imath [k_{i}r_{ib} + \mathbf{k}_{i}\mathbf{r}_{ib}])$$

$$\times M_{c} {}_{1}F_{1}(\imath \alpha_{ic}, 1, -\imath [k_{i}r_{ic} + \mathbf{k}_{i}\mathbf{r}_{ic}]),$$
(16)



with

$$M_{j} = \exp\left(-\pi \frac{\alpha_{ij}}{2}\right) \Gamma\left(1 - \imath \alpha_{ij}\right), \quad j = a, b, c \quad i = 1, 2.$$
(17)

Here the Sommerfeld parameter  $\alpha_{ij} = -Z_{ij}/k_i$  in the Kummer hypergeometric function, and

$$\mathbf{r}_{ia} = \mathbf{r}_i + \rho/2, \quad \mathbf{r}_{ib} = \mathbf{r}_i - \rho/2, \quad \mathbf{r}_{ic} = \mathbf{r}_i \quad i = 1, 2,$$
(18)

refer to the positions of the ejected electron with respect to the two oxygen and the central carbon atoms. As in [31], we will consider that the two oxygen centers are equivalent, so  $Z_{ia} = Z_{ib}$ . The asymptotic conditions impose that  $Z_{ia} + Z_{ib} + Z_{ic} = 2$  for the total charge 'seen' by an ejected electron. Thus, the charge corresponding to the carbon center will be given by  $Z_{ic} = 2(1 - Z_{ia})$ . Here, we will also assume that the two electrons being equivalent, the corresponding charges in the Sommerfeld parameter of final state wave function are identical. We will take in what follows  $Z_{1j} = Z_{2j} = Z_j$ , j = a, b, c.

The integrations run over the space coordinates of the two electrons, which are defined in the molecular frame of reference, whose origin is fixed on the carbon center of the molecule and whose z-axis is parallel to the internuclear vector  $\rho$  of constant modulus. To our knowledge, no MDCS values are available for the  $(\gamma, 2e)$  PDI of CO<sub>2</sub> with coincidence detection of the two ejected electrons and the residual  $CO_2^{2+}$  ion. In fact the lowest state of  $CO_2^{2+}$  is metastable and dissociates to CO<sup>+</sup>+ O<sup>+</sup> with a half-life of 2.3  $\pm$  0.2  $\mu$  sec [34]. Although it is relatively difficult, this makes it possible to determine the orientation of the target by detecting one of the emerging fragments, the  $O^+$  or the  $CO^+$ , in coincidence with the ejected electrons. The existing experiments mainly detect the two ejected electrons in coincidence, so we must integrate the MDCS over all directions of the molecular axis. This will give us the triple differential cross section (TDCS) measured by the experiment

$$\sigma^{(3)} = \frac{1}{4\pi} \int d\Omega_{\rho} \sigma^{(4)}(\rho).$$
<sup>(19)</sup>

#### 3. Results

As we mentioned above, our aim in this work is to study the variation of the MDCS of the PDI of  $CO_2$  in terms of the ejection energy and the ejection angles of the two  $1\pi_g$  bound electrons represented in the figures by their respective wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . To our knowledge, no such results concerning  $CO_2$  exist in previous literature. In the past, similar wave function approaches have succeeded in reproducing the experimental behavior of the variation of the TDCS of the PDI of H<sub>2</sub> [25] and N<sub>2</sub> [1]. We hope that our present results obtained by a similar approach extended to a three center  $CO_2$ 

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target will open the way for further developments and guide experiments in the near future.

In this paper we will only consider the equal energy sharing regime between the two ejected electrons, and the habitual situations where the vectors  $\mathbf{k}_1$ ,  $\mathbf{k}_2$  are coplanar with the polarization vector  $\epsilon$  which is parallel to the *z* axis of the laboratory frame.

We will consider four different values for the charges parameters. We Sommerfeld in the will take  $Z_a = 0.2, 0.4, 0.6, 0.8$  for which  $Z_c = 1.6, 1.2, 0.8, 0.4$ respectively. This will permit us to observe the influence of the nuclear charge distribution 'seen' by the ejected electrons, on the behavior of the TDCS. Now, for the choice  $(Z_a = 0.2,$  $Z_c = 1.6$ ), the external oxygen centers will have less influence than the carbon center situated at the origin. For the choice  $(Z_a = 0.8, Z_c = 0.4)$  the influence of the external oxygen centers becomes more important and the multi-center aspect more pronounced than that of the carbon center. We will also present the results obtained by the best fit of the Gaussian parametrization formula proposed in [33], using the procedure described in [1].

We start by looking for ejection energy values, which give the largest cross section. In figure 1, for the case  $Z_a = 0.2$  we show the variation of the TDCS with  $\theta_2$  for different values of the ejection energy. We use the polar representation, where the polar angle represents  $\theta_2$ , and the polar radius, the magnitude of the TDCS. We see that the results obtained for the case  $E_1 = E_2 = 10$  eV present the optimal situation. In all cases not shown here for which we have taken other values for  $Z_a$  like  $Z_a = 0.4$ , 0.6, 0.8, the 10 eV case always gives the optimal values for the TDCS. We will thus only show the results for this particular value of the energy of the ejected electrons in what follows.

To see the global structure of the variation of the TDCS with the ejection angles, in figures 2 (a), (b) and (c), we give the variations, in gray scale (color scale online), in terms of the ejection angles  $\theta_1$  and  $\theta_2$  simultaneously. As expected, the results obtained by the best fit of the Gaussian parametrization formula [33] following the procedure described in [1] show the habitual distribution obtained for the double ionization of helium type one-center targets. The results for  $(Z_a = 0.2,$  $Z_c = 1.6$ ) are given in figure 2 (b) and that of ( $Z_a = 0.8$ ,  $Z_c = 0.4$ ) in figure 2 (c). We see that all the panels show distributions which respect symmetry properties in the equal energy sharing regime, namely  $\sigma^{(3)}(\theta_1, \theta_2) = \sigma^{(3)}(\theta_2, \theta_1)$ , and  $\sigma^{(3)}(\theta_1, \theta_2) = \sigma^{(3)}(2\pi - \theta_1, 2\pi - \theta_2)$ . We have also two lines  $\theta_1 = \theta_2 - \pi$  and  $\theta_1 = \theta_2 + \pi$ , which are also axes of symmetry. For the first axis we have for  $0 \leq \theta_1 \leq \pi$  and  $\pi \leqslant \theta_2 \leqslant 2\pi, \sigma^{(3)}(\theta_1, \theta_2) = \sigma^{(3)}(\theta_2 - \pi, \theta_1 + \pi)$  and for the second we have for  $\pi \leqslant \theta_1 \leqslant 2\pi$  and  $0 \leqslant \theta_2 \leqslant \pi$ ,  $\sigma^{(3)}(\theta_1, \theta_2) = \sigma^{(3)}(\pi + \theta_2, \theta_1 - \pi)$ . As mentioned above, taking  $Z_a = 0.2$  and  $Z_c = 1.6$  in the ThCC function puts most of the charge seen by the ejected electrons in the carbon center situated at the mid-point of the molecule, thus reducing the three-center character of the ThCC. This can be seen in the relative similarity of the structure of figure 2(b) to that of figure 2(a). The situation changes when we take  $Z_a = 0.8$  and  $Z_c = 0.4$  attributing a bigger charge to the two exterior

oxygen centers. We see in figure 2(c) that the structure has undergone some modifications in the region around  $\theta_1 = \theta_2 - \pi$ . We also see that between the two maxima the valley is now replaced by a smaller maximum. To analyze these observations, in what follows we will consider some particular geometries and study the variations quantitatively.

In figure 3 we consider the variation of the TDCS with  $\theta_2$ and we impose the condition  $\theta_1 + \theta_2 = 2\pi$ . This corresponds to the variation taken along the diagonal passing by 360° of figure 2. Four cases corresponding to  $Z_a = 0.2, 0.4, 0.6, 0.8$ and the Gaussian fit [1] are presented. Let us study the different behaviors for the particular direction  $\theta_2 = 90^\circ$  $(\theta_1 = 270^\circ)$  with respect to  $\epsilon$ . For these angles the final state electron-electron correlation, which is the principal cause of double ionization, is not very important in the one-center case. This is confirmed by the structure of the dash-dot-dot curve corresponding to results obtained by the Gaussian fit approach for which double ionization in this direction is forbidden. Now in our calculations, where we have introduced the molecular aspect of the process, this direction is no longer forbidden. It passes from an unfavorable situation for  $Z_a = 0.2$  (dashed curve) to a rather favorable one for  $Z_a = 0.8$  (continuous line). This shows the necessity of the introduction of the multi-center factor in the initial and final state of the process. Let us now consider the ejection direction around  $\theta_2 = 50^\circ$  and consequently  $\theta_1 = 310^\circ$  which is a favorable direction for all the curves with an angular deflection of about ten degrees between the mono-centric and multicentric approaches.

In the same way, in figure 4 we consider the variations of the TDCS with  $\theta_2$  for two particular values of  $\theta_1$  and for each value giving the results for the five cases mentioned above. In 4 (a) we have the variation of the TDCS for  $\theta_1 = 60^\circ$  which corresponds to the variation of the TDCS along the line  $\theta_1 = 60^\circ$  in figure 2. In the same manner as in (3), we observe the evolution of the structure for different charges  $Z_a = 0.2, 0.4, 0.6, 0.8$  and the Gaussian fit [1]. For the atomic case of the Gaussian fit, parallel and anti-parallel ejection for both electrons is forbidden, but in the multi-center case anti-parallel ejection is possible. We also observe that the maxima of the curves corresponding to  $Z_a = 0.2, 0.4, 0.6, 0.8$  are situated around  $\theta_2 = 320^\circ$ , which corresponds to a relative angle of about 100° between the ejection directions of the two electrons as in the preceding case. In figure 4 (b) we show the case of  $\theta_1 = 180^\circ$ . The particularity of this case is that parallel and antiparallel ejection is forbidden in all five choices. This is due to the fact that  $\mathbf{k}_1$  is aligned with  $\epsilon$ . In this geometry the molecule behaves like an atom with a slight deviation for the multicenter case for the optimal ejection directions perpendicular to  $\mathbf{k}_1$  around 90°.

#### 4. Conclusion

By extending the two correlated two-center coulomb continuum descriptions to the three-center problem, and by using Dyson type orbitals for the initial state wave function, we have calculated the TDCS of the PDI of  $CO_2$  in equal ejection energy regime employing the velocity gauge. We have also introduced adjustable charges for the two oxygen and the carbon centers of this linear molecule based on the asymptotic conditions. To guide experiments in the near future, we have studied and analyzed the variation of the TDCS with the ejection energy and the ejection directions and compared it to those obtained by the gaussian parametrization formula. The results verify the symmetry conditions of the TDCS and show the optimal ejection directions for an equal energy sharing geometry. They also show the necessity of using higher values of  $Z_a$ , the Sommerfeld parameter of the oxygen center. In the near future, we intend to adapt our procedure and the three- center continuum function to other triatomic molecules in which the atoms are not aligned as in H<sub>2</sub>S, for example.

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