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Three-centre continuum wavefunction: application to the (e, 2e) simple ionization of the $1\pi_g$, $1\pi_u$ and $3\sigma_u$ molecular orbitals of CO₂ by fast electron impact

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Abstract

With the aim of finding an appropriate description of the state of an ejected electron from a linear three-centre molecular target, a wavefunction is constructed in a closed analytical form by solving the Schrödinger equation of an unbound electron (with wave vector \mathbf{k}) in a Coulomb field of three fixed charged nuclei. The model, which is an extension of a two-centre model developed in the past, fulfils the correct boundary conditions asymptotically up to the order $O((kr)^{-2})$. It is employed, in the frame of a perturbative first Born three-centre procedure, to the determination of the multiply differential cross sections (MDCS) of the (e,2e) simple ionization of the valence $1\pi_g$ level of CO₂, for which experimental results were given recently. The ionization of the inner $1\pi_u$ and $3\sigma_u$ levels of CO₂ are also investigated by this approach. The study of the variation of the MDCS with the direction of the scattered electron and the ejected electron in the case of oriented three-centre targets shows interference patterns similar to those created by the diffraction of light by three apertures.

1. Introduction

The scattering of an electron by two- or three-centre targets is one of the basic problems in collisional processes involving diatomic and polyatomic linear molecular targets [1]. In the case of simple (e, 2e) ionization experiments, where the ejected and the scattered electrons are detected in coincidence (see [2] and [3] for a general review), the basic difficulty for diatomic targets, besides that of the separation of the vibrational and rotational movements of the nuclei [4], consists of the determination of the continuum wavefunction of the slow ejected electron in the attractive field of the fixed centres. Usually one-centre approximate models are used by constructing large partial one-centre Coulomb or distorted waves [5] centred on one of the nuclei of the linear molecule for the homo-nuclear targets like Li₂ [6], or centred on the heaviest atom of the target, as in the case of H₂O [7]. Serov and collaborators [8] have used the exact solutions of the two-centre Schrödinger equation, which is separable in prolate spheroidal coordinates, to construct the wave, describing

the relatively slow (10 eV) ejected electron in the (e, 2e) experiments of H₂⁺ [8] and H₂ [9].

We have proposed in the past an elegant two-centre Coulomb continuum (TCC) wavefunction [10] satisfying the correct boundary conditions, which produces results of the same quality as the exact solutions for the ionization of H₂⁺. This function is now considered by different groups [11–13] as a very good choice in the study the two-centre aspects in a variety of situations, where diatomic systems are involved, beyond strictly electron–molecule collision processes. The original TCC model has slightly been modified [14] by the introduction of a supplementary parameter, which adds a certain flexibility to the function and adapts it to more general situations. We will refer to this as the modified two-centre continuum (MTCC).

The aim of the present work is to extend the TCC model to the three-centre case and apply it to the ionization of CO₂, which is the most common linear three-centre target, for which (e, 2e) experiments have been realized [15, 16]. Besides the direct interest of modelling the experiments, we want

to verify if the variation of the multiply differential cross section (MDCS) of a three-centre target with the scattering and ejection angles can show interference patterns similar to those already predicted for the two-centre case [10].

2. Theory

For the determination of the MDCS of the (e, 2e) simple ionization of CO₂, where the ejected and scattered electrons are detected in coincidence, which will be considered as a three-centre collinear molecule, we will employ, as in our previous publication [14], a first-order Born series perturbative procedure. The MDCS of a general out-of-plane detection of the scattered and ejected electrons in the case of an oriented linear CO₂ target is fourfold given by

$$\sigma^{(4)}(\rho) = \frac{d^4\sigma}{d\Omega_\rho d\Omega_s d\Omega_e d(k_e^2/2)} = \frac{k_s k_e}{k_i} \times \begin{cases} 2^{-1} (|T_{fi}^{m=-1}|^2 + |T_{fi}^{m=1}|^2) & \text{for } 1\pi_g \text{ and } 1\pi_u, \\ |T_{fi}^{m=0}|^2 & \text{for } 3\sigma_u, \end{cases} \quad (1)$$

where $d\Omega_s$, $d\Omega_e$ and $d\Omega_\rho$ are respectively the elements of the solid angles for the orientations of the scattered and the ejected electrons and the internuclear axis ρ . k_i , k_s and k_e represent respectively the moduli of the wave vectors of the incident, scattered and ejected electrons. m is the electronic magnetic quantum number corresponding to the level from which the electron will be ejected.

In the case of randomly oriented targets, we must pass to the triple differential cross section (TDCS) by integrating over all possible and equally probable directions of the molecule in space:

$$\sigma^{(3)} = \frac{1}{4\pi} \int d\Omega_\rho \sigma^{(4)}(\rho). \quad (2)$$

The conservation of the kinetic energy is given by

$$E_i = E_s + E_e + I, \quad (3)$$

where E_i , E_s and E_e represent respectively the energy values of the incident, scattered and ejected electrons. I gives the energy necessary to eject an electron from the particular level of the CO₂ target [15, 17]:

$$I = \begin{cases} 13.77 \text{ eV} & \text{for } 1\pi_g, \\ 17.31 \text{ eV} & \text{for } 1\pi_u, \\ 18.07 \text{ eV} & \text{for } 3\sigma_u. \end{cases} \quad (4)$$

In the limits of the ‘frozen-core’ model of the electronic structure of the target, the T matrix element T_{fi}^m involves only two electrons, the fast incident (scattered) and the bound (slow ejected) electrons. It is given here as the matrix element of the first term of the Born perturbative series:

$$T_{fi}^m = \frac{1}{2\pi} \int d\mathbf{r} \int d\mathbf{R} \exp(i(\mathbf{k}_i \mathbf{R} - \mathbf{k}_s \mathbf{R})) \times \bar{\lambda}_f(\mathbf{r}, \rho) V \lambda_i^m(\mathbf{r}, \rho). \quad (5)$$

Here, the fast incident and scattered electrons are reasonably described by plane waves, $(2\pi)^{-3/2} \exp(i\mathbf{k}_i \mathbf{R})$ for the incident electron and $(2\pi)^{-3/2} \exp(i\mathbf{k}_s \mathbf{R})$ for the scattered. $\lambda_i^{m=\pm 1}(\mathbf{r}, \rho)$ can be identified as a Dyson orbital [18, 19] of the bound electron in the initial state in the body fixed system of reference, and $\lambda_f(\mathbf{r}, \rho)$ the wavefunction of the ejected electron in the final state. The carbon atom is found at the origin of the system of reference, and the two oxygen atoms on the z axis, respectively, at $-\rho/2$ and $\rho/2$. $\mathbf{r} = \mathbf{r}_C$ refers to the position of the bound (ejected) electron with respect to the carbon centre. The position of this electron with respect to the two oxygen centres O₁ and O₂ is given by $\mathbf{r}_{O_1} = \mathbf{r} + \rho/2$ and $\mathbf{r}_{O_2} = \mathbf{r} - \rho/2$. The potential V represents the interaction between the incident electron and the target, which will be approximated here by the Coulomb interactions of the incident electron with the bound electron and the screened carbon and oxygen nuclei:

$$V = -\frac{Z_{O_1}}{|\mathbf{R} + \rho/2|} - \frac{Z_C}{R} - \frac{Z_{O_2}}{|\mathbf{R} - \rho/2|} + \frac{1}{|\mathbf{R} - \mathbf{r}|}. \quad (6)$$

The positive charges of the three-centres given by $Z_{O_1} \geq 0$, $Z_C \geq 0$, $Z_{O_2} \geq 0$ satisfy the condition $Z_{O_1} + Z_C + Z_{O_2} = 1$ as the target is globally neutral. They will be chosen empirically.

Using the Bethe transformation for \mathbf{R} in equation (5)

$$\int d\mathbf{R} \frac{\exp(i\mathbf{K}\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} = \frac{4\pi \exp(i\mathbf{K}\mathbf{r})}{K^2}, \quad (7)$$

with $\mathbf{K} = \mathbf{k}_i - \mathbf{k}_s$ being the momentum transfer, the transition matrix element T_{fi}^m will be reduced to

$$T_{fi}^m = \frac{2}{K^2} \int d\mathbf{r} \bar{\lambda}_f(\mathbf{r}, \rho) \lambda_i^m(\mathbf{r}, \rho) (-Z_{O_1} \exp(-i\mathbf{K}\rho/2) - Z_C - Z_{O_2} \exp(i\mathbf{K}\rho/2) + \exp(i\mathbf{K}\mathbf{r})), \quad (8)$$

where the integrations is over the space coordinates of the ejected electron. The orientation of the molecule will be given by ρ of constant modulus $\rho = 4.39$ au for the equilibrium position of CO₂.

2.1. The initial state wavefunctions

The initial ground-state configuration of CO₂ is given by [20, 21]

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4. \quad (9)$$

We will consider the (e, 2e) ionization of the three outermost levels. For each of these bound levels, we will present results obtained by two different bases. One is obtained by the molecular orbitals given by Mulligan [20], which we will designate by the minimal basis and the other obtained by the application of a molecular orbital obtained by the Slater-Type Orbital Package (STOP) [22, 23], which we will designate as the extended basis. The molecular orbitals proposed by McLean [21] give very similar results to those of [20], so we will not present them here.

The molecular orbitals of the extended bases corresponding to the above three levels are constructed by the

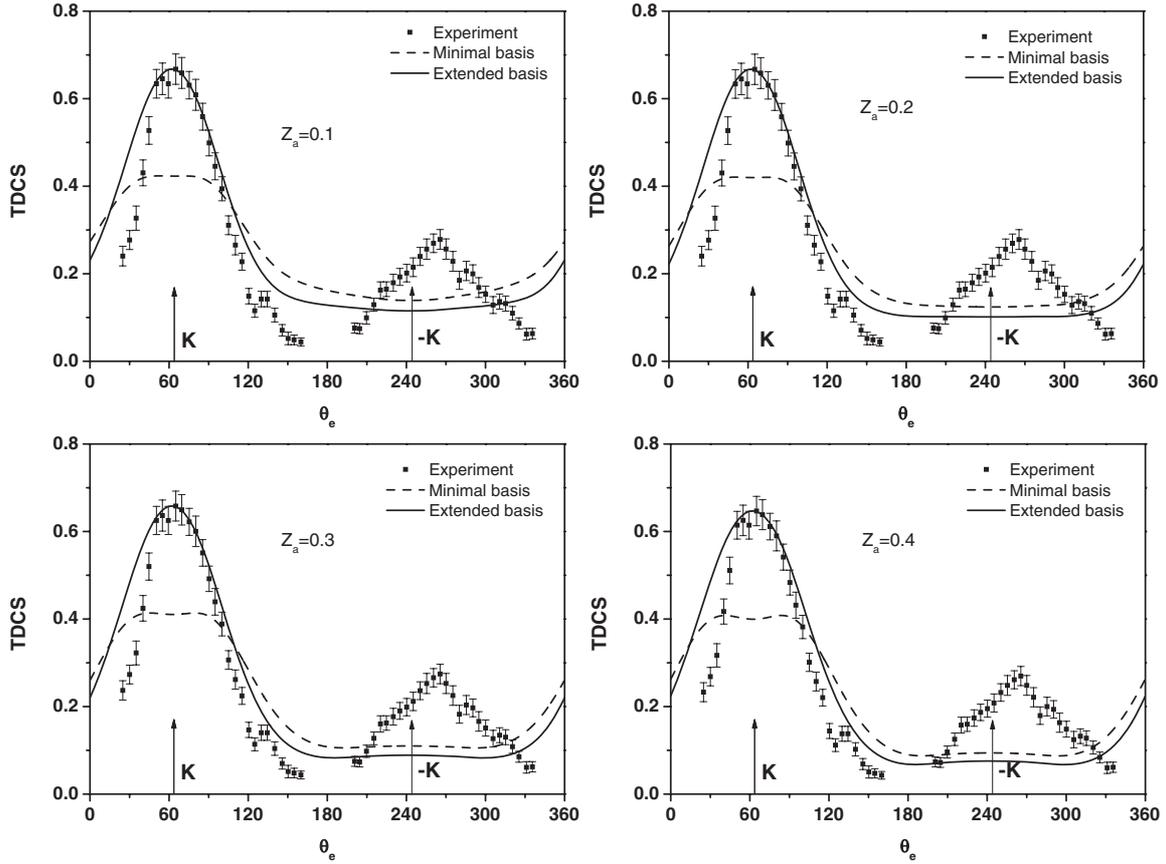


Figure 1. Variation of the TDCS in terms of the ejection angle θ_e of the ionization of the $1\pi_g$ level of CO_2 for different values of the parameters $Z_a = Z_b = 0.1(0.1)0.4$ and $Z_c = 1 - 2Z_a$. The energy of the scattered electron $E_s = 500$ eV which is detected at an angle $\theta_s = -6^\circ$ in coincidence with the ejected electron with the energy $E_e = 37$ eV. Full line: the extended basis set [25]. Dashed line: the minimal basis set [20]. The experimental cross section [16] normalized on the binary pick of the theoretical cross section with the extended basis set.

linear combinations of Slater-type 1s, 2s, 2p and 3d orbitals that we define in the following way:

$$1s = \sqrt{\frac{\xi_1^3}{\pi}} \exp(-\xi_1 r),$$

$$2s = \sqrt{\frac{\xi_2^5}{3\pi}} r \exp(-\xi_2 r), \quad 2p_z = \sqrt{\frac{\xi_3^5}{\pi}} z \exp(-\xi_3 r),$$

$$2p_x = \sqrt{\frac{\xi_3^5}{\pi}} x \exp(-\xi_3 r), \quad 2p_y = \sqrt{\frac{\xi_3^5}{\pi}} y \exp(-\xi_3 r),$$

$$3d_{zz} = \sqrt{\frac{\xi_4^7}{18\pi}} (2z^2 - x^2 - y^2) \exp(-\xi_4 r),$$

$$3d_{xz} = \sqrt{\frac{2\xi_4^7}{3\pi}} xz \exp(-\xi_4 r), \quad 3d_{yz} = \sqrt{\frac{2\xi_4^7}{3\pi}} yz \exp(-\xi_4 r).$$

They will be centred on each atom designated here by O_1 , C and O_2 .

For the $1\pi_g$ level, the following function is used $\lambda_i^{m=\pm 1}(\mathbf{r}, \rho) = 2^{-1/2}(f_g \pm i g_g)$ with

$$f_g = C_1(2p_x^{O_2} - 2p_x^{O_1}) + D_1(3d_{xz}^{O_2} + 3d_{xz}^{O_1}) + F_1 3d_{xz}^C, \quad (10)$$

$$g_g = C_1(2p_y^{O_2} - 2p_y^{O_1}) + D_1(3d_{yz}^{O_2} + 3d_{yz}^{O_1}) + F_1 3d_{yz}^C,$$

satisfying the gerade inversion symmetry $\lambda_i^{m=\pm 1}(\mathbf{r}, \rho) = \lambda_i^{m=\pm 1}(-\mathbf{r}, \rho)$. Here, the upper index indicates the atom on which a given orbital is centred.

For the $1\pi_u$ level, we constructed the molecular orbital satisfying the ungerade inversion symmetry $\lambda_i^{m=\pm 1}(\mathbf{r}, \rho) = -\lambda_i^{m=\pm 1}(-\mathbf{r}, \rho) = 2^{-1/2}(f_u \pm i g_u)$ with

$$f_u = C_2(2p_x^{O_2} + 2p_x^{O_1}) + D_2(3d_{xz}^{O_2} - 3d_{xz}^{O_1}) + E_2 2p_x^C, \quad (11)$$

$$g_u = C_2(2p_y^{O_2} + 2p_y^{O_1}) + D_2(3d_{yz}^{O_2} - 3d_{yz}^{O_1}) + E_2 2p_y^C.$$

For the $3\sigma_u$ level, the molecular orbital that we constructed satisfies $\lambda_i^{m=0}(\mathbf{r}, \rho) = -\lambda_i^{m=0}(-\mathbf{r}, \rho)$ and has the form

$$\lambda_i^{m=0}(\mathbf{r}, \rho) = A_3(1s^{O_2} - 1s^{O_1}) + B_3(2s^{O_2} - 2s^{O_1}) + C_3(2p_z^{O_2} + 2p_z^{O_1}) + D_3(3d_{zz}^{O_2} - 3d_{zz}^{O_1}) + E_3 2p_z^C. \quad (12)$$

Here, the Mulligan convention [20] is used, where all one-centre orbitals have the same z axis along the internuclear axis ρ , and they all are positive in the positive z direction.

The optimized orbital exponents ξ_1 , ξ_2 , ξ_3 and ξ_4 of oxygen and carbon [24, 25] are shown in table 1. The corresponding coefficients A_i , B_i , C_i , D_i , E_i , F_i ($i=1-3$) of the $1\pi_g$, $1\pi_u$ and $3\sigma_u$ levels displayed in table 2 have been obtained as mentioned above by the Fortran code STOP [22, 23].

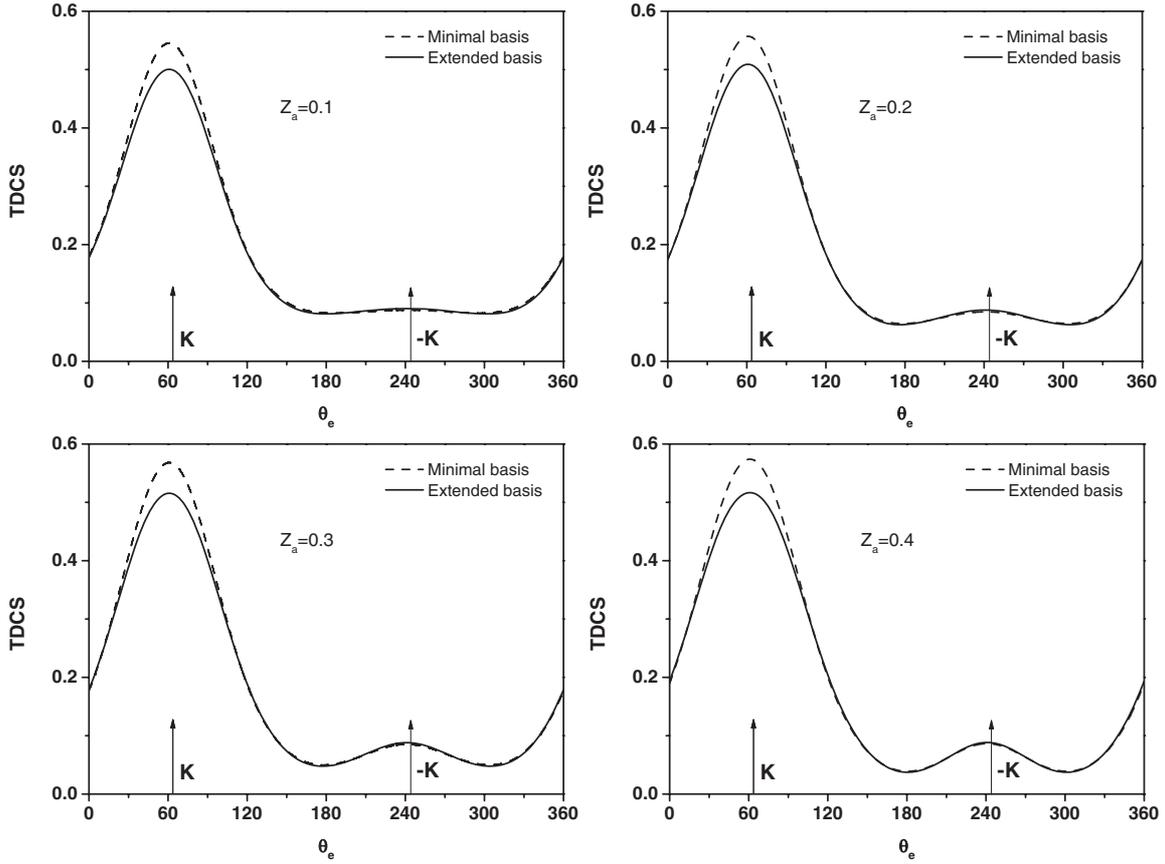


Figure 2. Same as in figure 1 from the $1\pi_u$ molecular orbital.

Table 1. Optimized orbital exponents ξ_1, ξ_2, ξ_3 and ξ_4 of oxygen and carbon [24, 25].

	ξ_1	ξ_2	ξ_3	ξ_4
O	7.657 90	2.220 96	2.254 68	2.522 79
C	5.672 70	1.850 38	1.774 43	1.143 02

2.2. The final state wavefunction: the three-centre electronic continuum

In the final state, the ejected electron is found in the field of three fixed nuclei. It will be described by what we will call the three-centre Coulomb continuum wavefunction designated by $\chi(\mathbf{k}, \mathbf{r}, \rho)$, where \mathbf{k} represents the wave vector of the electron. This function will replace $\lambda_f(\mathbf{r}, \rho)$ in the expression of the transition matrix element equation (8). We extend here the procedure described in [14] for two-centre targets to the three-centre case in the following manner.

Let us consider the electron moving in the field of three fixed collinear nuclei of charges $Z_a = Z_{O_1}$, $Z_c = Z_C$ and $Z_b = Z_{O_2}$. The vectors $\mathbf{r}_a = \mathbf{r} + \rho/2$, $\mathbf{r} \equiv \mathbf{r}_c$ and $\mathbf{r}_b = \mathbf{r} - \rho/2$ refer to the positions of the electron with respect to these nuclei. The Schrödinger equation has, in atomic units, the following form:

$$\left(-\frac{\Delta_{\mathbf{r}}}{2} - \frac{Z_a}{r_a} - \frac{Z_c}{r} - \frac{Z_b}{r_b} - \frac{k^2}{2}\right)\chi(\mathbf{k}, \mathbf{r}, \rho) = 0. \quad (13)$$

We seek a solution of this equation in the form of a product of three functions

$$\chi(\mathbf{k}, \mathbf{r}, \rho) = \zeta_a(Z_a, \mathbf{k}, \mathbf{r}_a)\zeta_c(Z_c, \mathbf{k}, \mathbf{r}_c)\zeta_b(Z_b, \mathbf{k}, \mathbf{r}_b), \quad (14)$$

with

$$\zeta_j(Z_j, \mathbf{k}, \mathbf{r}_j) = \exp\left(i\frac{\mathbf{k}\mathbf{r}_j}{3}\right)\vartheta_j(Z_j, \mathbf{k}, \mathbf{r}_j), \quad j = a, c, b. \quad (15)$$

Substituting this function into equation (13) and multiplying the left-hand side by the factor $\exp(-i\mathbf{k}\mathbf{r})$, we get the following equation:

$$\begin{aligned} &\left(\vartheta_c\vartheta_b\left[\frac{1}{2}\Delta_{\mathbf{r}_a} + i\mathbf{k}\nabla_{\mathbf{r}_a} + \frac{Z_a}{r_a}\right] + \frac{1}{2}\{\vartheta_c\nabla_{\mathbf{r}_b}\vartheta_b + \vartheta_b\nabla_{\mathbf{r}_c}\vartheta_c\}\nabla_{\mathbf{r}_a}\right)\vartheta_a \\ &+ \left(\vartheta_a\vartheta_b\left[\frac{1}{2}\Delta_{\mathbf{r}_c} + i\mathbf{k}\nabla_{\mathbf{r}_c} + \frac{Z_c}{r_c}\right] + \frac{1}{2}\{\vartheta_a\nabla_{\mathbf{r}_b}\vartheta_b + \vartheta_b\nabla_{\mathbf{r}_a}\vartheta_a\}\nabla_{\mathbf{r}_c}\right)\vartheta_c \\ &+ \left(\vartheta_c\vartheta_a\left[\frac{1}{2}\Delta_{\mathbf{r}_b} + i\mathbf{k}\nabla_{\mathbf{r}_b} + \frac{Z_b}{r_b}\right] + \frac{1}{2}\{\vartheta_c\nabla_{\mathbf{r}_a}\vartheta_a + \vartheta_a\nabla_{\mathbf{r}_c}\vartheta_c\}\nabla_{\mathbf{r}_b}\right)\vartheta_b = 0. \end{aligned} \quad (16)$$

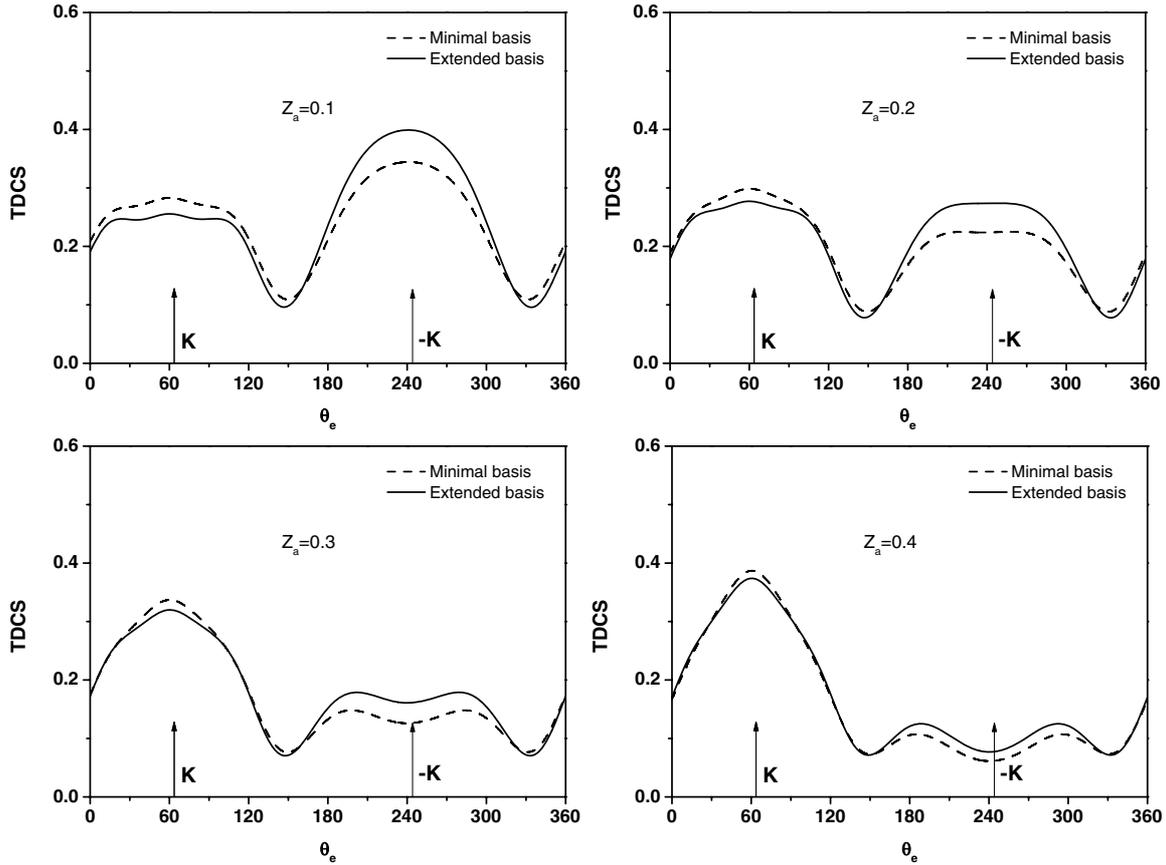


Figure 3. Same as in figure 1 from the $3\sigma_u$ molecular orbital.

Now in equation (16) we neglect as in [14] the last terms with the cross scalar products in each parentheses and obtain three separate equations for \mathbf{r}_a , \mathbf{r}_c and \mathbf{r}_b :

$$\left[\frac{1}{2} \Delta_{\mathbf{r}_j} + i \mathbf{k} \nabla_{\mathbf{r}_j} + \frac{Z_j}{r_j} \right] \vartheta_j(Z_j, \mathbf{k}, \mathbf{r}_j) = 0, \quad j = a, c, b. \quad (17)$$

These equations have the conventional solutions

$$\vartheta_j(Z_j, \mathbf{k}, \mathbf{r}_j) = {}_1F_1(i\alpha_j, 1, -i[kr_j + \mathbf{k}\mathbf{r}_j]), \quad j = a, c, b, \quad (18)$$

where ${}_1F_1$ is the Kummer confluent hypergeometric function and $\alpha_j = -Z_j/k$ is the Sommerfeld parameter. The wavefunction of the ejected electron can then be written in the following form:

$$\begin{aligned} \chi(\mathbf{k}, \mathbf{r}, \rho) = & \frac{\exp(i\mathbf{k}\mathbf{r})}{(2\pi)^{3/2}} M_{a1} F_1(i\alpha_a, 1, -i[kr_a + \mathbf{k}\mathbf{r}_a]) \\ & \times M_{c1} F_1(i\alpha_c, 1, -i[kr_c + \mathbf{k}\mathbf{r}_c]) \\ & \times M_{b1} F_1(i\alpha_b, 1, -i[kr_b + \mathbf{k}\mathbf{r}_b]), \end{aligned} \quad (19)$$

with the normalization factors

$$M_j = \exp\left(-\pi \frac{\alpha_j}{2}\right) \Gamma(1 - i\alpha_j), \quad j = a, c, b. \quad (20)$$

The neglected terms in equation (16) have the order $O(kr)^{-2}$ at $kr \rightarrow \infty$ (see details in [14]).

Taking $Z_a = Z_b$ which correspond to the two external centres, the final state wavefunction $\lambda_f(\mathbf{r}, \rho)$ will be symmetrical with respect to the exchange of the vectors \mathbf{r}_a and \mathbf{r}_b . It will also satisfy the asymptotic condition

$$\lim_{r \rightarrow \infty} \chi(\mathbf{k}, \mathbf{r}, \rho) \rightarrow \frac{\exp(i\mathbf{k}\mathbf{r})}{(2\pi)^{3/2}} \exp(-i(\alpha_a + \alpha_c + \alpha_b)) \times \ln(kr_c + \mathbf{k}\mathbf{r}_c). \quad (21)$$

We see that $\alpha_a + \alpha_c + \alpha_b = (-Z_a - Z_b - Z_c)/k = -1/k$, which shows the exact asymptotic charge seen by the ejected electron at large distances.

3. Results and discussion

As we have mentioned above, the main aim of the present work is to propose an appropriately approximated wavefunction for the state of an unbound electron in the field of three attractive fixed centres and give some guidance to ionization experiments. Stable three-centre triatomic systems are relatively rare. The linear H_3^+ system, which could be the perfect example for testing our model [26], is not stable. Similarly Li_3^{2+} is not easy to obtain and manipulate. The CO_2 molecule, which will be considered as a linear system having relatively loosely attached valence electrons with an ionization energy comparable to the hydrogen atom (0.506 au), can be a good choice for a target in our application.

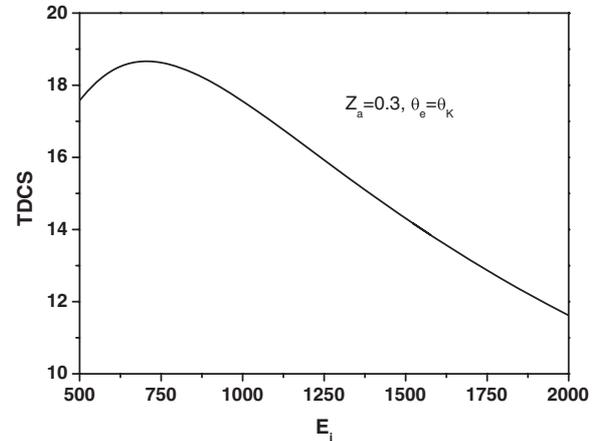
Recently experiments were performed [16] for the measurement of the TDCS of the simple (e, 2e) ionization

Table 2. The coefficients A_i , B_i , C_i , D_i , E_i and F_i ($i=1-3$) for the optimized orbital exponents ξ_1 , ξ_2 , ξ_3 and ξ_4 of the $1\pi_g$, $1\pi_u$ and $3\sigma_u$ molecular orbitals of CO_2 .

	A_i	B_i	C_i	D_i	E_i	F_i
$1\pi_g$			0.591 432	-0.022 054		0.248 423
$1\pi_u$			0.493 777	-0.031 866	0.508 353	
$3\sigma_u$	0.067 139	-0.395 932	-0.537 740	0.029 015	0.356 080	

of the valence $1\pi_g$ level with fast electrons. We have thus performed our calculations for the same conditions as these experiments, namely the detection of the fast $E_s = 500$ eV scattered electron at an angle $\theta_s = -6^\circ$ with respect to the incidence direction in coincidence with the ejected electron of $E_e = 37$ eV. Here, the incident energy is deduced from equation (3). We apply the ‘frozen-core’ approximation and choose four different values for $Z_a = Z_b$ in the perturbation potential V in equation (6), and determine for each case the TDCS by applying as mentioned above two different bound state functions: the minimal basis set proposed by Mulligan in [20] and the extended basis set presented in table 2, which has the peculiarity of having 3d orbitals. In figure 1, we show the variation of the TDCS with the ejection angle. We observe that the expected binary peak around the direction of the momentum transfer $\mathbf{K} = \mathbf{k}_i - \mathbf{k}_s$, i.e. $\theta_e = \theta_K$ is obtained only by the extended basis and that the minimal basis does not reproduce the appropriate structure of the curve in this region. This means that the 2p orbitals in the $1\pi_g$ wavefunction equation (10) are not sufficient to give the exact behaviour of the wavefunction and that 3d orbitals (see equation (10)) are necessary. This observation shows the role that (e, 2e) simple ionization experiments can have as probes to the electronic structure of atoms and molecules. We also observe that around the binary peak the results are not much affected by the nuclear charges. The recoil peak $\theta_e = \theta_K + \pi$ is absent for both bases, especially in the first three cases. A very small recoil peak is observed for the case $Z_a = 0.4$. This disagreement between experimental and first Born results was attributed in the past in the case of the ionization of N_2 [27] to the magnitude of the impact energy (~ 600 eV). In this regime, non-first Born effects, which are not taken into account in our procedure, are expected to start playing a role.

In figures 2 and 3 we present respectively the variation of the TDCS of the simple ionization of the $1\pi_u$ and $3\sigma_u$ levels of CO_2 for the same experimental conditions. As actual experimental energy resolution varies between 0.5 and 4 eV, the TDCS of these two levels are not resolved in an (e, 2e) experiment (see for example figure 2 in [15]) and coincidence counts around 18 eV must be attributed to the ionization $1\pi_u$ and $3\sigma_u$. This means that the TDCS determined separately for the $1\pi_u$ and $3\sigma_u$ levels by our procedure must be combined before being compared to experimental results. To our knowledge, there are no experimental results for the high impact energy regime of these levels, so we present them separately. As for the first case, here also the two different basis functions are used: a minimal basis given by Mulligan and the extended basis defined respectively in equations (11) and (12). In contrast to the $1\pi_g$ case, figure 1, we see that

**Figure 4.** Variation of the TDCS with the incident energy for the ionization of the $1\pi_g$ level of CO_2 when the ejection direction is parallel to the momentum transfer $\theta_e = \theta_K$ and $\phi_p = 0^\circ$, $\theta_s = -1^\circ$ with $Z_a = Z_b = 0.3$ and $Z_c = 1 - 2Z_a$.

the minimal basis produces the same structure as the extended bases showing that the d orbitals in equations (11) and (12) add little information on the electronic structure. We can also observe that for these states the recoil peak is affected by the nuclear charges Z_a especially in the case of $3\sigma_u$ case. This, we think, is due to the presence of 1s and 2s atomic orbitals, whose matrix elements are more sensitive to the nuclear charge of the final state function.

In what follows, we will study the MDCS equation (1) of the ionization of $1\pi_g$ corresponding to a given orientation of the molecule. This reveals some interesting characteristics pertaining to the linear three-centre nature of the target. To chose the optimal value of the energy of the incident electron, we have first studied the variation of the TDCS of the ionization of the $1\pi_g$ level in terms of the incident energy. We have chosen the most favourable ejection direction, which corresponds to an ejection in the direction of the momentum transfer. The scattering angle $\theta_s = -1^\circ$, which is also a favourable direction. Figure 4 shows that for the given conditions the highest cross section corresponds to an incident energy $E_i \approx 700$ eV. We will thus chose this value for the following two variations of the MDCS in terms of the scattering angle, presented in figure 5 for the most favourable ejection direction, which, as we said, corresponds to an ejection in the direction of the momentum transfer, and in terms of the ejection angle for a fixed scattering angle presented in figure 6. In both case the internuclear axis of the molecule is perpendicular to the incidence direction. As expected, we observe in figure 5 very typical interference patterns in the variation of the MDCS, like those of the variation of the intensity of light

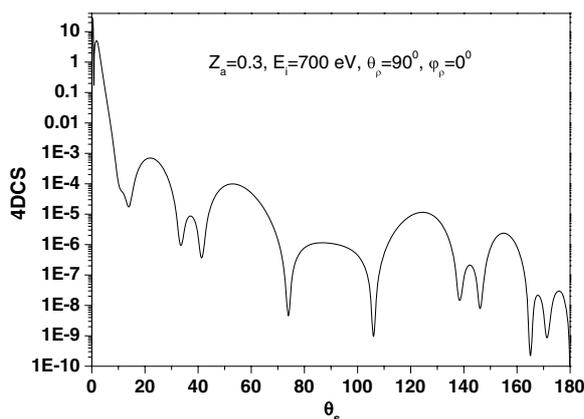


Figure 5. Variation of the 4DCS with the scattering angle for the ionization of CO₂ from the $1\pi_g$ molecular orbital for a given orientation $\theta_e = \theta_K$, $\theta_\rho = 90^\circ$ and $\phi_\rho = 0^\circ$ with $Z_a = Z_b = 0.3$ and $Z_c = 1 - 2Z_a$. Here, $E_i = 700$ eV.

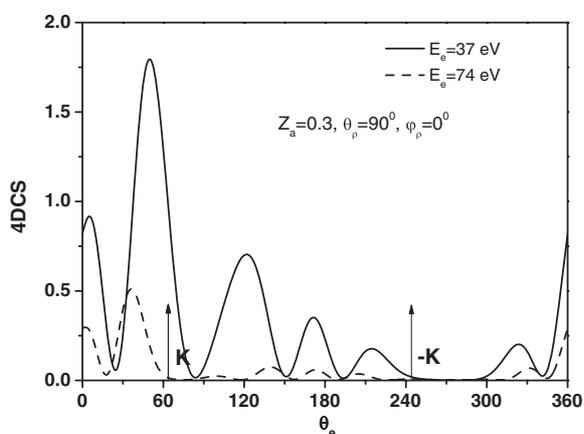


Figure 6. Variation of the 4DCS with the ejection angle for the ionization of CO₂ from the $1\pi_g$ molecular orbital for a given orientation $\theta_\rho = 90^\circ$ and $\phi_\rho = 0^\circ$ with $Z_a = Z_b = 0.3$ and $Z_c = 1 - 2Z_a$. Full line: $E_e = 37$ eV. Dashed line: $E_e = 74$ eV.

on a screen in a light diffraction–interference experiment by three slits or obstacles. We think that the observed minima correspond to the situations where the ionization of the electron for these particular conditions is forbidden. The three-centre character of the target manifests itself also in figure 6 in the variation of the MDCS by the appearance of repeated maxima and minima which change the position, when the energy of the ejected electron is changed, passing from 37 to 74 eV. The experimental verification of these observations can be performed only by the preparation of the aligned targets which can be obtained by the excitation of the rotational levels by appropriately polarized lasers.

4. Conclusion

We have applied a three-centre Coulomb continuum function, obtained in a closed analytical form by the Schrödinger equation of an unbound electron (with wave vector \mathbf{k}) in Coulomb field of three fixed charged nuclei, to the (e, 2e)

ionization of CO₂, whose electronic structure is described by molecular orbitals constructed by LCAO Slater-type orbitals. Our results reproduce the experimental binary peak of the ionization of the $1\pi_g$ level when 3d orbitals are introduced to the basis. With the aim of showing the multicentric character of the target, we have studied the variation of the MDCS for a given orientation of the molecular axis. This shows, as expected, an oscillatory behaviour due to three-centre interferences.

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