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Abstract. Cross sections for the ionization of N₂, CO and O₂ diatomic molecules by electron impact are calculated. The applied distorted wave model is based on our previous studies for positron impact, the molecular orbitals being described by Gaussian wavefunctions. Our study emphasizes the importance of electron exchange and of using correct distorted waves for the ejected electron.

PACS. 34.80.Gs Molecular excitation and ionization by electron impact

1 Introduction

Collision phenomena between electrons and atomic systems have several important practical applications in plasma related processes, astrophysics, atmospheric sciences and several other fields.

In the last decades both theoretical and experimental studies of the ionization of atoms and molecules by electron impact have attracted much interest. Experimental ionization cross sections were measured for a large number of atoms and molecules. A few experimental studies concerning with the ionization of the N₂, CO and O₂ molecules are available [1–6]. For these molecules theoretical calculations were made by Hwang et al. [7]. Their binary-encounter Bethe (BEB) model successfully combines the binary-encounter theory for low projectile energies with the Bethe theory for high impact energies. The model gives an analytic formula for the calculation of the orbital ionization cross section. For each orbital, the corresponding cross section is expressed in terms of the impact energy and a few molecular constants: the binding and kinetic energies of the bound electron and the orbital occupation number, respectively. The total cross section is obtained by summing the contributions from the different molecular orbitals. The BEB model provides good agreement with the available experimental data for a large number of molecules, including N₂, CO and O₂.

Recently we have studied the direct ionization of several molecules (H₂ [8], N₂ [9], O₂ [10], CO [11], CO₂ [11] and CH₄ [12]) by positron impact. These studies were based on the CPE (Coulomb plus plane waves with full energy range) model. The CPE model uses Coulomb or plane waves in order to describe the incident, scattered and ejected particles. We have described the initial state

of the active electron by multi-center Gaussian-type wavefunctions. In a recent paper [13], we have refined the calculations by describing the ejected electron and the projectile by the more realistic distorted waves. In the framework of the distorted wave Born approximation (DWBA) we have solved numerically the radial Schrödinger equation in the field of the spherically averaged potential created by the nuclei and the bound electrons. In this study two models were introduced in order to investigate the effect of the screened potentials on the direct ionization cross section, the ES (electron screening) and TS (total screening) models. The ES model describes the ejected electron with a distorted wave, while for the description of the incident and scattered positron uses Coulomb or plane waves. In the TS model the wavefunction of the incident and the scattered projectile is also calculated numerically in the potential created by the molecule. These distorted-wave models have improved the theoretical cross sections relative to the CPE results.

In the present work we apply these methods in the study of electron impact ionization of some diatomic molecules. Changing the projectile not only implies the change of the projectile charge sign, but it also implies taking into account the exchange effects. The models CPE, ES and TS were used to obtain direct and the total (i.e. direct plus exchange) cross sections for N₂, CO and O₂ molecules.

2 Theory

Previously we have developed a method for calculating the ionization cross section of molecules by positron impact [8–12]. For linear molecules like the ones studied in this work it used an expansion of the molecular orbitals in terms of Legendre polynomials. Now we adopt this method

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for electron impact, taking into account the exchange effects. Below we present the main steps of the theory.

The triple differential cross section for the ionization of molecules by charged particles may be written as

$$\frac{d^3\sigma}{d\hat{\mathbf{k}}_f d\hat{\mathbf{k}}_e dE_e} = \sum_r \frac{(2\pi)^4}{E_i} |f_t^r|^2, \quad (1)$$

where the sum runs over all occupied molecular orbitals. $\hat{\mathbf{k}}_f$ and $\hat{\mathbf{k}}_e$ stand for the direction of the momenta of the scattered and the ejected particles respectively. E_i is the impact energy, while E_e is the energy of the ejected electron. The square of the modulus of the total scattering amplitude may be written [14] in terms of the direct and exchange amplitudes

$$|f_t^r|^2 = |f_d^r|^2 + |f_e^r|^2 - \alpha |f_d^r| |f_e^r|, \quad (2)$$

here, α is a phase factor, while f_d^r and f_e^r stand for the direct and exchange scattering amplitude, respectively. As in [14], the value of α was chosen to be equal with one. The direct and the exchange amplitudes may be written as

$$f_d^r = \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi_b^r(\mathbf{r}_2) \rangle, \quad (3)$$

$$f_e^r = \langle \phi_e(\mathbf{r}_1) \phi_f(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi_b^r(\mathbf{r}_2) \rangle, \quad (4)$$

here ϕ_f and ϕ_e are the wavefunctions of the scattered and ejected electron, respectively. ϕ_i denotes the wavefunction of the projectile. The position vector of the incident and scattered electron is given by \mathbf{r}_1 , while \mathbf{r}_2 gives the position of the active electron. The initial, bound state of the active electron, the ϕ_b^r molecular orbital, has been constructed as a linear combination of Gaussian-type atomic orbitals, obtained as contractions of Gaussian-type functions. Details on this procedure is given in [8] for s orbitals and in [9] for p orbitals. In order to obtain functions with a given angular momentum, for all studied cases (N_2 , CO , O_2), the wavefunction of the active electron has been expanded in terms of the Legendre polynomials

$$\phi_b^r(\mathbf{r}_2) = \sum_{l_b} y_{l_b}^r(r_2, R) P_{l_b}(\cos \omega_2), \quad (5)$$

where the expansion coefficient may be expressed as

$$y_{l_b}^r(r_2, R) = \frac{2l_b + 1}{2} \int_{-1}^1 d(\cos \omega_2) P_{l_b}(\cos \omega_2) \phi_b^r(\mathbf{r}_2). \quad (6)$$

In the above equations, R stands for the internuclear distance (taken to be constant at the equilibrium value), l_b is the orbital angular momentum quantum number of the bound electron and ω_2 is the angle between \mathbf{r}_2 and \mathbf{R} . The wavefunctions of the incident, scattered and ejected particles have been expanded in terms of the partial waves. After performing the integration over the direction of the momenta of the scattered and ejected electron, and over the energy range of the ejected electron, one obtains from equation (1) the total ionization cross section as given in [14]

$$\sigma = \int_0^{E/2} \sigma(E_e, E_i) dE_e, \quad (7)$$

where the single differential cross section $\sigma(E_e, E_i)$ may be written as

$$\sigma(E_e, E_i) = \frac{16}{\pi E_i} \sum_r \sum_{l_b l_i l_e l_f L} (2L + 1) |f_t^r|^2, \quad (8)$$

here $E = E_i - I = E_f + E_e$ is the total kinetic energy of the two emerging electrons, I is the ionization energy, while L denotes the total orbital angular momentum of the molecule-electron system. Because the two emerging electrons are indistinguishable, by definition we consider the slower one to be the ejected electron, while the scattered electron is regarded to be the one with the greater energy. Therefore, the integration over the energy of the ejected electron in equation (7) is carried out only up to the half of the maximum allowed energy.

Performing the integrals over the angles in the matrix elements (3) and (4), the amplitudes may be written as

$$f_d^r = \sum_{\lambda} f_{\lambda}(l_b l_i l_e l_f L) \times \int dr_1 dr_2 y_{l_f}(r_1) y_{l_e}(r_2) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} y_{l_i}(r_1) y_{l_b}^r(r_2, R) \quad (9)$$

$$f_e^r = \sum_{\lambda} f_{\lambda}(l_b l_i l_f l_e L) \times \int dr_1 dr_2 y_{l_e}(r_1) y_{l_f}(r_2) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} y_{l_i}(r_1) y_{l_b}^r(r_2, R) \quad (10)$$

where $f_{\lambda}(l_b l_i l_e l_f L)$ and $f_{\lambda}(l_b l_i l_f l_e L)$ are angular factors, l_i , l_e and l_f are the orbital angular momentum quantum numbers of the incident, ejected and scattered electrons, respectively. We have marked by $r_{<}$ ($r_{>}$) the smaller (larger) between r_1 and r_2 . The functions y_{l_f} , y_{l_e} and y_{l_i} are radial wavefunctions and were obtained by solving numerically the radial Schrödinger equation.

As in our work for positron impact [13], we investigate the ionization process in the framework of two distorted-wave models, adapted to the ionization by electron impact. These models use distorted waves to represent the incident, scattered and ejected electrons. The distorted waves were calculated by solving the radial Schrödinger equation using the spherically averaged potential created by the nuclei and electrons. Further, we compare the results of our distorted-wave models with the experimental data, the results of the simple CPE model and the theoretical BEB results of Hwang et al. [7].

In the CPE model the projectile is described by a plane wave. The model regards the ejected (the slower) electron as moving in the potential field of the positive molecular ion, while the scattered (the faster) is approximated by a plane wave, since the positive charge of the residual ion is screened by the slower ejected electron.

The first distorted-wave model, named ES, introduces the distorted-wave representation only for the ejected electron. Here, the ejected electron moves in the averaged potential field of the nuclei screened by the spherically averaged field of the remaining electrons. Our spherically averaging method was described in [13]. In addition, the model assumes that both the incident and scattered electron is described by a plane wave, respectively. If we denote by V_i , V_e and V_f the potential energies of the incident, ejected and scattered electrons, respectively, the mathematical formulation of the ES model may be written as

$$\begin{aligned} V_i &= 0, \\ V_e &= -V_{nuclei} + V'_{electrons}, \\ V_f &= 0, \end{aligned} \quad (11)$$

where V_{nuclei} is the spherically averaged potential created by the nuclei and $V'_{electrons}$ stands for the spherically averaged field of the residual electrons.

Our second model introduces the distorted-wave representation for all the freely moving particles. The ejected electron moves in the spherically averaged potential field of the nuclei screened by the spherically averaged field of the residual electrons, while both the incident and scattered electron move in the averaged potential field created by the nuclei screened by the averaged field of all electrons. This model, named TS, may be formulated as

$$\begin{aligned} V_i &= -V_{nuclei} + V_{electrons}, \\ V_e &= -V_{nuclei} + V'_{electrons}, \\ V_f &= -V_{nuclei} + V_{electrons}, \end{aligned} \quad (12)$$

where $V_{electrons}$ denotes the spherically averaged potential created by all electrons of the target molecule.

3 Results and discussion

Our cross sections for the ionization of the N_2 , CO and O_2 molecules are presented in Figures 1–3 along with the experimentally determined cross sections of Straub et al. [1] for the N_2 molecule and the experimental data of Mangan et al. [4] for the CO molecule. In the case of the O_2 molecule our results were compared with the experimental measurements of Straub et al. [1] and Krishnakumar and Srivastava [6]. In all three cases, the figures also show the theoretical BEB cross sections of Hwang et al. [7].

These figures present two types of cross sections. The curves containing asterixes correspond to direct ionization cross sections. The models based on the calculation of the direct scattering amplitudes (9) were denoted with CPE, ES and TS. The curves without asterixes were obtained with our distorted-wave models, which contain contributions from both the direct and the exchange processes. These models were denoted with $CPE(t)$, $ES(t)$ and $TS(t)$. The t character in the bracket refers to the total scattering amplitude (2), which includes the exchange effect.

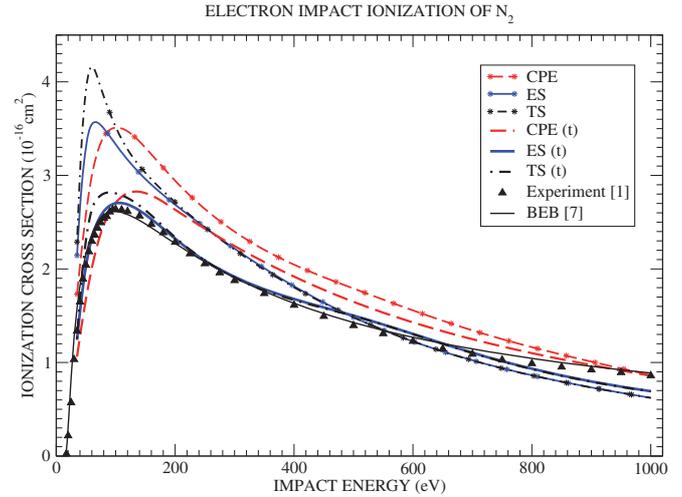


Fig. 1. (Color online) Calculated direct and total cross sections for the ionization of the N_2 molecule by electron impact as a function of the impact energy compared with the experimental data [1] and the theory of Hwang et al. [7].

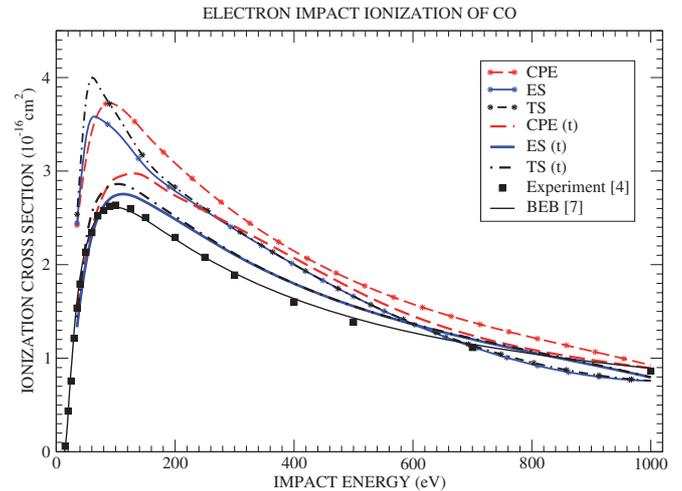


Fig. 2. (Color online) The same as Figure 1, but for the CO molecule. The experimental points are from [4].

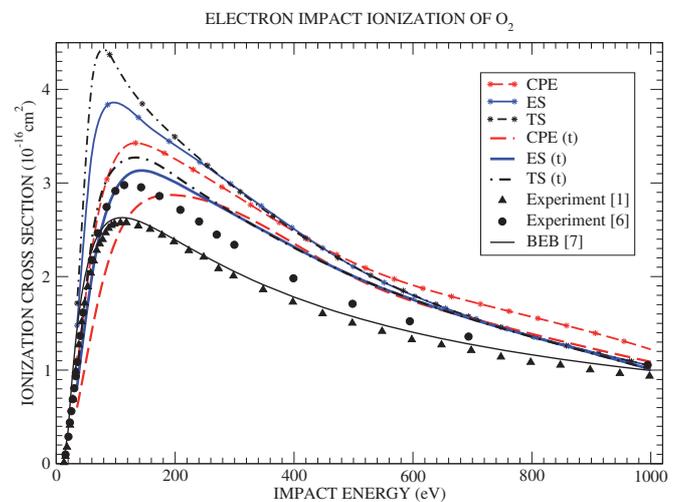


Fig. 3. (Color online) The same as Figure 1, but for the O_2 molecule, compared with the experiments [1,6].

Figure 1 shows our results for the ionization of the molecular nitrogen by electron impact. As expected, the curves corresponding to the direct ionization are higher than the experimental data, especially at low impact energies. Taking into account the exchange interaction, the results of the CPE(t), ES(t) and TS(t) models show better agreement with the experiment. However, the CPE(t) results overestimate the ionization cross sections mainly at intermediate energies. The best agreement was found in the case of the ES(t) model. While one would expect the TS(t) model to be the most accurate, it leads to slightly larger results than the experiment (and the ES(t) model) in the peak region. One possible explanation is, that in the TS(t) model the interaction between the two outgoing electrons is described by a static potential considering the ejected electron still in the initial (bound) state. This approximation is not suitable for the cases when the ejected electron has the energy comparable to that of the scattered electron. In these cases the ES(t) model, which describes the scattered electron by plane waves, seems to be more correct. For higher energies there is a perfect agreement between the ES(t) and TS(t) results. For low and intermediate energies our ES(t) model shows minimal differences relative to the theoretical BEB cross section. However, for energies higher than 700 eV our results are a slightly lower than the BEB and the experimental data.

Figure 2 presents the results for the ionization of the CO molecule. The behavior of our models is quite similar for CO as it was for N₂. The best agreement with experiment was found in the case of the ES(t) and TS(t) models. The latter shows minimal differences relative to the ES(t) results in the region of the peak. The CPE(t) model gives higher ionization cross sections than the experimental ones for impact energies lower than 700 eV. Our ES(t) model produces somewhat higher results than the BEB model and the experiment, mainly in the energy range from 100 eV to 700 eV. This disagreement, which was not present in the N₂ case, might be explained by a smaller electron screening effect in the case of CO. For impact energies higher than 700 eV our ES(t) model is in perfect agreement with the experiment.

The results for the O₂ molecule are presented in Figure 3. Similar to the case of N₂ and CO, taking into account the exchange interaction, leads to lower values for the ionization cross sections relative to the case when only the direct process is considered. However, for this molecule, the results obtained with our distorted-wave models ES(t) and TS(t) are higher than the CPE(t) results, mainly in the region of the peak. The different behavior of the O₂ cross sections relative to the previous ones may be due to the more complicated structure of the molecule, having two unpaired electrons on the outer orbital. The BEB calculations of Hwang et al. agree well with the experimental data of [1], but are lower than the measurements of [6] for energies lower than 400 eV. Our models are in better agreement with the experimental data of Krishnakumar et al. [6] than with the experimental measurements of Straub et al. [1]. The differences between models are significant only for impact energies below 250 eV.

4 Conclusions

We have carried out DWBA calculations for the ionization of the N₂, CO and O₂ diatomic molecules by electron impact. Our calculations indicate that the employed distorted-wave models and the description of the molecule by using Gaussian-type orbitals, applied previously for the ionization of molecules by positron impact, work well also for the description of the ionization by electrons. As expected, electron exchange lowers the calculated cross section values. The electron screening influences the ionization cross sections mostly in the region of the peak.

We may conclude, that both screening and exchange interaction effects are important in order to obtain reliable cross sections. Our ES(t) and TS(t) results are in a good agreement with the experimental data in the case of the N₂ and CO molecules, while for the O₂ molecule the theoretical cross sections are a slightly higher than the experimental values.

The applied method is simple, effective, and leads to reliable results both for electron and positron impact ionization. It may be applied with minor adoptions to other diatomic or polyatomic molecules. Unlike the BEB model, our method allows for a study of the screening effects and the dependence of the cross section on the projectile charge sign.

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