Semiclassical model for calculating fully differential ionization cross sections of the H$_2$ molecule

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Abstract

Fully differential cross sections are calculated for the ionization of H$_2$ by fast charged projectiles using a semiclassical model developed previously for the ionization of atoms. The method is tested in the case of 4 keV electron and 6 MeV proton projectiles. The obtained results show good agreement with the available experimental data. Interference effects due to the two-centre character of the target are also observed and analysed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last few decades there has been a considerable development in the theoretical description and experimental measurement of differential cross sections for charged particle impact ionization of atoms and molecules [1–4]. Nowadays, the interest is focused on the in-detail analysis of the electron ejection from atomic or molecular targets [5–10]. These analyses may be performed by measuring and calculating fully differential cross sections which give us the most complete information about an ionization process. These quantities describe the entire energy and angular distribution of the ionized electron, residual ion and projectile.

Previously, based on the semiclassical impact parameter method we have constructed a theoretical model to calculate fully differential cross sections for single ionization of light atoms. This model takes into account the projectile–target nucleus interaction classically. The method was tested in the case of the single ionization of helium produced by a C$^{+}$ ion projectile with an energy of $E_0 = 100$ MeV/u and good agreement with the experiments was achieved in the scattering plane, while in the perpendicular plane a structure similar to that observed experimentally was obtained [11, 12].

More complex and interesting features appear when the target is a molecule. Due to the multicentre character of the target, interference patterns occur in the ejected electron spectra. This phenomenon was observed in the double differential cross section (DDCS) data for the ionization of hydrogen molecule by fast ions by Stolterfoht et al [13] and has been analysed theoretically by several groups [14–18].

Recently, fully differential cross sections were measured and calculated for the ionization of H$_2$ by both fast and slow electrons [9, 19, 20], and interference effects were analysed in these data series. However, while several attempts have been made in the description of the interference effects in the double differential cross sections, and these effects are relatively well understood [14, 16], it was shown recently [21] that an accurate description of the role of the projectile–target nucleus interaction remains a major challenge to theory. There are even many more details to clarify for these effects, if they appear in the total differential cross section.

Interference effects due to indistinguishable diffraction of the incoming projectile from the two atomic centres were identified in the DDCS as a function of scattering angle for a fixed ejected electron energy [22]. It was shown that these kinds of interference structures can be more pronounced than those in the ejected electron spectrum.

The goal of the present paper is to adopt our previous semiclassical method [11] to calculate fully differential cross sections (FDCS) for the ionization of the hydrogen molecule, and to evidence the interference effects due to the two-centre character of the target. In this model, the description of the molecule is similar to that from paper [23], where total cross sections are calculated and are compared to the experimental data. Due to the limitations of a semiclassical model, we study
the ionization induced by fast charged projectiles, and analyse the interference structures only in the ejected electron spectra.

As a test case, the single ionization of the hydrogen molecule by 4 keV electron and 6 MeV proton projectiles is considered. FDCS are calculated and compared in the scattering plane with the experimental data of Cherid et al [24] and Dimopoulou et al [8]. Results in the perpendicular plane are also presented. In order to evidence the interference effects due to the two-centre character of the target, the fully differential ionization cross sections for the H$_2$ molecule and H atom are compared.

2. Semiclassical theory

In the semiclassical approximation the projectile is treated separately and it moves along a classical trajectory. This implies that only the electron system needs to be described by a time-dependent Schrödinger equation, while the projectile follows the classical laws of motion.

2.1. General theory

In order to study the ionization process of a small molecule induced by fast charged projectiles, first the ionization amplitudes have to be calculated.

As described in [16], the first-order transition amplitude for a projectile with impact parameter $b$, velocity $v$ and charge $Z_p$, and a certain orientation of the molecular axis $\mathbf{D}$ may be written as

$$a(b, \mathbf{k}, \mathbf{D}) = \frac{i Z_p}{v} \int_{-\infty}^{+\infty} \mathrm{d}z \ e^{i \frac{\Delta E}{\hbar} z} (\psi_k(r) \left| \frac{1}{|r - R|} \psi_i(r, \mathbf{D}) \right|),$$

(1)

where $\mathbf{r}$ is the position vector of the active electron and $R = b \mathbf{e}_x + z \mathbf{e}_z$ is the position of the projectile along the trajectory with $z = vt$. Here the origin is considered in the centre of the molecule. $\Delta E = E_i + \frac{\hbar^2}{2m} \frac{\Delta \zeta^2}{\hbar^2}$ is the energy transfer to the active electron, where $E_i$ stands for the ionization energy. The initial and final state of the active electron is denoted by $\psi_i(r, \mathbf{D})$ and $\psi_k(r)$, with $\mathbf{k}$ being its momentum vector. In the calculations the Coulomb interaction $\frac{1}{|r - R|}$ is expanded into a multipole series.

The transition probability for a given impact parameter and orientation of the molecular axis is the square of the transition amplitude modulus:

$$w(b, \mathbf{k}, \mathbf{D}) = |a(b, \mathbf{k}, \mathbf{D})|^2.$$  
(2)

Because in experiments the molecular orientation is usually unknown, the transition probabilities are averaged over molecular orientation:

$$w(b, \mathbf{k}) = \frac{4\pi}{4\pi} \int \mathrm{d}\Omega_D \int \mathrm{d}\theta_D \sin \theta_D w(b, \mathbf{k}, \mathbf{D}).$$

(3)

Finally, the triple differential cross section (TDCS) for the electron ejected into the energy range $[E_i, E + \Delta E]$ and into the solid angle $d\Omega$, and the projectile scattered into the solid angle $d\Omega_p$ can be expressed as

$$\frac{\mathrm{d}^3\sigma}{\mathrm{d}\Omega_p \mathrm{d}\Omega \mathrm{d}E} = \frac{b}{\sin \theta_p} \left| \frac{\mathrm{d}b}{\mathrm{d}\theta_p} \right| w(b, \mathbf{k}).$$

(4)

Because some experimental data [8] are differential relative to the perpendicular momentum transfer $\mathbf{q}_\perp$ and not of the scattering angle:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\mathbf{q}_\perp \mathrm{d}\Omega} = b \frac{\mathrm{d}b}{\mathrm{d}q} \ w(b, \mathbf{k}).$$

(5)

An important part of the model is to assign impact parameter values to certain projectile scattering angles. As described in detail in [12], this may be achieved using the transverse momentum balance [2], which states that the momentum transfer is the sum of the transverse components of the electron’s and residual ion’s momenta. Further it is assumed that the impact parameter is related to the momentum transfer to the residual ion, and we take into account the projectile–electron interaction separately. Thus, in this model, the projectile–target nucleus interaction is accounted for. By this point of view two main collision types are possible: (a) binary collision where most of the momentum transfer is taken by the electron and (b) recoil collision where most of the momentum transfer is taken by the target nucleus. Accordingly, two different impact parameter values have to be used in these collision regimes. The transition between these impact parameters is realized smoothly in the transition regions.

The projectile scattering is treated as a classical potential scattering problem in the field of the target system with nuclear charge $Z_t$ [25]. The simplest way to include the effect of the electrons around the target nucleus is to consider the potential to be a product of the Coulomb potential and the Bohr-type screening function [26]. Here it has to be mentioned that using this potential we assume that the projectile scattering is produced by a spherical potential. This implies that in the description of the projectile scattering the two-centre nature of the molecule is neglected. While in the analysis of the cross section as a function of the projectile scattering angle the correct description of the projectile–target nucleus interaction is important [21], we assume that the present approximation does not influence significantly the character of our results as a function of electron ejection angle.

2.2. The particular case of hydrogen molecule target

In the particular case of the hydrogen molecule the initial state is represented by a Heitler–London type molecular wavefunction. Written only for the active electron

$$\psi_i(r, \mathbf{D}) = N(e^{-\alpha|\mathbf{r} - \mathbf{D}|/2} + e^{-\alpha|\mathbf{r} + \mathbf{D}|/2}),$$

(6)

where $\alpha$ is the effective charge, $\mathbf{D}$ is the vector associated with the internuclear distance and $N$ denotes a normalization factor. In order to separate the dependence on the direction $\mathbf{D}$ of the molecular axis, this is expanded into a Legendre series [23]. In this series each term is characterized by the quantum numbers $l_i, m_i$. In what follows, the expansion coefficients depending only on the molecular distances will be denoted by $c_{l_i}(r, \mathbf{D})$.

The $\psi_k(r)$ continuum wavefunction is expanded into partial wave series, depending on angular momenta $l_f, m_f$ and phase shift $\sigma_{l_f}$. The radial part $R_{l_f}(kr)$ is a wavefunction
of the continuum electron moving in the mean field of the residual H$_2^+$ molecular ion approximated by the potential

$$V(r) = \begin{cases} \frac{1}{r}, & r > \frac{D}{2} \\ \frac{2}{r}, & r \leq \frac{D}{2}. \end{cases}$$

(7)

This wavefunction is calculated numerically.

By these considerations the ionization amplitude will be [23]

$$a(b, k, \hat{D}) = \frac{(4\pi)^{3/2} Z_n N_i}{2 N_f} \times \sum_{l_f,l_l} \frac{i^{-l_f} e^{-im_f \theta}}{\sqrt{(2l_f + 1)(2l_l + 1)(2l_l + 1)}} C_{l_f,0,l_l}^{l_f,0} \times \sum_{l_f,l_l} C_{l_f,m_l,l_l,m_l}^{l_f,0} Y_{l_f,m_l}(\hat{D}) Y_{l_l,m_l}(\hat{k}) e^{i m_l \phi_l}(k, b, D),$$

(8)

where $N_i$ and $N_f$ are the normalization factors of the initial and final state target wavefunctions, respectively. The quantum numbers $l_c, m_c$ correspond to the multipole expansion of the Coulomb interaction and

$$G_{l_f,l_l}^{m_l}(k, b, D) = \int_{-\infty}^{+\infty} dz e^{i k z} Y_{l_f,m_l}(\hat{R}) \times \int_0^\infty dr^2 r_{l_f}(kr) r_{l_l}(2r) c_{l_c}(r, D).$$

(9)

is the integral over the projectile trajectory.

Using this expression, the transition probability is calculated and averaged over molecular orientation. The FDCS for ionization of the hydrogen molecule will look like

$$\sigma_{\text{FDCS}} = K \left( \frac{N_i}{N_f} \right)^2 \times \sum_{l_f,l_l} \frac{i^{-l_f} e^{i(\sigma_{l_f} - \sigma_{l_l})}}{(2l_f + 1)(2l_l + 1)(2l_l + 1)} \times C_{l_f,0,l_l}^{l_f,0} \sum_{m_c,m_c'} C_{l_f,m_c,l_l,m_c'}^{l_f,0} C_{l_c,m_c,l_c,m_c'}^{l_c,0} Y_{l_f,m_c}(\hat{k}) \times Y_{l_l,m_c'}(\hat{k}) G_{l_f,l_l}^{m_c,m_c'}(k, b, D),$$

(10)

where $K$ is a constant depending on projectile charge, velocity and scattering angle, target charge and ejected electron momentum and it differs for the different kinds of FDCSs mentioned earlier (see equations (4) and (5)). While our results will be represented scaled to unity at their highest value in the scattering plane, in our following discussion the $K$ constant will play the role of a simple scaling constant.

3. Results and discussion

In order to test the validity of the results of the semiclassical model for the H$_2$ ionization, calculated FDCS for fast electron and proton projectile impact are compared to the available experimental data [8, 24].

Figure 1 shows fully differential cross sections for the ionization of the hydrogen molecule by 4.087 keV electron impact. The projectile scattering angle is $1^\circ$ and the ejected electron energy is 20 eV. The top panel of the figure shows TDCS in the scattering plane, while the bottom panel shows the same data in the perpendicular plane. Experimental and theoretical data are each scaled to unity at their highest value in the scattering plane. Together with the results for the molecule (continuous line), TDCS are shown for the same collision process with atomic H target are represented by dashed lines.

Further comment needs the fact that the TDCS in the scattering plane for atomic hydrogen target show shoulder structures at angles around 45° and 135°. Such structures cannot occur for pure first-order ionization from an isotropic 1s state. As presented above, in order to take into account the projectile–target nucleus interaction, a certain impact parameter is assigned for every kinematic condition. Two different impact parameter values are used in the two collision regimes. The transition between these impact parameters is realized smoothly in the $\theta_e = 0^\circ,\ldots,50^\circ$ and $\theta_e = 130^\circ,\ldots,180^\circ$ transition regions. The shoulders appear due to this impact parameter adaption mechanism.

In the scattering plane the theory reproduces well in shape the binary and the recoil peak structure. However, the semiclassical first-order results show a shift of the binary peak with some $10^\circ$ relative to the experimental data, which have the angular resolution of less than $1^\circ$ [24]. Such peak shifts indicate that the first-order approximation may not be sufficiently accurate.

Experimental data in the perpendicular plane for this particular process were not found. As in the case of our previous studies of the He ionization [12], the semiclassical theoretical results show a double-lobe structure similar to that reported in the literature for slower collision processes [20].

In order to evidence the interference effects due to the two-centre nature of the target, TDCS for the H$_2$ molecule and H atom are compared in figure 1. The only difference between these calculations is that the one-centre
wavefunction describing the H atom is replaced by a two-centre wavefunction in the case of the molecular target. At the first look the TDCS distributions for H₂ molecule and H atom are very similar. However, the recoil peak for the H₂ target is larger than that for the H atom. The interference effects are analysed later by means of the interference factor. We note here that we obtain the interference structures by comparing the theoretical results for H₂ and H. Because the agreement between our calculations and the experimental data is not perfect, we cannot say that we have identified the interference effects in the experimental data.

We have identified the interference effects in the electron ejection spectrum, due to the coherent ejection from the two centres of the molecule. This effect is obtained by describing the molecular electron by a two-centre wavefunction. We assume that neglecting the two-centre character of the target in the description of the projectile scattering does not influence the obtained interference patterns.

The interference structures in the ejected electron spectrum are analysed through the interference factor defined by the ratio of the cross section obtained for the molecule and of two independent hydrogen atoms [9, 17]:

\[ I = \frac{\sigma_{H_2}}{2\sigma_H}. \]  

This interference effect may be detected in the TDCS distribution from nonoriented molecules. The interference factor may be expressed by an analytical approximate formula [9]

\[ I = 1 + \frac{\sin(Dq')}{Dq'}, \]  

where \( q' = q - k \) is the momentum imparted to the recoil ion. In figure 2 the interference factor obtained from our calculations (continuous line) is shown for the ionization process discussed earlier and it is compared to the analytical form (12) (dashed line). The top panel of the figure shows the interference factor in the scattering plane. As expected, it has oscillatory behaviour with a strong maximum in the vicinity of the recoil peak. The semiclassical theory predicts another smaller maximum in the binary peak region, too, suggesting a more complicated behaviour than that given by the analytical formula. In the perpendicular plane due to the kinematic conditions the \( q' \) momentum is constant: (1) the transverse component of the recoil momentum \( q' \) parallel to \( q \) is constant because the electron momentum is zero in that direction and \( q' \) is fixed; (2) the transverse component of \( q' \) perpendicular to \( q \) is constant because \( q \) is zero in that direction and the electron energy is fixed. Accordingly, the analytical formula gives a constant interference factor. In contrast to this result, the semiclassical theory predicts some oscillations symmetric relative to the 180° direction (bottom panel of the figure).

TDCS distributions for other projectile energies and scattering angles are analysed in figure 3. The top and middle panels present scattering plane TDCS results for 4.087 keV electron projectile with 1.5° and 3° scattering angles. The ionized electron is ejected with 20 eV energy. The results are in good agreement with experiments both in the shape of the distribution and in the position of binary and recoil peaks.

The bottom panel of figure 3 shows results for 4.167 keV projectile energy and a larger 8.2° scattering angle. The electron is ejected with a higher energy, of 100 eV. In this...
case the experiments show a narrow binary peak, which is well reproduced by our calculations.

Figure 4 shows FDCS results of the semiclassical model for ionization of hydrogen molecule by 6 MeV proton projectile impact. In this case the experimental data of Dimopoulou et al [8] are differential in ejected electron momentum vector and the perpendicular momentum transfer vector. The comparison is made for different electron ejection energies and momentum transfers.

On one hand, for larger electron energies, of \( E_e = 2.6 \text{ eV} \) (top panels of the figure), the agreement between the experimental data and the present, semiclassical theory is reasonably good. Beside of this, it has to be noted that our first-order results show a shift of the binary peak with some 10°, but because of the experimental errors in the cross section this shift cannot be determined precisely. The cross section ratios for the binary and recoil peaks are also well reproduced.

On the other hand, for lower electron energies, of \( E_e = 0.2 \text{ eV} \) (bottom panels of the figure), there is a discrepancy between the experimental and theoretical FDCS distributions. In experiments the cross section ratio of the binary and recoil peaks is almost 1. This feature is not reproduced by the semiclassical model. The explanation is the same as in the case of CDW-EIS model [8]: the FDCS distribution in the sub-eV region is influenced by the presence of the vibrational autoionizing channel (not included into the semiclassical model) which leads to the ejection of very low energy electrons. The angular distribution of the autoionized electrons is essentially a dipolar one with respect to the momentum transfer axis.

4. Conclusions

In conclusion, the theoretical model based on the first-order, semiclassical, impact parameter approximation used to calculate fully differential cross sections for single ionization of light atoms has been adopted to calculate fully differential cross sections for the ionization of diatomic molecules. The method has been tested in the case of the ionization of \( \text{H}_2 \) by 4 keV electron and 6 MeV proton projectiles. Except for some special cases, the obtained results in the scattering plane show good agreement with the experiments [8, 24], and are in agreement with other theories [8, 9, 19]. The double-lobe structure reported in the perpendicular plane is also reproduced. However, for low electron ejection energies the semiclassical model fails to reproduce the experimentally observed more symmetrical electron emission patterns in the scattering plane. In order to analyse the effect of the two scattering centres of the molecule on the cross section, we have compared the TDCCS for the \( \text{H}_2 \) with the TDCCS obtained for independent atoms. Higher cross sections were obtained for molecules in the region of the recoil peak, and also the width of the binary peak was changed. These differences may be interpreted as interference effects.

The aim of this work was to test that the semiclassical model, in its simple form, is able to treat complex colliding systems and describe interference patterns in the fully differential cross sections, too.

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