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The effect of target representation in positron-impact ionization of molecular hydrogen

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Abstract

Ionization cross sections for positron collisions with hydrogen molecules have been calculated using a two-center molecular representation. The results are compared with our previous work which used spherically averaged H_2 wavefunctions as well as with existing experimental results. The use of a two-centre wave function for the molecular target, either of the Heitler–London type or a Gaussian representation, produces results which lie between the two most recent sets of experimental data. We find that our CPE4 model produces results in better agreement with experiment over the whole energy range than our CPE model. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Positron impact ionization of molecules has received significant attention recently. On the experimental side most of the work has been carried out for the ionization of molecular hydrogen. These experiments produced integrated [1–4] and triple differential cross sections [5]. Other experiments have measured the ionization of O_2 [6], N_2 [7], CO [8], CO_2 [8,9] and even organic molecules [10].

So far, theoretical studies of this process have been limited to molecular hydrogen, where distorted wave calculations produced integrated [11,12] and triple differential cross sections [13]. The paper by Chen et al. [12] studied the ionization problem using two-center wavefunctions for the electrons, where the calculation was done first for a fixed molecular orientation and then averaged over nuclear orientations. The paper by Campeanu et al. [11] uses a one-center formalism with the hydrogen molecular orbitals spherically averaged before the ionization calculations.

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This Letter has two goals. First, we want to assess the accuracy of our previous spherically averaging method by performing the same calculation in a two-center approximation. Secondly, we want to explore the use of a Gaussian representation for the molecular target, which can be readily used for other, more complex targets. We shall present results in both the CPE and CPE4 approximations, two ionization models which were shown to produce reliable theoretical cross sections for positron impact ionization of noble gases and hydrogen [14]. Model CPE4, which is considered to be superior to CPE, assumes that the ejected electron feels the effect of both the faster scattered positron and the residual molecular ion.

2. Theory

Starting from the expression for the ionization amplitude given in [12], the triple differential cross section for the ionization of the hydrogen molecule by positron impact can be shown to be

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

where E_i is the energy of the projectile, E_e the energy of the ejected electron, while $\hat{\mathbf{k}}_e$ and $\hat{\mathbf{k}}_f$ stand for the direction of the momenta of the ejected electron and scattered positron, respectively. The amplitude can be written as

$$f = \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) \phi_{\text{H}_2^+}(\mathbf{r}_3) | V(r_{12}) | \phi_i(\mathbf{r}_1) \Psi_{\text{H}_2}(\mathbf{r}_2, \mathbf{r}_3) \rangle, \quad (2)$$

where ϕ_i and ϕ_f stand for the wavefunction of the incident and scattered positron, respectively, ϕ_e is the wavefunction of the ejected electron, while Ψ_{H_2} describes the initial state of the target and $\phi_{\text{H}_2^+}$ the residual ion. In order for (1) to be valid, the ejected electron wave function must be orthogonalized to the target wave function for H_2 as detailed below. In the above amplitude \mathbf{r}_1 is the position vector of the positron, while \mathbf{r}_2 and \mathbf{r}_3 stand for the position vectors of the active and the passive electron, respectively. The fact that each of the electrons can be active is reflected in the factor 2 in the expression of the cross section (1).

We have used two different wavefunctions to describe the ground state of the hydrogen molecule. Firstly, we have adopted the Heitler–London type wavefunction of Wang [15]. It has the form

$$\Psi_{\text{H}_2}(\mathbf{r}_2, \mathbf{r}_3) = N_{\text{H}_2} [\phi(r_{a2})\phi(r_{b3}) + \phi(r_{b2})\phi(r_{a3})], \quad (3)$$

where $\phi(r)$ is the hydrogenlike $1s$ wavefunction (with the effective charge 1.166), while r_{ai} and r_{bi} denote the distances between nucleus a or b and the i th electron with position vector \mathbf{r}_i ($i = 2, 3$) relative to the centre of the molecule. These can be expressed as

$$\mathbf{r}_{ti} = \mathbf{r}_i \mp \frac{\mathbf{R}_0}{2} \quad (4)$$

\mathbf{R}_0 being the internuclear separation. Here t denotes the two atoms a and b with corresponding signs ‘ $-$ ’ and ‘ $+$ ’, respectively. In this case the orthogonalization condition imposed is that

$$\langle \phi_e(\mathbf{r}_3) | \phi(r_{t3}) \rangle = 0 \quad (5)$$

where as above t denotes the atoms a and b . Note that it is sufficient to impose this condition on one of the wavefunctions ϕ and the other will be automatically orthogonal as well. Since the speed of the ejected electron is generally much faster than the nuclear motion, in the final state of the residual ion the internuclear separation and the orientation of the molecular axis are taken as the same as in the initial state (Born–Oppenheimer separation) so that we can describe the residual ion by a linear combination of atomic orbitals

$$\phi_{\text{H}_2^+}(\mathbf{r}_3) = N_{\text{H}_2^+} [\phi(r_{a3}) + \phi(r_{b3})] \quad (6)$$

$\phi(r)$ being the same atomic orbitals as for the initial state of H_2 .

Using expressions (3) and (6) for the molecular wave functions, the scattering amplitude can be written as

$$\begin{aligned} f &= N_{\text{H}_2^+} N_{\text{H}_2} \left\{ \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi(r_{a2}) \rangle [\langle \phi(r_{a3}) | \phi(r_{b3}) \rangle + \langle \phi(r_{b3}) | \phi(r_{b3}) \rangle] \right. \\ &\quad \left. + \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi(r_{b2}) \rangle [\langle \phi(r_{a3}) | \phi(r_{a3}) \rangle + \langle \phi(r_{b3}) | \phi(r_{a3}) \rangle] \right\} \\ &= N_{\text{H}_2^+} N_{\text{H}_2} (1 + S) \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) [\phi(r_{a2}) + \phi(r_{b2})] \rangle, \end{aligned} \quad (7)$$

where $S = \langle \phi(r_{a3}) | \phi(r_{b3}) \rangle$ is the overlap integral between the two atomic orbitals centered on different nuclei. Taking into account that $N_{\text{H}_2^+} = 1/\sqrt{2(1+S)}$ and introducing the notation

$$\phi_g(\mathbf{r}_2) = N_g [\phi(r_{a2}) + \phi(r_{b2})], \quad (8)$$

where $N_g = N_{\text{H}_2}/(2N_{\text{H}_2^+})$, the amplitude can be written simply as

$$f = \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi_g(\mathbf{r}_2) \rangle. \quad (9)$$

Alternatively, we have used Gaussian wavefunctions for the description of the ground state of the molecule with a basis set of 3 or 6 basis functions. In this case, because the wavefunction for H_2 is a product of two molecular orbitals of the form given in (8), integration over the coordinates \mathbf{r}_3 can be carried out leading directly to the expression (9) for the amplitude. Here the orthogonalization condition is $\langle \phi_e(\mathbf{r}_3) | \phi(r_{a3}) + \phi(r_{b3}) \rangle = 0$ which only affects the ejected partial waves of even parity. The hydrogen $1s$ orbitals have been constructed as contractions of $1s$ Gaussian type functions (CGF) [16]

$$\phi_{1s}^{\text{CGF}} = \sum_{p=1}^L d_p \phi_p^{\text{GF}}(\alpha_p, r), \quad (10)$$

where L is the length of the contraction and d_p a contraction coefficient. The Gaussian primitives have the general form

$$\phi_p^{\text{GF}}(\alpha_p, r) = (2\alpha_p \gamma^2 / \pi)^{3/4} e^{-\alpha_p \gamma^2 r^2}, \quad (11)$$

γ being a scaling factor used to scale all the exponents in the related Gaussians.

A standard value of 1.24 is normally used for γ in ab initio calculations for polyatomic molecules [17]. However, for the hydrogen molecule in its ground state an optimum scale factor of 1.19 has been obtained [18]. In our calculations we have used two different basis sets, namely STO-3G and STO-6G [19].

In both cases, as in a previous paper [20], we expand the wavefunction of the active electron into a Legendre series

$$\phi(r_{a2}) + \phi(r_{b2}) = \sum_{l_b} c_{l_b}(r_2, R_0) P_{l_b}(\cos \omega_2), \quad (12)$$

where ω_2 stands for the angle between \mathbf{r}_2 and \mathbf{R}_0 . The expansion coefficients can be expressed with the following integral

$$c_{l_b}(r_2, R_0) = \frac{2l_b + 1}{2} \int_{-1}^{+1} dx P_{l_b}(x) \left[\phi\left(\sqrt{r_2^2 + R_0^2/4 - r_2 R_0 x}\right) + \phi\left(\sqrt{r_2^2 + R_0^2/4 + r_2 R_0 x}\right) \right]. \quad (13)$$

In order to separate the angular dependences on the position of the electron and the orientation of the molecular axis, the Legendre polynomial is expanded in terms of spherical harmonics

$$P_{l_b}(\cos \omega_1) = \frac{4\pi}{2l_b + 1} \sum_{m_b} Y_{l_b m_b}^*(\hat{\mathbf{R}}_0) Y_{l_b m_b}(\hat{\mathbf{r}}_2). \quad (14)$$

Using the above, we have expressed the two-centre wavefunction as a sum of products of a one-centre (atomic) wavefunction characterized by angular momentum l_b

$$\phi_{l_b m_b}(\mathbf{r}_2) = \frac{4\pi N_g}{2l_b + 1} c_{l_b}(r_2, R_0) Y_{l_b m_b}(\hat{\mathbf{r}}_2), \quad (15)$$

and a spherical harmonic expressing the dependence on the orientation of the molecular axis $Y_{l_b m_b}^*(\hat{\mathbf{R}}_0)$.

Using the above expansion, the amplitude can be written as

$$f = \sum_{l_b, m_b} \langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi_{l_b m_b}(\mathbf{r}_2) \rangle Y_{l_b m_b}(\hat{\mathbf{R}}_0). \quad (16)$$

The cross section (1) calculated with this amplitude will depend on the orientation of the molecular axis $\hat{\mathbf{R}}_0$. In the usual experimental setup this dependence cannot be detected. In order to compare the theoretical results with the experiments, we average the cross section over all the possible angles $\hat{\mathbf{R}}_0$, similar to Chen et al. [12]. Taking into account the orthogonality properties of the spherical harmonics, the averaged differential cross section becomes

$$\frac{d^3 \sigma_{AV}}{d\hat{\mathbf{k}}_f d\hat{\mathbf{k}}_e dE_e} = 2 \frac{(2\pi)^4}{4\pi E_i} \sum_{l_b, m_b} |\langle \phi_f(\mathbf{r}_1) \phi_e(\mathbf{r}_2) | V(r_{12}) | \phi_i(\mathbf{r}_1) \phi_{l_b m_b}(\mathbf{r}_2) \rangle|^2. \quad (17)$$

Further, in the calculation of the total cross section, one must average over the angles of the outgoing electron and positron as well as the energy of the electron as described in [21] for the atomic case. In the expansion on l_b for homopolar molecules only the terms with even l_b are nonzero. In our present calculations we have taken into account only the terms with $l_b = 0$ and 2. The terms with $l_b > 2$ contribute less than 0.5%, to the total cross sections and have been neglected.

3. Results and discussion

In Figs. 1 and 2 we present the integrated ionization cross sections corresponding to the models CPE and CPE4 respectively. In each figure we show three theoretical curves which converge at high impact energies, but show greater differences in the region of the maximum cross section. In both figures the top curve corresponds to our one-center calculation [11] using the spherically averaged target representation of Wang [15], the lowest curve corresponds to the two-center calculation with Wang's target representation and the middle curve corresponds to the two-center calculation with a 6-term gaussian representation of H_2 .

Figs. 1 and 2 also include the experimental results. The results of Chen et al. [12] using a two-center approximation and Wang's target representation lie consistently below our results and are not shown. The ionization model employed by Chen et al. was a "truncated" CPE, in which the scattered positron is always faster than the ejected electron and this might explain the difference from our middle curve in Fig. 1.

The various experiments seem to disagree significantly in the region of the maximum of the cross section. They all used coincidence techniques combined with time-of-flight measurements to ensure that the direct ionization data is not affected by the positronium formation. The data of Moxom et al. [3] were obtained by eliminating the background caused by random extraction of ions in the original work of Knudsen et al. [2]. The data of Jacobsen et al. [4] lie considerably below the other experimental results and our theoretical calculations.

Our Figs. 1 and 2 shows that the one-center calculations using the spherically averaged target representation produce data in best agreement with Moxom et al. [3]. However, compared with our two-center calculations these results are higher in the region of the maximum by 13% for CPE and 16% for CPE4. Our current two-center work and that of Chen et al. [12] produce data which lay between the most recent experimental sets of results [3,4].

Finally, changing the molecular representation from Wang's model to a gaussian set does not significantly change the ionization cross sections. We have also investigated the effect of increasing the gaussian set and the 6-terms set produced almost the same results as the 3-terms set.

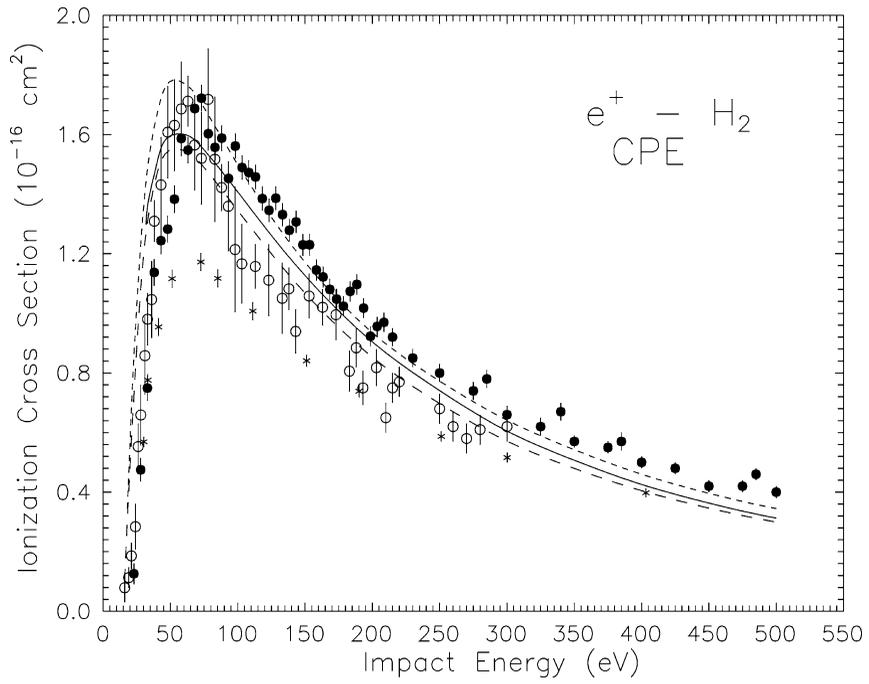


Fig. 1. CPE model results: solid curve, two-centre Gaussian wave functions; long-dash curve, two-centre Wang wave functions; short-dash curve, spherically-averaged Wang wave functions. Experimental results: ● [3], ○ [2], * [4].

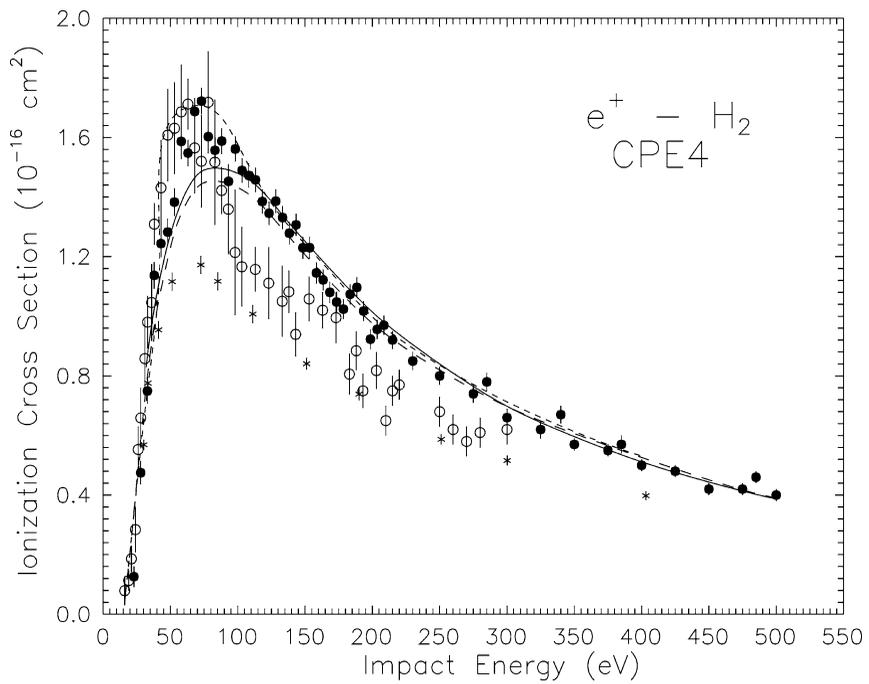


Fig. 2. CPE4 results. The legend is the same as for Fig. 1.

4. Conclusions

Our calculations show that the results at higher energies are not particularly sensitive to the wave functions used. The CPE4 results seem to be in better agreement at these energies. However, in the region of the maximum, the use of spherically averaged molecular orbitals in the one-center ionization model produces significantly higher results for the integrated cross sections. Both two-center models produce data which lie between the two most recent sets of measurements.

We also find that the use of Gaussian representations of molecular orbitals produces ionization cross sections very similar to those obtained with the Heitler–London model for H₂ obtained by Wang [15]. The use of Gaussian molecular representations has the advantage of providing a relatively simple approach to the ionization of more complex molecules, a task that we intend to undertake in the near future.

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