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Interference effects in the photoionization of molecular hydrogen

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Abstract

Photoionization cross sections for the hydrogen molecule have been calculated, emphasizing the interference effects due to the two-center character of the target. In order to easily identify the main features of the interference, a simplified description of the final state has been adopted. Because of the approximate description of electron states, results are gauge-dependent. Interference pattern, identified in the in the experimental data, is well reproduced by our length form results.

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1. Introduction

The wave properties of the electrons make possible the arise of interference effects. The two nuclei of a diatomic molecule are analogous to the two slits from the classical Young experiment for light. The possibility of the interference effects in the ejected electron spectra due to the two-center character of a molecular target have been predicted for the first time by Cohen and Fano [1] for the photoionization. The phenomenon have been analyzed in more detail by Walter and Briggs [2], including photo-double ionization. In the last two years much interest have been given to the interference effects observed in the ejected elec-

tron spectra in case of the ionization of the hydrogen molecule by fast charged projectiles. It has been observed experimentally by Stolterfoht and coworkers [3,4] that the cross section ratios obtained for the hydrogen molecule and hydrogen atom shows an oscillatory pattern. These interference patterns have been investigated theoretically by several groups [5–9].

Although there are much experimental data [10–13] and theoretical descriptions [14–19] for the photoionization of the hydrogen molecule, except for Cohen and Fano [1] and Walter and Briggs [2], the interference effects due to the two-center character of the molecule were not analyzed.

The photoionization process may be treated in different gauges (using length, velocity or acceleration form of the dipole operator). If the wavefunctions of the initial and the final states are exact (as it can be done easily for the H atom), results are gauge-inde-

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pendent. However, for atoms and molecules with more electrons, the electronic states cannot be described exactly, and usually the obtained results depend on the gauge. This is the case also for the relatively elaborate calculations done for the helium [20] or hydrogen molecule [16]. However, some approximations, as the random phase approximation (RPA) [16,19] may lead to gauge-independent results.

Our aim in the present letter is to investigate how the two-center character of the molecule influences the photoionization cross section and the angular distribution of the ejected electron. In order to express the interference patterns by simple analytic formulae, we have described the ejected electron by plane waves. This may seem a too simplistic approach, and does not produce reliable values for the absolute cross sections, but makes possible to emphasize the interference effects. We analyze the character of the results using both velocity and length forms of the dipole operator.

2. Theory

The differential photoionization cross section for a linearly polarized radiation may be expressed as

$$\sigma = \frac{4\pi\alpha}{\omega} |M_{fi}(\omega)|^2, \quad (1)$$

where α is the fine-structure constant, ω the photon angular frequency and $M_{fi}(\omega)$ the transition matrix element. The matrix element is given by

$$M_{fi}(\omega) = k^{1/2} \langle \Psi_f | e^{i\mathbf{K}\mathbf{r}} \boldsymbol{\epsilon} \nabla_r | \Psi_i \rangle \quad (2)$$

with Ψ_i and Ψ_f the initial and final states of the active electron, respectively. \mathbf{K} is the wave vector and $\boldsymbol{\epsilon}$ the polarization vector of the photon, while \mathbf{k} is the wave vector of the ejected electron. The factor $k^{1/2}$ occurs if the continuum wavefunction is normalized to momentum. In dipole approximation the matrix element may be written as

$$M_{fi}(\omega) = k^{1/2} \langle \Psi_f | \boldsymbol{\epsilon} \nabla_r | \Psi_i \rangle \quad (3)$$

in velocity form, while in length form we have

$$M_{fi}(\omega) = -k^{1/2} \omega \langle \Psi_f | \boldsymbol{\epsilon} \mathbf{r} | \Psi_i \rangle. \quad (4)$$

Applying the above formulae for the hydrogen atom (or a hydrogen-like ion with nuclear charge ρ)

with

$$\Psi_i(\mathbf{r}) = \sqrt{\frac{\rho^3}{\pi}} e^{-\rho r} \quad (5)$$

and approximating the final state by plane waves

$$\Psi_f(\mathbf{k}, \mathbf{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\mathbf{r}}, \quad (6)$$

one obtains in velocity form

$$\sigma_V = \frac{32\alpha}{\omega} \frac{\rho^5 k}{(\rho^2 + k^2)^4} (\boldsymbol{\epsilon}\mathbf{k})^2, \quad (7)$$

while in the length form we get

$$\sigma_L = 512\alpha\omega \frac{\rho^5 k}{(\rho^2 + k^2)^6} (\boldsymbol{\epsilon}\mathbf{k})^2. \quad (8)$$

Taking into account that for a one-electron atom

$$\omega = \frac{k^2}{2} + \frac{\rho^2}{2}, \quad (9)$$

one observes that in length form the cross section is exactly 4 times larger than in velocity form. The asymptotic behavior for high photon energies in both gauges is the correct $\sigma \propto \omega^{-7/2}$. Comparing these findings to the exact result obtained with Coulomb wavefunctions, which is gauge-independent (see, e.g., [21])

$$\sigma = \frac{64\pi\alpha}{\omega} \frac{\rho^6 e^{-4\eta \operatorname{arccot} \eta}}{(1 - e^{-2\pi\eta})(\rho^2 + k^2)^4} (\boldsymbol{\epsilon}\mathbf{k})^2, \quad (10)$$

(with $\eta = \rho/k$) we may state, the plane-wave approximation leads to the correct result only for high photon energies and in velocity form (see Fig. 1).

For the hydrogen molecule the initial state of the active electron is approximated by a linear combination of two atomic orbitals

$$\Psi_i = \frac{1}{\sqrt{2(1+S)}} [\Psi_0(\mathbf{r}_a) + \Psi_0(\mathbf{r}_b)]. \quad (11)$$

Here $\Psi_0(\mathbf{r}_{a,b})$ are the atomic $1s$ orbitals given by (5) centered to the nuclei a or b , while S is the overlap integral between these two orbitals.

Using plane waves for the final state the (3) matrix element in velocity form may be written as

$$M_{fi}(\omega) = \frac{k^{1/2}\boldsymbol{\epsilon}}{(2\pi)^{3/2}\sqrt{2(1+S)}} \times \int d\mathbf{r} e^{i\mathbf{k}\mathbf{r}} \nabla_r [\Psi_0(\mathbf{r}_1) + \Psi_0(\mathbf{r}_2)], \quad (12)$$

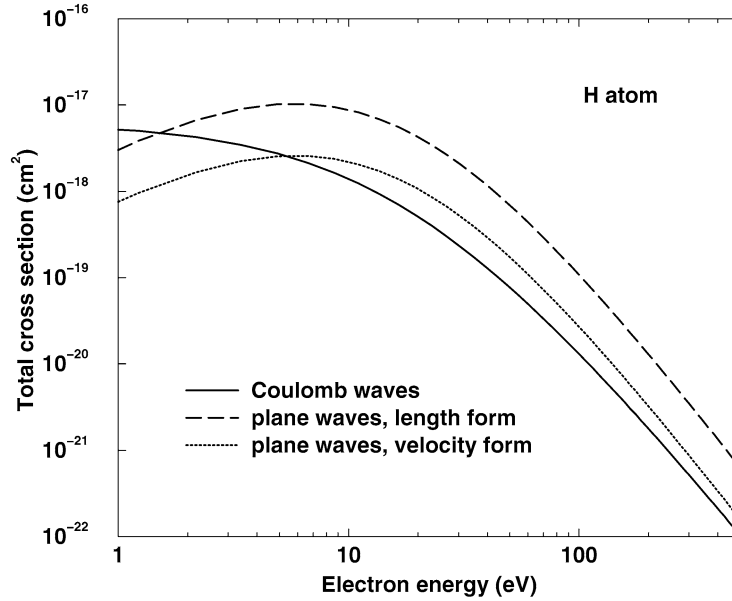


Fig. 1. Total photoionization cross section for the hydrogen atom as a function of the ejected electron energy. The exact results (using Coulomb waves) are compared to the cross sections obtained with a plane-wave approximation for the continuum electron in two different gauges.

and after performing the calculations one obtains

$$M_{fi}(\omega) = -\frac{4\rho^{5/2}}{\pi\sqrt{1+S}} \frac{(\epsilon\mathbf{k})k^{1/2}\cos(\mathbf{k}\mathbf{D}/2)}{(\rho^2+k^2)^2}. \quad (13)$$

Using (1), the cross section for a fixed orientation of the molecular axis may be written

$$\sigma_V(\hat{\mathbf{D}}) = \frac{128\rho^5\alpha}{\omega\pi(1+S)} \frac{(\epsilon\mathbf{k})^2k\cos^2(\mathbf{k}\mathbf{D}/2)}{(\rho^2+k^2)^4}, \quad (14)$$

where a factor of 2 occurs because of the two electrons of the molecule. This result was given first by Cohen and Fano [1] and then recalculated by Walter and Briggs [2]. The $\cos(\mathbf{k}\mathbf{D}/2)$ factor is responsible for the interference effects for a fixed orientation of the molecular axis. Because in most experiments the orientation of the molecule is not detected, in order to compare the results with experimental data, one has to average the cross section over the angles

$$\sigma_V = \frac{1}{4\pi} \int d\hat{\mathbf{D}} \sigma(\hat{\mathbf{D}}). \quad (15)$$

The calculations can be done analytically to obtain

$$\sigma_V = \frac{64\rho^5\alpha}{\omega(1+S)} \frac{\cos^2\theta_\epsilon k^3}{(\rho^2+k^2)^4} \left[1 + \frac{\sin(kD)}{kD} \right] \quad (16)$$

with $\cos\theta_\epsilon = \epsilon\hat{\mathbf{k}}$.

If one applies for the calculations the matrix element written in length form (4), the results will be different. Introducing the notation $\mathbf{r}_{fi} = \langle \Psi_f | \mathbf{r} | \Psi_i \rangle$ we have

$$\mathbf{r}_{fi} = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} e^{i\mathbf{k}\mathbf{r}} \mathbf{r} \Psi_i. \quad (17)$$

Using $\mathbf{r}e^{-i\mathbf{k}\mathbf{r}} = i\nabla_{\mathbf{k}}e^{-i\mathbf{k}\mathbf{r}}$ we obtain

$$\mathbf{r}_{fi} = \frac{i\nabla_{\mathbf{k}}}{(2\pi)^{3/2}} \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} \Psi_i = i\nabla_{\mathbf{k}} \tilde{\Psi}_i(\mathbf{D}, \mathbf{k}), \quad (18)$$

where $\tilde{\Psi}_i(\mathbf{D}, \mathbf{k})$ is the initial state in momentum representation. This may be expressed in terms of the atomic wavefunction

$$\tilde{\Psi}_i(\mathbf{D}, \mathbf{k}) = \frac{2\cos(\mathbf{k}\mathbf{D}/2)}{\sqrt{2(1+S)}} \tilde{\Psi}_0(\mathbf{k}), \quad (19)$$

where

$$\begin{aligned} \tilde{\Psi}_0(\mathbf{k}) &= \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} N(\rho) e^{-\rho r} \\ &= \frac{4N(\rho)\rho}{\sqrt{2\pi}(\rho^2+k^2)^2} \end{aligned} \quad (20)$$

with $N(\rho) = \sqrt{\rho^3/\pi}$ a normalization factor.

Using the above result, for the (4) matrix element we obtain

$$\begin{aligned} M_{fi}(\omega) &= \omega \epsilon \frac{8i\rho N(\rho)k^{1/2}}{\sqrt{4\pi(1+S)}} \nabla_k \frac{\cos(\mathbf{kD}/2)}{(\rho^2 + \mathbf{k}^2)^2} \\ &= \frac{8i\omega\rho N(\rho)k^{1/2}}{\sqrt{4\pi(1+S)}} \\ &\quad \times \left[\frac{\sin(\mathbf{kD}/2)\epsilon\mathbf{D}}{2(\rho^2 + \mathbf{k}^2)^2} + \frac{4\cos(\mathbf{kD}/2)\epsilon\mathbf{k}}{(\rho^2 + \mathbf{k}^2)^3} \right]. \quad (21) \end{aligned}$$

Inserting the matrix element (21) to (1) and multiplying by 2 because of the two electrons, we obtain the cross section for a fixed position of the molecular axis

$$\begin{aligned} \sigma_L(\hat{\mathbf{D}}) &= \frac{128\alpha\omega\rho^5k}{\pi(1+S)} \\ &\quad \times \left[\frac{\sin(\mathbf{kD}/2)\epsilon\mathbf{D}}{2(\rho^2 + \mathbf{k}^2)^2} + \frac{4\cos(\mathbf{kD}/2)\epsilon\mathbf{k}}{(\rho^2 + \mathbf{k}^2)^3} \right]^2. \quad (22) \end{aligned}$$

Comparing this result in length form to that obtained in velocity form (14) one may observe, that not only the magnitude of the cross section is different, but also its dependence on the orientation of the molecular axis and on the electron ejection angle.

Averaging the cross section over all possible orientations of the molecular axis, after the analytical integration over the angles, we get

$$\begin{aligned} \sigma_L &= \frac{1024\omega\rho^5\alpha}{(1+S)(\rho^2 + k^2)^6} k^3 \cos^2\theta_\epsilon \left[1 + \frac{\sin(kD)}{kD} \right] \\ &\quad + \frac{16\omega\rho^5\alpha k}{(1+S)(\rho^2 + k^2)^4} \left[\frac{D^2}{3} - \frac{D}{k} \cos^2\theta_\epsilon \sin(kD) \right] \\ &\quad + \frac{1}{k^2} (1 - 3\cos^2\theta_\epsilon) \left(\cos(kD) - \frac{\sin(kD)}{kD} \right) \\ &\quad + \frac{256\omega\rho^5\alpha k}{(1+S)(\rho^2 + k^2)^5} \cos^2\theta_\epsilon \\ &\quad \times \left[\frac{\sin(kD)}{kD} - \cos(kD) \right]. \quad (23) \end{aligned}$$

Beside the difference in magnitude between the expression above obtained in length form and the (16) expression obtained in velocity form observed also for atoms, in case of the molecules the angular dependence, too is obtained to be different in the two gauges. While in velocity form for molecules one obtains the same $\cos^2\theta_\epsilon$ angular dependence as for atoms, in length form we obtain a more complicated dependence, and there is electron ejection even for $\theta_\epsilon = 90^\circ$.

3. Results and discussion

The polar graphs on Figs. 2–4 show differential cross sections for the photoionization of the hydrogen molecule for various photon energies and fixed orientation of the molecular axis, normalized to the maximum value. Our results using the velocity form (14) and the length form (22) are represented along the random phase approximation (RPA) results of Semenov and Cherepkov [19], and the few available experimental data [22]. In Fig. 2 is represented the cross section for the molecular axis parallel to the polarization vector. At low photon energies all the results are in good agreement with each other, length and velocity forms lead to the same angular distribution. This distribution is a typical dipole one, governed by $\cos^2\theta_\epsilon$, because for low energies in Eq. (14) the $\cos^2(\mathbf{kD}/2)$ is close to 1, and in (22) the term with $\sin(\mathbf{kD}/2)$ is negligible. Discrepancy begins to occur at higher energies. At 54.4 eV the differences between the three models become visible, and at 84.2 eV are already essential. At this energy the probability of ejecting an electron at 0 degrees relative to the polarization vector (and to the molecular axis) in velocity form becomes very small, because $\cos(kD/2)$ is close to 0 (being exactly 0 at 82 eV). The shape of the polar graph in length form is somehow different, because it does not reduce to zero at 0 degrees, but disagreement with the RPA results of Semenov and Cherepkov [19] is total—their differential cross section has a maximum value at 0 degrees.

Our results for the molecular axis at 45° relative to the polarization vector are represented on Fig. 3. It is worth to notice the main difference between the results in the two gauges—while the cross section is velocity form is always zero at a perpendicular direction to the polarization vector, in length form this is not the case, mainly for high energies. In this sense, present length form results (using plane waves) are similar to that obtained by Walter and Briggs [2] using continuum waves distorted by Coulomb functions (2C). However, the details of the angular distributions are different.

If the molecular axis is perpendicular to the polarization vector, nothing interesting happens, our results for the angular distribution in the different gauges and those of Semenov and Cherepkov [19] are in perfect agreement (Fig. 4).

However, in most experiments the orientation of the molecule is not detected, and worth to investigate

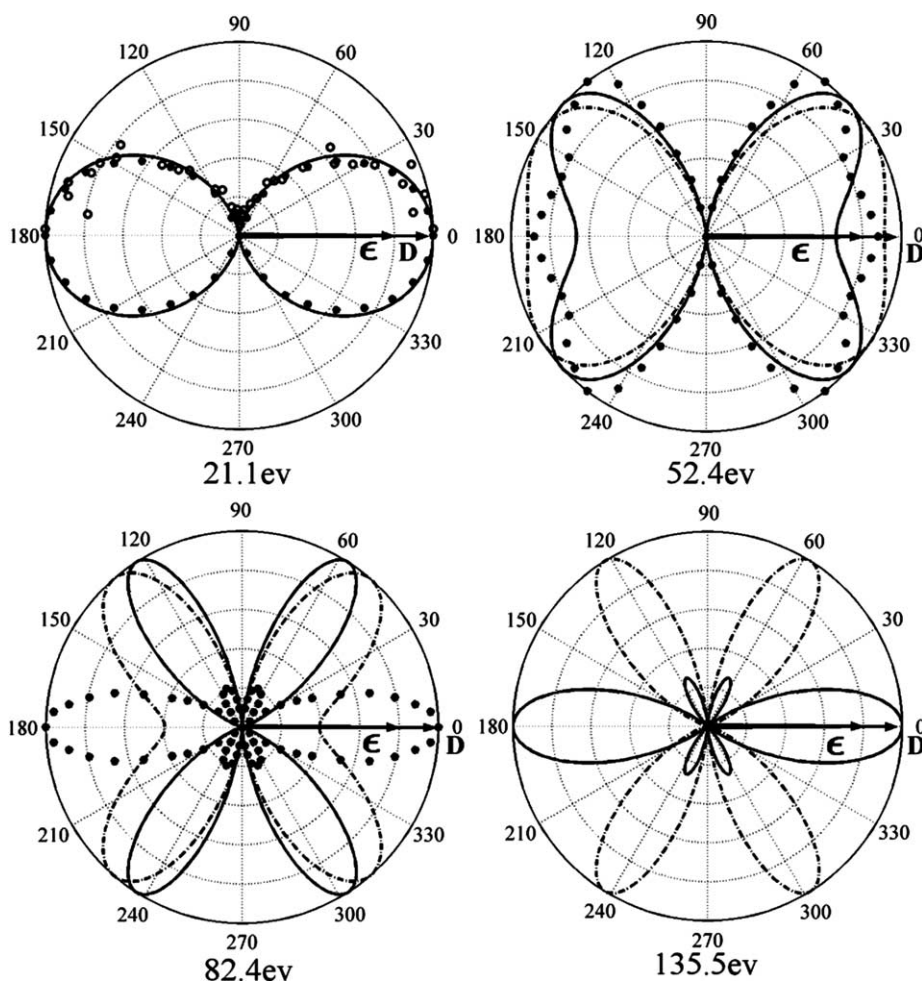


Fig. 2. Polar representation of the differential photoionization cross section of the H_2 for the molecular axis parallel to the polarization vector, for different photon energies. Cross sections are normalized to the maximum value. Solid lines—velocity form results, dashed line—length form results, full circles—RPA results of Semenov and Cherepkov [19], open circles—experimental data [22].

the angular behavior of the averaged photoionization differential cross section relative to the orientation of the molecular axis. Results in velocity and length forms, based on formulae (16) and (23), respectively, are plotted on Fig. 5 for two photon energies. At low energies the differences obtained in the two gauges are negligible, while at high energies the already mentioned difference becomes visible—in length form there is possible the electron ejection perpendicular to the polarization vector, while in velocity form it is not. Here again we can state, that length form results using plane waves are similar to the 2C results of Walter and Briggs [2].

The differences between the results obtained in the two different gauges may be expressed using the β asymmetry parameter. In velocity form the β parameter is constantly 2, as for the hydrogen atom, but in the length form its value is lower and decreases with increasing photon energy. On Fig. 6 we have represented the asymmetry parameter in both gauges along with the RPA results of Cacelli et al. [16] and the experimental data [23,24]. The obtained values in length form are closer to the experimental data and the RPA results, than our velocity form values.

Finally, in order to emphasize the interference effects in the photoionization due to the two-center char-

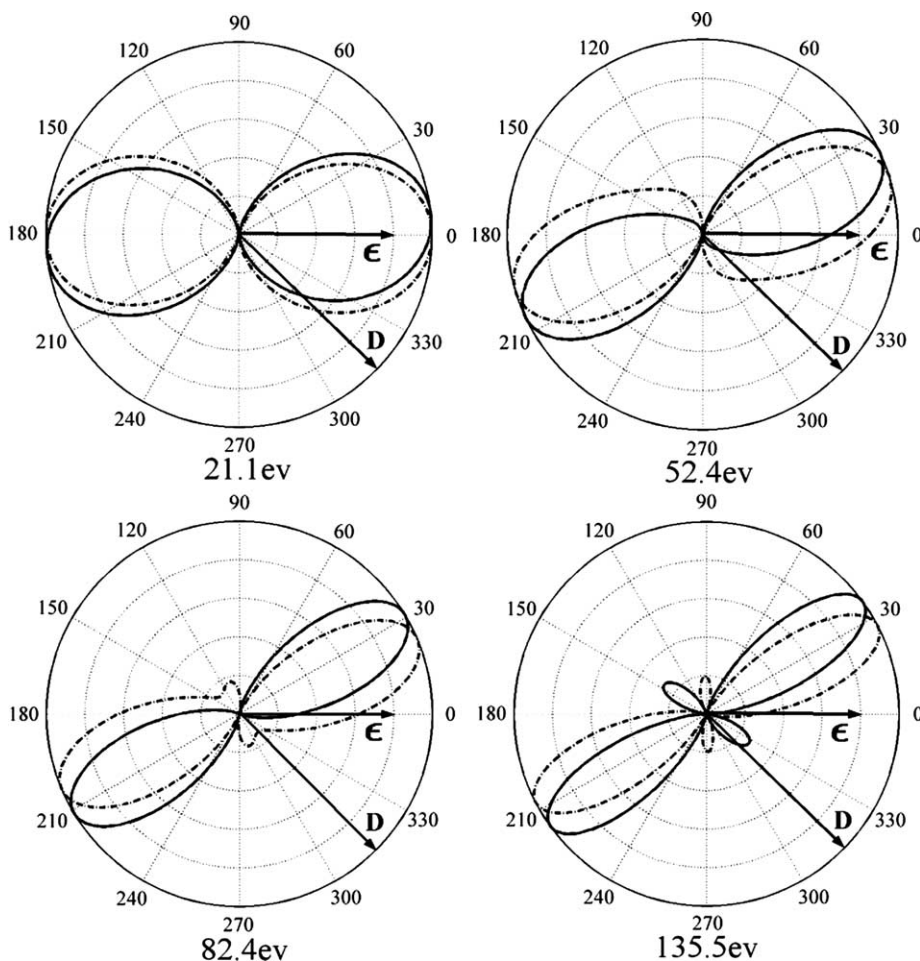


Fig. 3. Same as Fig. 2, but for 45° between the molecular axis and the polarization vector.

acter of the molecule, we have plotted on Fig. 7 the cross section ratio $\sigma(\text{H}_2)/2\sigma(\text{H})$. This method, used first by Stolterfoht et al. [3] for the ionization by ion impact gives the possibility to observe oscillations in the molecular cross sections, i.e., maxima and minima due to the interference. Our theoretical ratios are represented along the experimental photoionization cross section of the H_2 of Samson and Haddad [13] divided by the double of the theoretical total cross section of the H atom calculated from formula (10), using the same ionization potential for the atom as for the molecule. Theoretical ratios are calculated using plane waves for the ejected electron in velocity and length forms. As may be observed from (16), in velocity form the differential cross section has the same

angular distribution as for atoms, and the ratio does not depend on the electron ejection angle. This is not the case for the length form (23), and the cross section ratio depends on the ejection angle. This ratio increases for higher velocities and angles close to 90° , where the cross section for atoms tends to 0.

In their RPA calculation, Semenov and Cherepkov [19] have found in the $p\sigma$ component of the cross section a minimum at around 80 eV photon energy, which they call ‘Cooper-like’. They state, that this minimum is related to the non-spherical shape of the molecular potential. This is certainly true, but we can add, that this minimum is caused by the interference of the electron waves emitted by the two centers of the molecule. If the electron is ejected parallel to

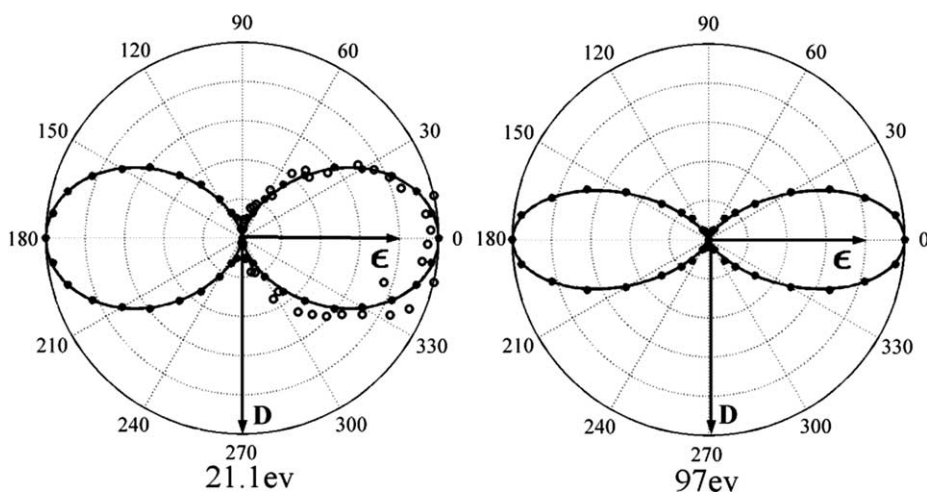


Fig. 4. Same as Fig. 2, but for 90° between the molecular axis and the polarization vector.

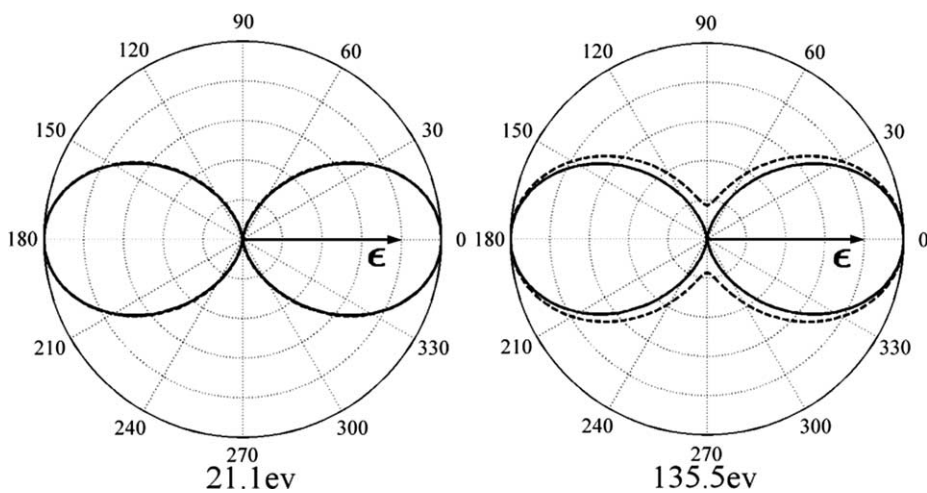


Fig. 5. Same as Fig. 2, but averaged over the orientation of the molecular axis.

the molecular axis ($\mathbf{k} \parallel \mathbf{D}$), the expression $\cos(\mathbf{kD}/2)$ from (14) is exactly zero for 82 eV photon energy (corresponding to 2.21 a.u. electron velocity), leading to a zero differential cross section for this ejection angle. In length form the differential cross section does not reach zero, but the minimum still exists. If one integrates over all possible orientations of the molecular axis, instead of the pronounced minimum observed for electrons ejected parallel to the molecular axis, one observes a broad minimum shifted to higher energies (see Fig. 7). The minimum is obtained at higher electron velocities in length form than in veloc-

ity form. The cross section ratios obtained in length form fits very well the experimental ratios.

4. Conclusions

Interference effects caused by the two-center character of the target in the photoionization of the hydrogen molecule have been studied. In order to express the factors in the cross section due to the interference in closed analytic form, we have approximated the final state of the ejected electron by plane waves. In these conditions the calculations performed in dif-

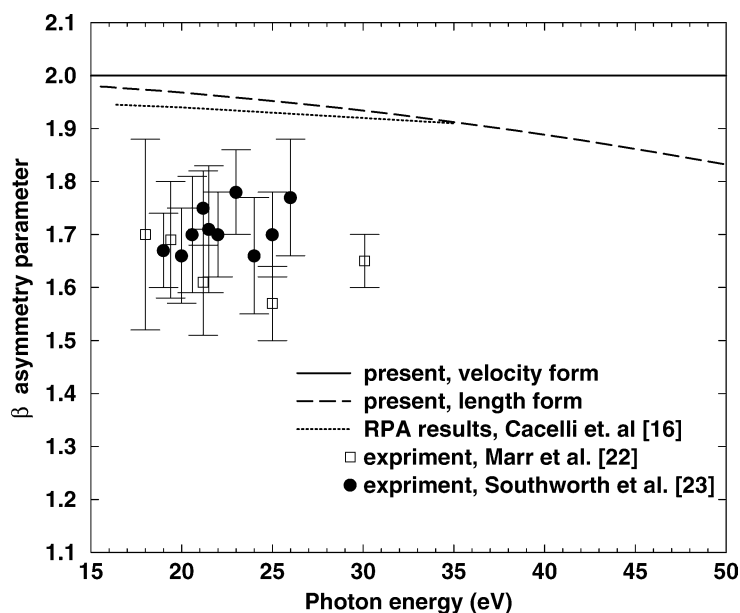


Fig. 6. The β asymmetry parameter for the photoionization of the H_2 as a function of the photon energy.

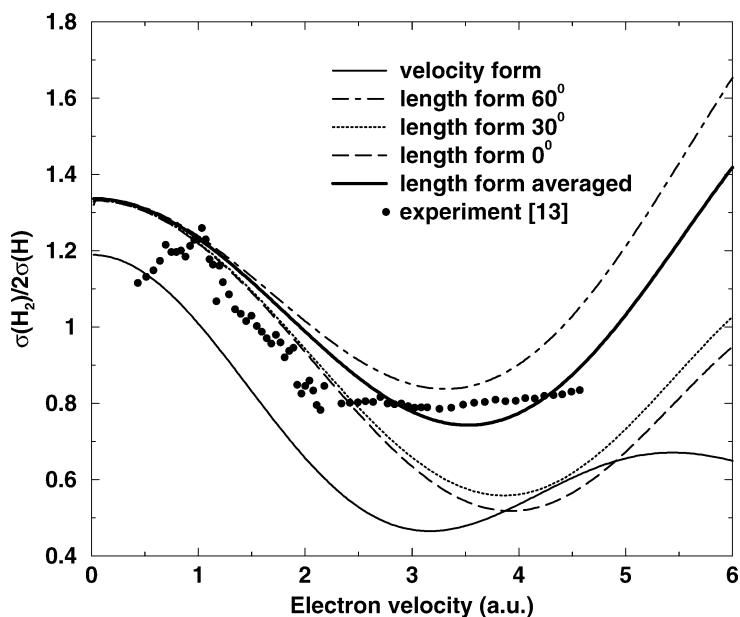


Fig. 7. Photoionization cross section ratios $\sigma(H_2)/2\sigma(H)$ as a function of the ejected electron velocity. In length form the ratios are represented for different electron ejection angle, and also for total ionization cross sections (or averaged over the angles). Experimental points are obtained by dividing the H_2 data of Samson and Haddad [13] by the double of the theoretical atomic total cross section obtained from (10).

ferent gauges lead to different results for the absolute value of the cross section and angular distributions of the ejected electron. For the absolute value, velocity

form lead to better results (cross sections obtained in length form are too high), but for the angular distribution length form seems to give more interesting and

reliable results. When averaged over the orientation of the molecular axis, velocity form calculations give the same $\cos^2 \theta_\epsilon$ angular distribution as for atoms [2], while in length form calculations lead to more complicated angular distributions. In the latter case there is possible the ejection of the electron even perpendicular to the polarization vector, as in case of the use of more evaluated wavefunctions [2].

As previously for ion impact [5], we have studied the ratio of the differential ionization cross sections for the H_2 molecule and the H atom as a function of the ejected electron velocity. Maxima and minima are obtained as a clear evidence for the interference effects. These oscillations in velocity form does not depend on the ejection angle as have been observed for ion impact. However, in length form an angular dependence of the ratio have been observed, because of the different angular distribution of the photoelectron for the atom and the molecule. When integrated over the angles, our predictions obtained in length form for these oscillations are in good agreement with the experiment.

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