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Study of the interference effects in the ionization of H_2 by the use of two-center wavefunctions

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Abstract

Photoionization cross section for the hydrogen molecule has been calculated using two-center wavefunctions for the description of the initial and final states. Interference effects which appears due to the two-center character of the molecular target were identified and analyzed. The angular distribution of outgoing electron and the contribution of partial waves have been also studied. The obtained results are very sensitive to the description of the final state.

Keywords: Photoionization; Interference effects; Two-center wavefunctions

1. Introduction

Interference effects, which are analogous with the Young's two slit interference, may occur in the photoionization of molecular hydrogen due to the two-center character of the target molecule. The possibility of such kind of interference phenomena in the ejected electron spectra have been predicted for the first time by Cohen and Fano (1966).

Similar effects were observed by Stolterfoht and coworkers (Stolterfoht et al., 2001, 2003) in the case of ionization of hydrogen molecule by fast charged projectiles where the ratio of the molecular and atomic cross section shows an oscillatory pattern.

There are many experimental data (Backx et al., 1976; Samson, 1976; Lee et al., 1976; Samson and Haddad, 1994) and theoretical descriptions (Cohen and Fano, 1966; Flannery and Öpik, 1965; Khare, 1968; Cacelli et al., 1993; Yan et al., 1998; Martín, 1999; Walter and Briggs, 1999; Semenov and Cherepkov, 2003; Nagy et al., 2004; Fojón et al., 2004) devoted to the photoionization of the hydrogen molecule, but only a few of them (Cohen and Fano, 1966; Walter and Briggs, 1999; Nagy et al., 2004; Fojón et al., 2004) analyze the interference effects.

In a previous paper, the photoionization cross section for hydrogen molecule has been calculated using a simplified description of the final state by plane waves (Nagy et al., 2004). This approximation provides a good description of the main features of interference effects, but it is gauge dependent (the angular distribution of the outgoing electrons depend on the used gauge and the cross section in length gauge is nearly four times higher then in velocity gauge, Nagy et al., 2004).

Our aim in the present paper is to analyze the influence of the two-center character of the final state on the interference effects. We also perform a deeper analysis of interference effects by the study of the contribution of different partial waves.

2. Theory

The differential cross section for a linearly polarized radiation is expressed as

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

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

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The transition matrix element in dipole approximation may be written in velocity form as

$$M_{fi}(\omega) = \hat{\boldsymbol{\varepsilon}}\langle\psi_f|\nabla|\psi_i\rangle, \tag{2}$$

while in length form is

$$M_{fi}(\omega) = \mathrm{i}\hat{\boldsymbol{\varepsilon}}\omega\langle\psi_f|\mathbf{r}|\psi_i\rangle. \tag{3}$$

Here, ψ_i and ψ_f are the initial and final states of the active electron, and $\hat{\boldsymbol{\varepsilon}}$ is the polarization vector of the photon.

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

$$\psi_i = \frac{1}{\sqrt{2(1+S)}}[\psi_0(r_a) + \psi_0(r_b)], \tag{4}$$

where $\psi_0(r_{a,b})$ are the atomic 1s orbitals centered to the nuclei a or b, with an effective charge of 1.16 (Shull and Ebbing, 1958). S is the overlap integral between the two atomic orbitals. The simplest description of the final state is a plane wave (Cohen and Fano, 1966; Nagy et al., 2004), neglecting all the nucleus–electron and electron–electron interaction in the final state. This description has the advantage that the results and the interference pattern can be expressed by simple analytic formulae, but the results strongly depend on the gauge, both for the angular distribution of the ejected electron and for the absolute value of the cross section (Nagy et al., 2004).

We investigate two methods of taking into account the nucleus–electron interaction in the final state. One is to multiply the plane wave with two Coulomb distortion factors (Walter and Briggs, 1999) centered to the nuclei a and b, which lead us to the $2C$ wavefunction

$$\begin{aligned}\psi_{2C} = {} & (2\pi)^{-3/2}\mathrm{e}^{-\pi\gamma}\mathrm{e}^{-\mathrm{i}\mathbf{rk}}\mathrm{e}^{\mathrm{i}k(r_a+r_b)}\Gamma^2(1+\mathrm{i}\gamma) \\ & \times H(1+\mathrm{i}\gamma, 1; -\mathrm{i}(kr_a - \mathbf{kr_a})) \\ & \times H(1+\mathrm{i}\gamma, 1; -\mathrm{i}(kr_b - \mathbf{kr_b})).\end{aligned} \tag{5}$$

Another simple final state wavefunction can be obtained by a linear combination of two Coulomb wavefunctions, which we call 2CA

$$\begin{aligned}\psi_{2CA} = {} & \tfrac{1}{2}(2\pi)^{-3/2}\mathrm{e}^{-\pi\gamma/2}\Gamma(1+\mathrm{i}\gamma) \\ & \times[\mathrm{e}^{\mathrm{i}kr_a}H(1+\mathrm{i}\gamma, 1; -\mathrm{i}(kr_a - \mathbf{kr_a})) \\ & + \mathrm{e}^{\mathrm{i}kr_b}H(1+\mathrm{i}\gamma, 1; -\mathrm{i}(kr_b - \mathbf{kr_b}))].\end{aligned} \tag{6}$$

This wavefunction also takes into account the two-center character of the final state. The 2CA wavefunction does not have a proper asymptotic behavior, but it describes well the active electron in the vicinity of nuclei, which is required in this case. The Coulomb distortion factor and the Coulomb wavefunction were used in a modified form (we applied the Kummer transformation (see Abramowitz and Stegun, 1972 relation 13.2.1) on the $\mathrm{H}(a,b;x)$ confluent hypergeometric function), where $\mathbf{k}$ is the wave vector of the ejected electron, $\mathbf{R_0}$ is the half of the nuclear separation and $\gamma = \rho/k$ is the Sommerfeld-parameter with ρ, the effective charge of nuclei "seen" by the active electron.

The influence of the electron–electron interaction on the final state was taken into account by the screening effect of the passive electron on the nucleus–electron interaction. This means that the effective charge of the nuclei a or b "seen" by the active electron depends on it's position. This screening effect was reproduced by a simple trial function

$$\rho(r) = \rho_\infty + \Delta\rho\frac{1}{1+\exp(r - r_h/c)}, \tag{7}$$

where r is the distance of the active electron from the center of the molecule, c and r_h are parameters which fix the shape of trial function. ρ_∞ was set to 0.5 a.u. and $\Delta\rho$ to 0.66 a.u. in order to fulfill the following requirements for the trial function:

- the asymptotic value of the effective charge has to be 0.5 a.u. (because the two nuclei are screened by one electron);
- the value of the effective charge in the region of the nuclei has to be 1.16 a.u., the same value as for the bound wavefunction (Shull and Ebbing, 1958);
- the final state wavefunction and it's first order derivate has to be continuous.

In order to study the contribution of the partial waves, the initial and final wavefunctions have been expanded into series of spherical harmonics

$$\psi_f = \sum_{l_1,m_1} c_{l_1,m_1} Y_{l_1}^{m_1}(\theta,\varphi), \tag{8}$$

$$\psi_i = \sum_{l_2,m_2} b_{l_2,0} D^{l_2}_{m_2,0}(\alpha,\beta,\gamma) Y_{l_2}^{m_2}(\theta,\varphi). \tag{9}$$

The final state wavefunction has been expanded in the laboratory frame (fixed to the polarization vector $\hat{\varepsilon}$), while the initial state wavefunction was expanded in the body-fixed frame and transformed into laboratory frame by the use of Wigner D-functions. The α,β,γ are the Euler angles of the frame rotation. By the use of the above formulae (8,9), the transition matrix element may be expressed as a sum of partial matrix elements as follows:

$$\begin{aligned}M_{fi} = {} & \mathrm{i}\omega_{fi}\hat{\boldsymbol{\varepsilon}}\sum_{l_1,l_2,m}\langle c_{l_1,m_1} Y_{l_1}^{m_1}(\theta,\varphi)|\mathbf{r}|b_{l_2,0} \\ & \times D^{l_2}_{m_2,0}(\alpha,\beta,\gamma) Y_{l_2}^{m_2}(\theta,\varphi)\rangle.\end{aligned} \tag{10}$$

The matrix elements were evaluated numerically by using Gauss quadratures and Simpson's method for the involved integrals. The total cross section was found after averaging over the molecular orientation and integrating over the ejected electron's polar angles of the differential cross section σ given by (1)

$$\sigma_{\mathrm{total}} = \frac{1}{4\pi}\int \mathrm{d}\hat{\mathbf{R}}_0 \int \mathrm{d}\hat{\mathbf{k}}\sigma. \tag{11}$$

3. Results and discussion

The polar graphs on Fig. 1 represent the differential cross sections for the photoionization of the hydrogen molecule for different photon energies and for fixed molecular orientation, if the molecular axis is parallel to the polarization vector. Our results using 2C and 2CA wavefunctions in length and velocity gauge are represented along the random phase approximation (RPA) results of Semenov and Cherepkov (2003), our previous results for plane waves (Nagy et al., 2004) in velocity and length gauge, and a few available experimental data (Hirosika and Eland, 2003). At low photon energies all the results are in good agreement with each other (all the curves are identical on Fig. 1a), length and velocity gauges lead to the same angular distribution, which is a typical dipole one.

It is not shown, but the angular distribution is not sensible to the used method in the case of the perpendicular orientation of the molecular axis to the polarization vector, for all energies. In this case interference effects are negligible.

Interference effects become important in case of the parallel orientation, at higher photon energies, around 80 eV. In this case the plane waves in different gauges lead to different angular distribution. (Results should be gauge-independent for exact wavefunctions.) This gauge dependence of angular distribution is reduced by the use of two-center wavefunctions. The 2C and 2CA wavefunctions at this photon energies lead to different angular distribution, but both are less gauge dependent than plane waves. Here is also a disagreement between our and RPA results. The cause of this disagreement is, that interference effects cause a very low minimum (in the cross section as a function of photon energy) for parallel ejection, but in different models this minimum is located at different energies.

On Fig. 2 we show the polar graphs of the contributions of different partial waves to the differential cross sections for the two significant photoionization channels ($0 \rightarrow 1$ and $2 \rightarrow 3$—the numbers are the orbital quantum numbers of the initial and final partial waves, respectively, see Eqs. (8) and (9)), and for various photon energies. There is

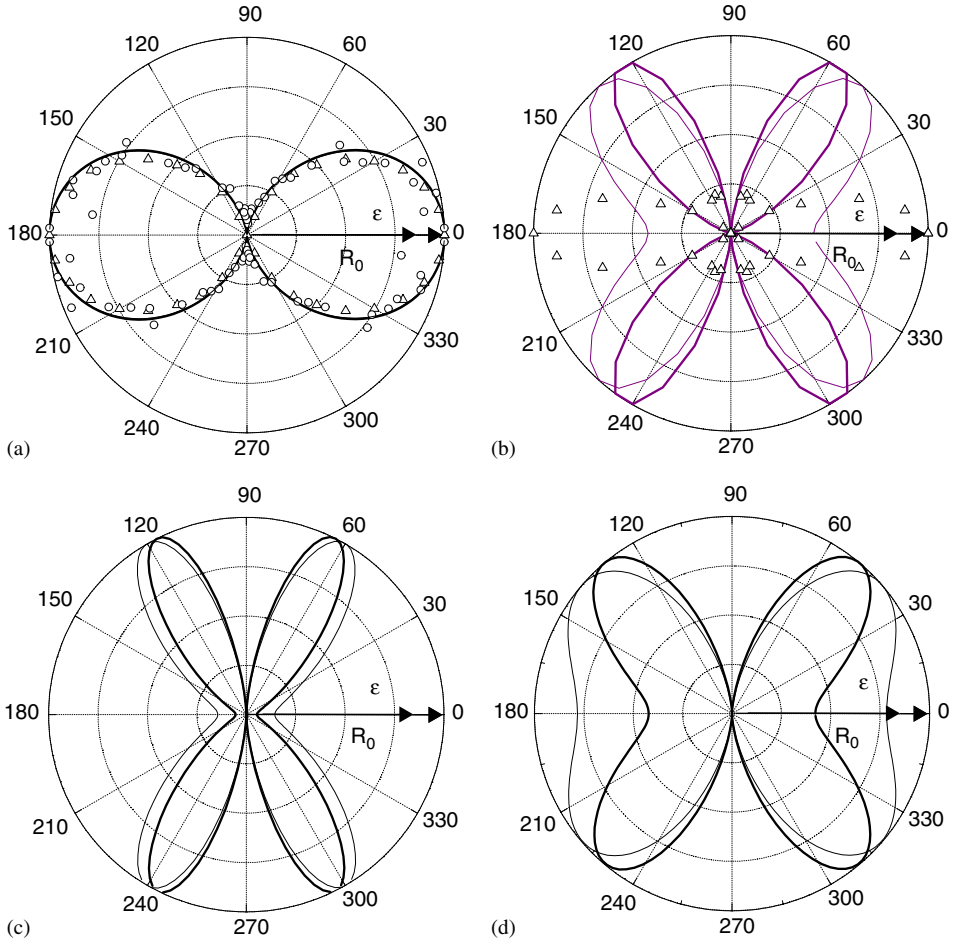

Fig. 1. Polar representation of the differential photoionization cross section of H_2, if the molecular axis is parallel to the polarization vector, for 21.1 eV (a) and 82.4 eV (b–d) photon energies. Cross sections are normalized to the maximum value. Open triangles—RPA results of Semenov and Cherepkov (2003), open circles—experimental data (Hirosika and Eland, 2003), Solid lines represent our calculations, using plane waves (a,b), 2CA (c) and 2C (d) approximations. The results in velocity gauge are represented by thick lines, while in length gauge by thin lines.

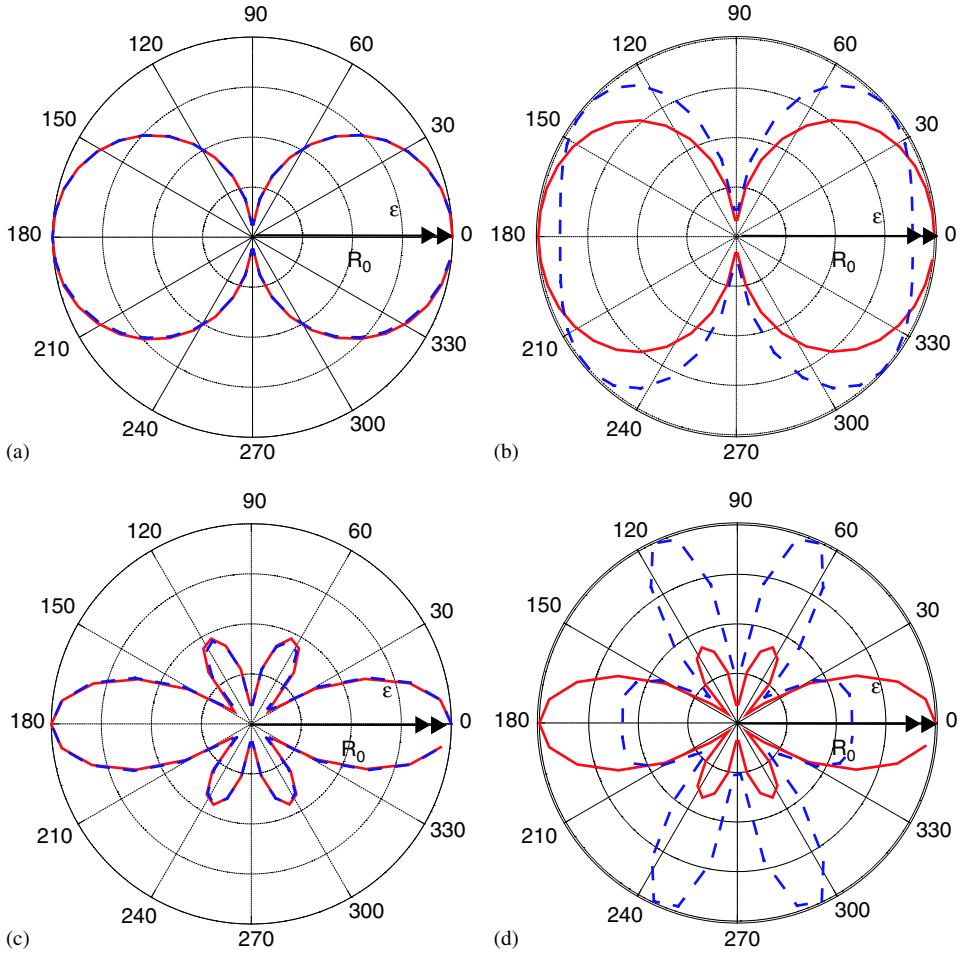

Fig. 2. Polar representation of the differential photoionization cross section of the H_2 for the molecular axis parallel to the polarization vector, for channels $0 \rightarrow 1$ (a, b) and $2 \rightarrow 3$ (c, d), while the photon energy is 21.1 eV (a, c) or 82.4 eV (b, d). Cross sections are normalized to the maximum value. Solid line—2C wavefunction length gauge, dashed line—2CA wavefunction length gauge.

for each partial photoionization channel a characteristic angular distribution, for channel $0 \rightarrow 1$ a p type, while for channel $2 \rightarrow 3$ an f type. The shape of angular distribution for a given channel varies very slow with the increasing photon energy, especially the 2C.

Fig. 3 shows the contribution of different partial waves to the differential cross section as a function of ejected electron momentum. Only channels $0 \rightarrow 1$ and $2 \rightarrow 3$ have significant influence on the value of the cross section. In the investigated energy region the contribution of channel $2 \rightarrow 1$ is negligible. Evidence of interference in the channels and between channels could be observed. For $k = 4$ the cross section has a very deep minimum, while partial channels have only smooth minima. The deep minimum forms because the two significant partial waves at this value of the momentum interferes destructively. This interesting feature is more visible when using 2C wavefunctions.

The total photoionization cross section (see Eq. (11)) was evaluated by Monte Carlo integration and the results are presented in Fig. 4. Our theoretical cross sections for 2C and 2CA wavefunctions with and without screening in velocity gauge are represented along the experimental data

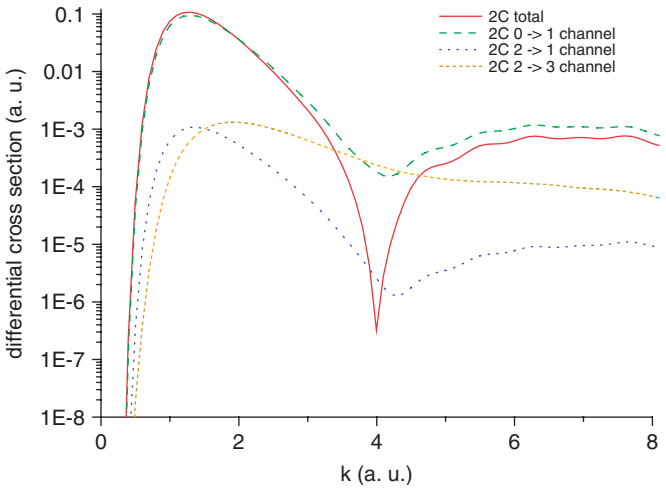

Fig. 3. Differential photoionization cross section for different channels as a function of the momentum of the ejected electron, for the molecular axis parallel to the polarization vector.

of Samson and Haddad (1994) with the theoretical results of Fojón et al. (2004) and our previous results obtained with plane waves (Nagy et al., 2004). For the total cross

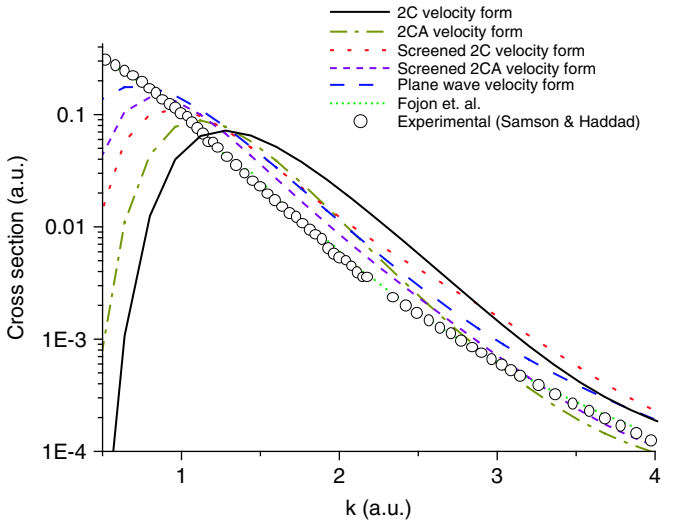

Fig. 4. Total photoionization cross sections as a function of the momentum of the outgoing electron.

section by the use of two-center but unscreened wavefunctions we get worse results than in case of plane waves. This tendency appears because in this approximation the electron–electron interaction is neglected and the nucleus–electron interaction is overestimated. By the introduction of the screening effect caused by the other electron, a significant improvement was obtained, and there is a reasonably good agreement between our screened 2CA result in velocity gauge and experimental data. The results presented on the previous figures, because of the better quality of the method, are those obtained with the screened wavefunctions. The screening effect was described by the trial function (7), where the shape-parameters were set to $r_h = 1.9$ a.u. and $c = 0.2$ a.u. values. In spite of this important improvement there is a significant difference between our results and experimental data at low electron velocities. Moreover, the absolute value of the cross sections show a significant gauge dependence. Fojón et al. (2004) has obtained results in very good agreement with the experiment, because they have used more sophisticated wavefunctions.

4. Conclusions

Interference effects caused by the two-center character of the target in the photoionization of hydrogen molecule have been studied. We have completed our previous calculations (Nagy et al., 2004) by taking into account the two-center character of the final state. By the two used models the previously observed gauge dependence of angular distribution of ejected electron has been reduced. It is obvious the different angular distributions of the photoelectrons relative to atomic case, when the molecular axis is parallel with the polarization vector. A partial wave analysis has been also performed, and interference between different partial waves has been investigated. We have also calculated total ionization cross sections. We have obtained results in reasonable agreement with the experiment only, if the screening effect has been taken into account. Better agreement with the experiment may be obtained only by the use of more sophisticated wavefunction. The strength of our method is simplicity, and the possibility of interpretation of interference effects.

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