Coherent electron emission for dissociative ionization of molecular hydrogen by electron impact

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Abstract. The single ionization of hydrogen molecules is studied theoretically as a function of the molecular alignment. Within the framework of the two-effective center model, multiple differential cross sections as a function of both electron momenta in the final channel of the reaction, and the internuclear orientation, are computed for both non-dissociative and dissociative final \( \text{H}_2^+ \) states. Preliminary results show that the interference pattern arising from the two-center character of the molecular target changes strongly with the final state of the residual molecular ion.

1. Introduction

In this work, the single ionization of \( \text{H}_2 \) molecules is studied theoretically as a function of the molecular alignment. The interest is focused here on the interference effects arising from the two-center nature of the molecular target. In a previous work [1], molecular transition amplitudes obtained within the framework of a two-effective center (TEC) approximation [2] were shown to be described as an effective one-center contribution modulated by an interference factor similar to the one appearing in Young-type experiments with light. Oscillatory patterns that depend markedly on the molecular orientation were predicted. Also, it was found that interference phenomena may be evident even in the integrated cross sections. It is worth noting that the ionization process was considered there as a pure vertical electronic transition from the ground electronic state (\( ^1\Sigma_g^+ \)) of \( \text{H}_2 \) target to the non-dissociative ground electronic state (\( ^2\Sigma_g^+ \)) of the residual \( \text{H}_2^+ \) [1]. This channel gives the dominant contribution for the electron ionization reaction. The TEC model was successfully used to explain many experimental evidences of interference patterns (see for instance Ref. [3] and references therein). It is worthy to mention that molecules were in general randomly oriented in those experiments.

Only recently, Senftleben and co-workers [4] presented experimental 5-fold differential cross sections (5DCS’s) in coplanar geometry of electron impact ionization of hydrogen molecules as a function of the molecular orientation. Indeed, dissociative ionization of the molecular target was considered in order to define the alignment of the internuclear axis. Under those conditions, it was found that experimental cross sections corresponding to molecules oriented along the momentum transfer direction are larger than the ones for molecular alignment perpendicular to the momentum transfer. Moreover, they showed that calculated triply differential cross sections of ionization of \( \text{He} \) targets multiplied by the interference factor predicted by Ref. [1] to the case of final non-dissociative state, exhibit the opposite behavior.
In the present work, single ionization of hydrogen molecules by the impact of fast electrons is studied for both non-dissociative gerade and dissociative ungerade final H$_2^+$ states. 5DCS’s in coplanar geometry as a function of the scattered and the ejected electron momenta, and of the internuclear orientation are computed by using the first-order TEC approximation. Interference effects due to the coherent electron emission from the molecular target are explored. Particular attention is paid to the influence of the final state of the residual H$_2^+$ molecular ion.

Atomic units will be used except where otherwise stated.

2. Theory

The reaction of interest is the electron-impact ionization of H$_2$ molecular targets, namely,

$$e^- + H_2^{(1\Sigma_g^+)} \rightarrow 2e^- + H_2^+(2\Sigma^\pm_{g,u})$$

The ionization process may be considered as a pure electronic transition by applying closure relations over all possible final rotational and vibrational states of the residual target [5, 6]. At the energies involved in this work, the molecule can be considered as frozen during all the reaction. As a consequence, only vertical transitions from the ground electronic state of the target to the specific final electronic state of the H$_2^+$ molecule are assumed. Also, exchange effects in the collision dynamics are disregarded in the present calculations.

The 5DCS in coplanar geometry is given then by the following expression [1]:

$$\sigma^{(5)} = \frac{d^5\sigma}{d\Omega_p d\Omega_e d\Omega_s d(k_e^2/2)} \approx 2(2\pi)^4 \frac{k_e k_s}{k_i} |t_{fi}(\rho_0)|^2$$

where the emitted electron is ejected with momentum $k_e$ into the differential solid angle $\Omega_e$ with respect to the incidence direction, and the projectile is scattered with momentum $k_s$ into the solid angle $\Omega_s$. The incidence direction is defined by the wave vector $k_i$ of the incident electron. In equation (2), $\rho_0$ denotes the equilibrium internuclear vector of the molecular target and $\Omega_p$, the corresponding solid angle.

The prior version of the transition matrix element reads

$$t_{fi}(\rho_0) = \langle \Psi_i^- (\rho_0, R, r_1, r_2) | \frac{1}{r_{1p}} + \frac{1}{r_{2p}} - \frac{Z_T}{R_a} - \frac{Z_T}{R_b} | \Psi_i^+(\rho_0, R, r_1, r_2) \rangle$$

where $\Psi_i^+$ is the non-perturbed electronic wavefunction in the initial channel and $\Psi_i^-$ is the final wavefunction, both satisfying the proper asymptotic boundary conditions. $Z_T = 1$ represents the charge of the molecular nuclei. Coordinates are illustrated in Fig. 1.
The initial wavefunction $\Psi_i^+$ is represented as

$$\Psi_i^+ = \frac{e^{ik_i R}}{(2\pi)^{3/2}} \Phi_i(\rho_0, r_1, r_2)$$  \hspace{1cm} (4)$$

where $\Phi_i$ is the initial molecular bound state described here by a simple Heitler-London type wavefunction [7],

$$\Phi_i(\rho_0, r_1, r_2) = N_{\text{HL}}(\rho_0) \{e^{-\beta_{1a}r_1} e^{-\beta_{2b}r_2} + e^{-\beta_{1b}r_1} e^{-\beta_{2a}r_2}\}$$  \hspace{1cm} (5)$$

with $\beta = 1.166$, $\rho_0 = 1.406$ and $N_{\text{HL}}$ the normalization function.

The final-state wavefunction is approximated as,

$$\Psi_f^- \simeq \frac{e^{ik_e R}}{(2\pi)^{3/2}} \Phi_{g,u}(\rho_0, r_2) \xi_e(k_e, r_1)$$  \hspace{1cm} (6)$$

where $\Phi_{g,u}$ represents the wavefunction corresponding to the gerade $^2\Sigma_{g}^+$ (ungerade $^2\Sigma_{u}^-$) state of the residual H$_2^+$ molecular ion. In the calculations, the wavefunctions $\Phi_{g,u}$ are represented by a simple linear combination of atomic orbitals

$$\Phi_{g,u}(\rho_0, r_2) = N_{g,u}(\rho_0) \{e^{-\alpha r_2a} \pm e^{-\alpha r_2b}\}$$  \hspace{1cm} (7)$$

with $N_{g,u}(\rho_0)$ the corresponding normalization factor and $\alpha = 1.3918$ the variational parameter.

In the first-order TEC model [2], the final continuum wavefunction $\xi_e$ is taken as

$$\xi_e(k_e, r_1) = \frac{e^{ik_e r_1}}{(2\pi)^{3/2}} C(k_e, r_{1j}, \gamma_e)$$  \hspace{1cm} (8)$$

where $j = a$ or $b$ indicates the center from which the target electron is ionized, $\gamma_e = -Z_T/k_e$ is the corresponding Sommerfeld parameter, and the Coulomb factor $C(k, r, \gamma)$ is given by

$$C(k, r, \gamma) = \Gamma(1 - i\gamma) \ e^{-\pi\gamma/2} _1F_1[i\gamma; 1; -i(kr + kr)]$$  \hspace{1cm} (9)$$

In preceding equations, it is assumed that electron 1 is ionized from the center labelled $j$ while the passive electron is supposed to screen completely the charge of the other nucleus from which ionization is not produced. This is the main assumption made in the TEC approximation. The exchange with electron 2 is taken into account by means of the factor 2 included in equation (2).

Using equations (4)-(9), the transition matrix element $t_\theta$ of equation (3) can be written as a sum of direct and indirect terms as follows,

$$t_\theta(\rho_0) = \frac{1}{(2\pi)^{9/2}} N N_{g,u}(\rho_0) N_{\text{HL}}(\rho_0) \sum_{j,l} (t_{j,l}^{\text{dir}} + t_{j,l}^{\text{ind}}) \hspace{1cm} j, l = a, b$$  \hspace{1cm} (10)$$

where

$$t_{j,l}^{\text{dir}} = \langle e^{ik_e r_1} _1F_1[i\gamma_e; 1; -i(k_e r_{1j} + k_e r_{1l})] (e^{-\alpha r_2j} \pm e^{-\alpha r_2l}) | \left( \frac{1}{R_{1p}} - \frac{1}{R_{j}} \right) | e^{iK.R} e^{-\beta r_{1j}} e^{-\beta r_{2l}} \rangle$$  \hspace{1cm} (11)$$
and

\[
\begin{align*}
\tau_{j,l}^{\text{ind}} &= \left< e^{iK \cdot r_i} F_1 \left[ \Gamma_{e}; 1; -i(k_e r_{1j} + k_e r_{1l}) \right] \left( e^{-\alpha r_{2j}} \pm e^{-\alpha r_{2l}} \right) \right> \\
&= e^{iKR} e^{-\beta r_{1j}} e^{-\beta r_{2j}}
\end{align*}
\]

(12)

Here, \( K = k_e - k_s \) is the momentum transfer and \( N = \Gamma(1-i\gamma_e) e^{-\pi\gamma_e/2} \). The direct and indirect terms can be interpreted as follows [8]. The direct terms describe ionization of electron 1 from center \( j = a \) (or \( b \)) by means of the interaction of the projectile with this electron and with center \( j \). The indirect terms consider also that the electron 1 is ionized from center \( j \) but not through the interaction of the projectile with the passive electron and with the other center labelled \( l \neq j \). As stated in Ref. [8], electrons are shared by both nuclei in the molecule but matrix elements allow this interpretation.

In the case in which the contribution of the indirect terms (12) may be neglected, the 5DCS given by equation (2) reduces to the approximate expression [1],

\[
\sigma_{g,u}^{(3)} \simeq 2 \left[ 1 \pm \cos(\chi \cdot \rho_0) \right] \sigma_{g,u}^{(3)}
\]

(13)

which depends on the symmetry of the \( H_2^+ \) final state, \( \chi = k_e - K \) and the internuclear vector \( \rho_0 \).

In equation (13), \( \sigma_{g,u}^{(3)} \) represents a one-center differential cross section corresponding to effective atoms placed at the position of either molecular nuclei [1]. Therefore, when the indirect terms are negligible, the interference pattern due to coherent emission from both molecular centers appears explicitly in the 5DCSs expression, and can be closely related with the one appearing in Young’s double-slit experiments. This latter can be considered in fact as one of the main virtues of the TEC model.

3. Results

In figure 2, TEC differential cross sections (thick lines) of ionization of \( H_2 \) molecules are presented as a function of the emitted angle \( \theta_e \) for the case of transitions to the \( gerade \) ground state of the residual \( H_2^+ \) molecular ion. These calculations are obtained by using the full transition matrix element given by equation (10). Three particular cases corresponding to molecules aligned at 0° (dotted lines), 45° (dashed lines) and 90° (full lines) relative to the momentum transfer direction are considered in the figure. The impact and emission energies are \( E_i = 4087 \) eV and \( E_e = 100 \) eV, respectively, whereas the scattering angle is fixed at angle \( \theta_e = -1^\circ \). This high energy regime is similar to the one analyzed in [1]. Approximate 5DCS’s obtained from equation (13) for \( gerade \) final \( H_2^+ \) state are also included in figure 2 (thin lines). At the energies considered here, differential cross sections are only slightly modified by neglecting the indirect terms contribution in the transition matrix element.

Interference patterns coming from the coherent electron emission from the different scattering centers in the molecule are observed in figure 2. As pointed out previously [1], particular regions in which the electron emission is more likely to happen are revealed in the figure. This behavior comes from the combined contribution of the interference factor \( 1 + \cos(\chi \cdot \rho_0) \) and the differential cross section corresponding to effective atoms placed at the position of each nucleus. A strong dependence on the internuclear vector of the 5DCS’s is observed also in figure 2. Hence, differential cross sections corresponding to molecules oriented parallel to the momentum transfer are lower than the ones obtained for molecules aligned in the perpendicular direction. This is the opposite behavior to that observed in recent measurements for the case of dissociative ionization [4].

Surprisingly, in the case of molecules oriented in the \( K \) direction, suppression of the binary peak is observed in figure 2. This is a really unexpected behavior because this direction is
Figure 2. 5DCS’s as a function of the ejection angle $\theta_e$ for H$_2$ molecules oriented at angles of 0° (dotted lines), 45° (dashed lines) and 90° (full lines) relative to the momentum transfer direction $\mathbf{K}$ with polar angle $\theta_K$. The results correspond to final gerade state of the residual H$_2^+$ molecular ion. The impact energy is $E_i = 4087$ eV, the emission energy is $E_e = 100$ eV and the scattering angle is $\theta_s = -1^\circ$. The positive orientation for the polar angles is taken clockwise. Thick lines, full TEC model. Thin lines: approximate TEC model obtained by neglecting indirect contributions (see text).

precisely the more favorable classical one for the electron emission. This effect comes from the interference factor which predicts total destructive interference when the condition $\chi \cdot \mathbf{p}_0 = l\pi$ is reached for some odd $l$ value. For the kinematical arrangement of figure 2, it can be shown easily that $k_e \sim \pi / \rho_0 + \mathbf{K}$ for $\theta_e = \theta_K$. This result can be related to the one obtained by Fernández and co-workers [9] for photoionization of H$_2$ molecules. In this case and when the molecule is aligned parallel to the polarization vector of the incidence radiation, no photoelectrons are emitted under certain similar conditions.

In figure 3, molecular TEC 5DCS’s as a function of the emitted electron angle are presented for the particular case in which the final state of the residual H$_2^+$ molecule corresponds to the $^2\Sigma_{u}^{-}$ state. The kinematical conditions here are the same as the ones considered in figure 2. In this case, the indirect terms are more important than in the case of the gerade H$_2^+$ final state. In particular, this contribution seems to be more important for the case of $\theta_e = \theta_K$. Also from figure 3, it can be seen that differential cross sections at different molecular orientations are reversed in order compared to the cases studied in the preceding figure. Therefore, cross sections for parallel alignment are in general greater than the ones for the perpendicular direction, in a similar way to that obtained in Ref. [4]. This difference in the relative order of the cross sections with the gerade state comes from the electronic distribution of the ungerade state. Moreover, this provokes the supression of both the binary and recoil peaks in the case of $\theta_e = \theta_K - 90^\circ$ because the ungerade state has a nodal plane at those directions.

4. Conclusions

To sum up, 5DCS’s of single ionization of H$_2$ molecules as a function of both electron momenta in the final channel of the reaction, and the internuclear orientation, were computed for both non-dissociative and dissociative final H$_2^+$ states within the two-effective center approximation. The
inclusion of indirect terms barely affects previous calculations [1] for the *gerade* state in which they were neglected. In contrast, some influences may appear for the *ungerade* state studied in this work. Present results at high enough impact energy show that the interference pattern changes strongly with the final state of the residual molecular ion. Moreover, interesting features are observed at the binary and recoil peaks for certain conditions. More elaborated results on this matter will be published soon elsewhere.

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