

Electronic correlation in the ionization of molecular hydrogen

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(Received 27 May 1994)

Cross sections for double ionization and ionization plus excitation of H₂ by high-energy charged particles are calculated as a function of the orientation of the H₂ internuclear axis. The contributions of the double collision, the shake-off or shake-up, and ground-state correlation mechanisms have been considered. The calculated cross sections have been compared with the data of Edwards *et al.* [Phys. Rev. A **42**, 1367 (1990); **44**, 797 (1991); **46**, 6970 (1992)]. Our results for double ionizations are acceptable, while the ionization-excitation cross sections have a strong dependence on the bound-state and continuum-state wave functions.

PACS number(s): 34.50.Gb, 34.90.+q

I. INTRODUCTION

Several experimental and theoretical investigations of the two-electron processes in electronic or ionic collisions have been performed; see Refs. [1, 2]. The accurate calculation of the cross sections requires a great effort even for the most simple two-electron target, the He atom [3]. In order to simplify the treatment of the many-body system one can use many-body perturbation theory and approximate the complex interactions in terms of some simple ones. Concerning the two-electron processes, they can be described by the following mechanisms [4, 5]: (a) double collision or TS2, considering two independent projectile-electron interactions with no electronic correlation involved; (b) shake-off and shake-up, when a single projectile-electron interaction is followed by an electron-hole interaction; (c) ground-state correlation, if the single projectile-electron interaction is preceded by an electron-electron interaction; and (d) TS1 where the projectile-electron interaction is followed by an electron-electron interaction. In cases (b) and (c) correlation is included in the final and initial asymptotic wave functions, respectively, so they can be termed as static correlations. In case (d) we have scattering correlation [4]. Except for the TS1, the transition amplitudes corresponding to the mechanisms above can be expressed in terms of single-electron amplitudes.

Cross sections for two-electron processes that occur during collisions of fast charged projectiles with H₂ were recently reported by Edwards *et al.* [5, 6]. These processes included double ionization, single ionization plus excitation, and double excitation. The production of these dissociative states were analyzed at specified angles of the molecular axis relative to the beam direction. Our aim is to reproduce these data by theoretical calculations.

The contribution of the double collision mechanism was investigated in our paper [7]. In the present work

we take into account the contribution of the shake-off, shake-up, and ground-state correlation mechanisms. We study the relative importance of these mechanisms in the different processes. Since our previous studies revealed a strong dependence of the ionization-excitation cross sections on the applied wave functions, more realistic initial-state and final-state wave functions are used.

II. THEORY

For the calculation of the cross sections we have used the semiclassical approximation, assuming a straight-line trajectory for the projectile. The probability amplitude of the transition from the initial state to the final state for the impact parameter \mathbf{B} is [4]

$$a(\mathbf{B}) = \langle \psi_f(\mathbf{r}_1, \mathbf{r}_2) | U(-\infty, +\infty) | \psi_i(\mathbf{r}_1, \mathbf{r}_2) \rangle. \quad (1)$$

The origin of the coordinate system is taken at the center of the molecule and the z axis is along the projectile trajectory. $U(-\infty, +\infty)$ is the evolution operator between the initial and the final state of the two electrons with coordinates \mathbf{r}_1 and \mathbf{r}_2 .

The initial-state two-electron wave function is constructed as a linear combination of several configurations as

$$\psi_i(\mathbf{r}_1, \mathbf{r}_2) = \sum_j c_j \phi_j(\mathbf{r}_1) \phi_j(\mathbf{r}_2). \quad (2)$$

The coefficients c_j are obtained by the diagonalization of the Hamiltonian matrix. The consideration of the configuration interaction corresponds to the inclusion of the ground-state correlation mechanism. We have applied the wave function of Hagstrom and Shull [8] and a second one constructed in a similar form. In our calculations only the four most important configurations are included

$$\psi_i = c_1(1\sigma_g)^2 + c_2(1\sigma_u)^2 + c_3(1\pi_u)^2 + c_4(2\sigma_g)^2. \quad (3)$$

The final-state wave function is taken as a product of one-electron wave functions

$$\psi_f = \phi_f(\mathbf{r}_1) \phi_f(\mathbf{r}_2). \quad (4)$$

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In order to obtain the probability amplitude for the double collision (TS2) mechanism, we use the independent-electron approximation. Then neglecting electron-electron correlations, the evolution operator reduces to a product of single-electron evolution operators [4]

$$U(-\infty, +\infty) = U_1(-\infty, +\infty)U_2(-\infty, +\infty) \quad (5)$$

and the TS2 amplitude can be written as

$$a(\mathbf{B})_{\text{TS2}} = \sum_j c_j \langle \phi_f(\mathbf{r}_1) | U_1(-\infty, +\infty) | \phi_j(\mathbf{r}_1) \rangle \\ \times \langle \phi_f(\mathbf{r}_2) | U_2(-\infty, +\infty) | \phi_j(\mathbf{r}_2) \rangle. \quad (6)$$

The amplitudes calculated with different configurations have the same magnitude, but the weight factors c_2 , c_3 , and c_4 are negligible and $c_1 \approx 1$. Therefore in calculating the double-collision cross sections we take into account only the basic configuration

$$a(\mathbf{B})_{\text{TS2}} = \langle \phi_f(\mathbf{r}_1) | U_1(-\infty, +\infty) | \phi_1(\mathbf{r}_1) \rangle \\ \times \langle \phi_f(\mathbf{r}_2) | U_2(-\infty, +\infty) | \phi_1(\mathbf{r}_2) \rangle. \quad (7)$$

Assuming a single projectile-electron interaction and taking into account only static correlation, which is included in the asymptotic wave functions, the evolution operator reduces to a single-electron one

$$U(-\infty, +\infty) = U_1(-\infty, +\infty). \quad (8)$$

The probability amplitude due to the static correlations, which include the shake-off or shake-up and the ground state correlation mechanisms, can be expressed by a sum of products of single-electron amplitudes and overlap integrals between initial and final wave functions

$$a(\mathbf{B})_{\text{ST}} = \sum_j c_j \langle \phi_f(\mathbf{r}_1) | U_1(-\infty, +\infty) | \phi_j(\mathbf{r}_1) \rangle \\ \times \langle \phi_f(\mathbf{r}_2) | \phi_j(\mathbf{r}_2) \rangle. \quad (9)$$

In order to calculate the one-electron amplitudes we apply first-order time-dependent perturbation theory

$$a_i(\mathbf{B}) = -\frac{i}{v} \int_{-\infty}^{+\infty} dz_i \exp\left(i\frac{\Delta E}{v}z_i\right) \\ \times \langle \phi_f(\mathbf{r}_i) | V(\mathbf{r}_i - \mathbf{R}_i) | \phi_j(\mathbf{r}_i) \rangle, \quad (10)$$

where we integrate along the projectile trajectory. ΔE is the energy transfer, v the projectile velocity, and $V(\mathbf{r}_i - \mathbf{R}_i)$ the Coulomb potential between the electron i and the projectile in position \mathbf{R}_i .

In the calculation of the cross section for a given process one has to square the sum of the amplitudes

$$\sigma \sim |a_{\text{TS2}} + a_{\text{ST}}|^2. \quad (11)$$

For the mechanisms studied it can be easily shown that if the TS2 amplitude is real then the static correlation amplitude is imaginary and vice versa. Thus we do not obtain an interference term which could depend on the sign of the projectile charge Z_p and we cannot explain the difference in experimental data for positively and negatively charged particle impact. In the absence of this interference term the total cross section is simply the sum

of the TS2 and static correlation cross sections and this is the same for positive and negative projectiles.

The explanation for this imperfection is that we have neglected time-ordering effects [9, 10]. In the expression of the evolution operator [4], the time-ordering operator which plays a role in the calculation of the second-order (TS2) amplitude occurs. McGuire and Straton [9] and Stolterfoht [10] have shown that including time-ordering leads to interference between first-order and second-order processes.

A. Double ionization

In calculation of the cross sections for double ionization we take into account only the basic configuration of the ground-state wave function and so it can be written as a product wave function. The calculation of the TS2 amplitude for double ionization was described in our previous paper [7]. The only change is in the use of a more realistic ground-state wave function. As can be seen from Eq. (7), the TS2 amplitude in this case is a product of one-electron amplitudes.

The shake-off amplitude from (9) for the \mathbf{k}_1 and \mathbf{k}_2 momenta of the outgoing electrons and the $\hat{\mathbf{R}}_0$ orientation of the molecular axis is

$$a(\mathbf{B}, \mathbf{k}_1, \mathbf{k}_2, \hat{\mathbf{R}}_0)_{\text{SO}} = \langle \phi_{\mathbf{k}_1}(\mathbf{r}_1) | U_1(-\infty, +\infty) | 1\sigma_g(\mathbf{r}_1) \rangle \\ \times \langle \phi_{\mathbf{k}_2}(\mathbf{r}_2) | 1\sigma_g(\mathbf{r}_2) \rangle. \quad (12)$$

The final-state continuum-electron wave function is expanded in partial-wave series

$$\phi_{\mathbf{k}_i}(\mathbf{r}_i) = \sum_{l_f} i^{l_f} \exp(i\sigma_{l_f}) R_{l_f}(k_i r_i) \\ \times \sum_{m_f} Y_{l_f m_f}(\hat{\mathbf{k}}_i) Y_{l_f m_f}^*(\hat{\mathbf{r}}_i). \quad (13)$$

As in our earlier papers [7, 11], the radial wave function $R_{l_f}(k_i r_i)$ is approximated as

$$R_{l_f}(k_i r_i) = \sqrt{\frac{2}{\pi}} \frac{1}{k_i r_i} F_{l_f} \left(-\frac{Z_{\text{eff}}}{k_i}, k_i r_i \right). \quad (14)$$

The Coulomb function $F_{l_f}(-\frac{Z_{\text{eff}}}{k_i}, k_i r_i)$ describes the motion of an electron in the field of an effective charge Z_{eff} positioned in the center of mass of the two target protons. The two-center initial-state wave function is expanded into series of Legendre polynomials with the angle between the molecular axis and the position vector of the electron in their argument

$$1\sigma_g(\mathbf{r}_1, \hat{\mathbf{R}}_0) = \sum_{l_g} c_{l_g}(r_1) P_{l_g}(\cos(\mathbf{r}_1, \hat{\mathbf{R}}_0)). \quad (15)$$

Writing the Legendre polynomials as a product of spherical harmonics

$$P_{l_g}(\cos(\mathbf{r}_1, \hat{\mathbf{R}}_0)) = \frac{4\pi}{2l_g + 1} \sum_{m_g} Y_{l_g m_g}(\hat{\mathbf{R}}_0) Y_{l_g m_g}^*(\hat{\mathbf{r}}_1), \quad (16)$$

the dependence on the orientation of the molecular axis can be separated. The Coulomb interaction between the projectile and the electron in Eq. (10) is expanded into partial-wave series

$$\frac{1}{|\mathbf{r}_i - \mathbf{R}_i|} = \sum_{l_c} \frac{4\pi}{2l_c + 1} \frac{r_{>}^{l_c}}{r_{<}^{l_c+1}} \sum_{m_c} Y_{l_c m_c}(\hat{\mathbf{R}}_i) Y_{l_c m_c}^*(\hat{\mathbf{r}}_i). \quad (17)$$

Following the steps described in [11] we obtain, for the one-electron amplitude,

$$a(\mathbf{B}, \mathbf{k}_1, \mathbf{R}_0) = \frac{i(4\pi)^{3/2} Z_p}{v} \sum_{l_f l_c l_g} \frac{i^{-l_f} \exp(-i\sigma_{l_f})}{[(2l_f + 1)(2l_c + 1)(2l_g + 1)]^{1/2}} (l_c 0 l_g 0 | l_f 0) \\ \times \sum_{m_f m_c m_g} (l_c m_c l_g m_g | l_f m_f) Y_{l_g m_g}(\hat{\mathbf{R}}_0) Y_{l_f m_f}^*(\hat{\mathbf{k}}_1) \exp(im_c \varphi_B) G_{l_f l_c l_g}^{m_c}(k, B, R_0), \quad (18)$$

where

$$G_{l_f l_c l_g}^{m_c}(k, B, R_0) = \int_{-\infty}^{\infty} dZ \exp\left(i \frac{\Delta E}{v} Z\right) Y_{l_c m_c}(\hat{\mathbf{R}}) \exp(-im_c \varphi_B) \int_0^{\infty} dr_1 r_1^2 R_{l_f}(kr_1) \frac{r_{<}^{l_c}}{r_{>}^{l_c+1}} c_{l_g}(r_1). \quad (19)$$

The overlap integral from (12) can be expressed as

$$\langle \phi_{\mathbf{k}_2}(\mathbf{r}_2) | 1s\sigma_g(\mathbf{r}_2) \rangle = \sum_{L_g} \frac{4\pi i^{-L_g} \exp(-i\sigma_{L_g})}{2L_g + 1} \int dr_2 r_2^2 R_{L_g}(k_2 r_2) c_{L_g}(r_2) \sum_{M_g} Y_{L_g M_g}(\hat{\mathbf{R}}_0) Y_{L_g M_g}^*(\hat{\mathbf{k}}_2). \quad (20)$$

The differential cross section with respect to the orientation of the molecular axis due to the shake-off mechanism can be obtained by squaring the amplitude (12) and integrating over \mathbf{k}_1 , \mathbf{k}_2 , B , and the azimuthal angle of the projectile position φ_B . Carrying out the calculations, the cross section can be expressed as

$$\frac{d\sigma(\mathbf{R}_0, E)_{\text{SO}}^{2+}}{d\mathbf{R}_0} = 2\pi(4\pi)^3 \left(\frac{Z_p}{v}\right)^2 \sum_L A_{L(\text{SO})}^{2+} P_L(\cos \theta_{R_0}), \quad (21)$$

where the Legendre coefficients are

$$A_{L(\text{SO})}^{2+} = \sum_{l_g l'_g L_g} \sum_{l_c l'_c l'_f} (-1)^{l'_g} \frac{(2L + 1)^{1/2}}{(2l_c + 1)^{1/2} (2l'_c + 1) (2L_g + 1)} (l_c 0 l_g 0 | l_f 0) \\ \times (l'_c 0 l'_g 0 | l'_f 0) (l_g 0 l'_g 0 | L 0) \left\{ \begin{matrix} l_g & l'_g & L \\ l'_c & l_c & l_f \end{matrix} \right\} \sum_{m_c} (l_c m_c L 0 | l'_c m_c) \\ \times \int_0^{\infty} B dB \int_0^{\infty} k_1^2 dk_1 G_{l_f l_c l_g}^{m_c}(k_1, B, R_0) G_{l_f l'_c l'_g}^{m_c*}(k_1, B, R_0) \int_0^{\infty} k_2^2 dk_2 \left| \int dr_2 r_2^2 R_{L_g}(k_2 r_2) c_{L_g}(r_2) \right|^2. \quad (22)$$

B. Ionization plus excitation

In calculating the ionization plus excitation cross sections for the excited states of the H_2^+ molecular ion we have used the exact wave functions [12]. We have performed calculations for the $2p\sigma_u$, $2s\sigma_g$, and $2p\pi_u$ excited states. The continuum wave functions are numerically generated by solving the Schrödinger equation in the cylindrical symmetric field of the residual ion. We obtain these continuum wave functions in the angular momentum representation. In this representation the amplitude depends on the ejected electron energy and on orbital and magnetic quantum numbers. The differential cross section dependence on the orientation of the molecular axis has the form

$$\frac{d\sigma(\hat{\mathbf{R}}_0)}{d\hat{\mathbf{R}}_0} = \sum_{LM} \int d\mathbf{B} \int dE |a_{LM}(\mathbf{B}, E, \hat{\mathbf{R}}_0)|^2. \quad (23)$$

Let us take first the probability amplitudes due to the static correlation. If the initial configuration ϕ_j from Eq. (9) is the basic one $1\sigma_g$, the mechanism is the shake-up. If ϕ_j is different from $1\sigma_g$, the mechanism of the ionization-excitation corresponds to the ground-state correlation.

In the case of the excitation of the $2p\sigma_u$ and $2p\pi_u$ states the $\langle \phi_f | 1\sigma_g \rangle$ overlap integral is vanishing, so there is no shake-up to these states. We obtain a transition amplitude as a contribution of the ground-state correlation mechanism

$$a(\mathbf{B}, E)_{GC}^{LM} = c_j \langle \phi_{LM}(E, \mathbf{r}_1) | U_1(-\infty, +\infty) | \phi_j(\mathbf{r}_1) \rangle \\ \times \langle \phi_f(\mathbf{r}_2) | \phi_j(\mathbf{r}_2) \rangle. \quad (24)$$

If the final excited state is $2p\sigma_u$, this can be produced if ϕ_j is $1\sigma_u$. For the excitation of $2p\pi_u$ the proper initial configuration is $1\pi_u$. The overlap integral between these initial and final states is rather large.

For the excitation of the $2s\sigma_g$ state we get two nonzero terms

$$a(\mathbf{B}, E)_{ST}^{LM} = c_1 \langle \phi_{LM}(E, \mathbf{r}_1) | U_1(-\infty, +\infty) | 1\sigma_g(\mathbf{r}_1) \rangle \\ \times \langle 2s\sigma_g(\mathbf{r}_2) | 1\sigma_g(\mathbf{r}_2) \rangle \\ + c_4 \langle \phi_{LM}(E, \mathbf{r}_1) | U_1(-\infty, +\infty) | 2\sigma_g(\mathbf{r}_1) \rangle \\ \times \langle 2s\sigma_g(\mathbf{r}_2) | 2\sigma_g(\mathbf{r}_2) \rangle. \quad (25)$$

The first term represents shake-up amplitude and the second term is due to ground-state correlation.

The overlap integrals in these formulas can be easily calculated. Let us concentrate upon the one-electron ionization amplitudes. In the expression (10) the Coulomb interaction is expanded like in Eq. (17). In the initial-state and final-state wave functions we separate the complex phase factor of the φ dependence

$$\phi_j(\mathbf{r}_1) = \phi_j(r_1, \theta'_1) e^{im_j \varphi'_1}, \quad (26)$$

$$\phi_{LM}(E, \mathbf{r}_1) = \phi_{LM}(E, r_1, \theta'_1) e^{iM\varphi'_1}, \quad (27)$$

where the primed angles are in the molecular frame. m_j is ± 1 for the $2\pi_u$ configuration and zero for the others. The r - and θ -dependent parts of the wave functions are expanded like in Eq. (15) into terms of Legendre series and the Legendre polynomials are written like a product of spherical harmonics

$$\phi_j(r_1, \theta'_1) \phi_{LM}(E, r_1, \theta'_1) \\ = \sum_{l_g} \frac{4\pi}{2l_g + 1} b_{l_g}^{LM}(E, r_1) \sum_{m_g} Y_{l_g, m_g}(\hat{\mathbf{r}}_1) Y_{l_g, m_g}^*(\hat{\mathbf{R}}_0). \quad (28)$$

The dependence on the orientation of the molecular axis $\hat{\mathbf{R}}_0$ occurs because θ'_1 is in the molecular frame and $\hat{\mathbf{r}}_1$ is in the laboratory frame, where the z axis is along the projectile trajectory. By integrating over \mathbf{r}_1 in the matrix element from Eq. (10) we transfer φ'_1 into the laboratory frame. We rotate the frame by θ , the angle between the molecular axis and the projectile trajectory

$$\cot \varphi'_1 = \cot \varphi_1 \cos \theta - \frac{\cos \theta_1 \sin \theta}{\sin \varphi_1}. \quad (29)$$

By integrating the matrix element over the angles we introduce the notation

$$J_{l_g, m_g, l_c, m_c, m_j, M}(\theta) = \int_0^{2\pi} d\varphi_1 \int_{-\pi/2}^{\pi/2} d\theta_1 \sin(\theta_1) Y_{l_g, m_g}(\theta_1, \varphi_1) Y_{l_c, m_c}^*(\theta_1, \varphi_1) e^{i(m_j - M)\varphi'_1} \quad (30)$$

and we obtain

$$\left\langle \phi_{LM}(E, \mathbf{r}_1) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} \right| \phi_j(\mathbf{r}_1) \right\rangle = \sum_{l_g, l_c} \frac{(4\pi)^2}{(2l_g + 1)(2l_c + 1)} \int_0^\infty dr_1 r_1^2 b_{l_g}^{LM}(E, r_1) \frac{r_1^{l_c}}{r_1^{l_c+1}} \sum_{m_g, m_c} J_{l_g, m_g, l_c, m_c, m_j, M}(\theta) \\ \times Y_{l_c, m_c}(\hat{\mathbf{R}}_0) Y_{l_g, m_g}^*(\hat{\mathbf{R}}_0), \quad (31)$$

where the coefficients $b_{l_g}^{LM}$ are defined by the expansion (28). After these transformations we can easily express the one-electron amplitude

$$a_1^{LM}(\mathbf{B}, E, \hat{\mathbf{R}}_0) = \frac{iZ_p}{v} \sum_{l_g, l_c} \frac{(4\pi)^2}{(2l_g + 1)(2l_c + 1)} \sum_{m_g, m_c} B_{l_g, l_c, LM}^{m_c}(B, E) e^{im_c \varphi_B} J_{l_g, m_g, l_c, m_c, m_j, M}(\theta) Y_{l_g, m_g}^*(\hat{\mathbf{R}}_0), \quad (32)$$

where

$$B_{l_g, l_c, LM}^{m_c}(B, E) = \int_{-\infty}^{+\infty} dz_1 \exp\left(i \frac{\Delta E}{v} z_1\right) Y_{l_c, m_c}(\hat{\mathbf{R}}_1) e^{-im_c \varphi_B} \int_0^\infty dr_1 r_1^2 \frac{r_1^{l_c}}{r_1^{l_c+1}} b_{l_g}^{LM}(E, r_1). \quad (33)$$

Squaring the amplitude and integrating over φ_B for the dependence on $\hat{\mathbf{R}}_0$ we get

$$\int_0^{2\pi} d\varphi_B |a_1^{LM}(\mathbf{B}, E, \hat{\mathbf{R}}_0)|^2 = 2\pi (4\pi)^3 \frac{Z_p^2}{v^2} \sum_{l_g, l'_g, L_0} \sum_{l_c, l'_c} \frac{1}{(2l_c + 1)(2l'_c + 1) \sqrt{(2l_g + 1)(2l'_g + 1)}} \\ \times (l_g 0 l'_g 0 | L_0) \sum_{m_g, m'_g} (-1)^{m_g} (l_g m_g l'_g - m_g | L_0) B_{l_g, l_c, LM}^{m_c}(B, E) B_{l'_g, l'_c, LM}^{m'_c}(B, E) \\ \times J_{l_g, m_g, l_c, m_c, m_j, M}(\theta) J_{l'_g, m'_g, l'_c, m'_c, m_j, M}(\theta) P_{L_0}(\cos \theta). \quad (34)$$

The cross section due to the static correlation can be calculated using the formula (23) combined with (25)

$$\frac{d\sigma(\hat{\mathbf{R}}_0)}{d\hat{\mathbf{R}}_0} = \sum_{LM} \int_0^{2\pi} d\varphi_B \int dB B \int dE \left| \sum_j a_{1j}^{LM}(\mathbf{B}, E, \hat{\mathbf{R}}_0) \langle \phi_f(\mathbf{r}_2) | \phi_j(\mathbf{r}_2) \rangle \right|^2. \quad (35)$$

Now let us treat the double collision (TS2) mechanism. As we have shown in Eq. (7), the TS2 amplitude is a product of one-electron amplitudes. The single-ionization amplitude is calculated like in the case of the static correlation. The excitation amplitude has a similar form

$$a_2^{\text{ex}}(\mathbf{B}, \hat{\mathbf{R}}_0) = \frac{iZ_p}{v} \sum_{L_g L_c} \frac{(4\pi)^2}{(2L_g + 1)(2L_c + 1)} \times \sum_{M_g M_c} D_{L_g L_c}^{M_c}(B) e^{iM_c \varphi_B} \times J_{L_g M_g L_c M_c m_1 M_f}(\theta) Y_{L_g M_g}^*(\hat{\mathbf{R}}_0), \quad (36)$$

where $D_{L_g L_c}^{M_c}$ is calculated like $B_{l_g l_c LM}^{m_c}$ from the integral (33), but the final wave function is of the excited state. The $J_{L_g M_g L_c M_c m_1 M_f}(\theta)$ integral is defined as in (30), with the initial-state magnetic quantum number $m_1 = 0$. As for the final state, in the case of the excitation of the $2p\sigma_u$ or $2s\sigma_g$ states $M_f = 0$ and for the $2p\pi_u$ state $M_f = \pm 1$. As one can see, for the first two the integrals reduce to $\delta_{L_g L_c} \delta_{M_g M_c}$. The expression of the cross sections for all the excited states due to the TS2 mechanism is obtained straightforwardly.

III. RESULTS AND DISCUSSIONS

Figures 1 and 2 represent the results for the energy and angular dependence for double ionization of the hydrogen molecule. In the considered energy interval the double collision and shake-off are the dominant processes. Shake-off becomes the most important mechanism above 700 keV proton energy. As for the angular dependence, our results are in better agreement with the data for positively charged projectile. The cross sections are not sensitive to the ground-state wave functions. The results

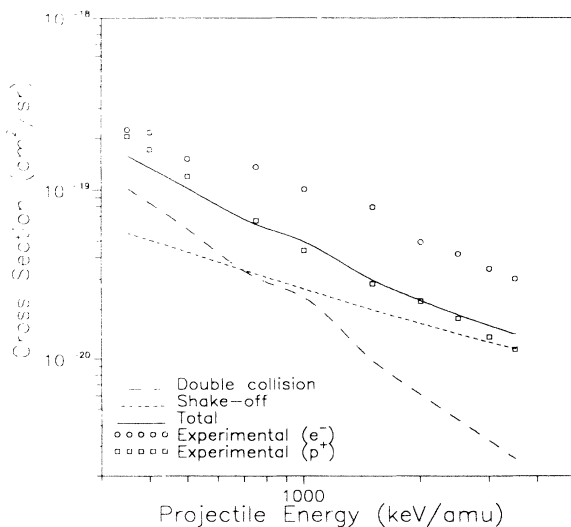


FIG. 1. Double-ionization cross sections of H_2 with the molecular axis oriented at 90° relative to the projectile motion as a function of the projectile energy. The experimental data were taken from Ref. [5].

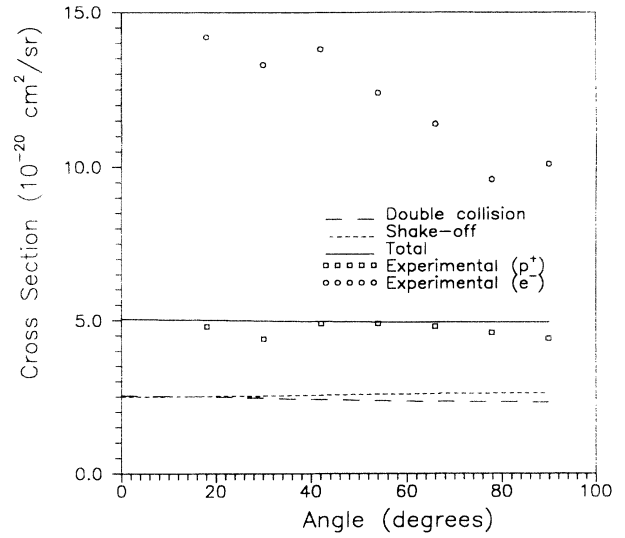


FIG. 2. Angular dependence of the double-ionization cross section on the orientation of the molecular axis relative to the projectile motion at 1 MeV/amu projectile energy. The experimental points are taken from Ref. [6].

presented in Figs. 1 and 2 are calculated using the wave functions taken from Ref. [8], but for the simple Heitler-London wave functions the results are about the same.

At the same time the ionization plus excitation cross sections are very sensitive to the applied wave functions. For the double collision mechanism the cross sections calculated with a Heitler-London-type ground-state wave function as in Ref. [7] and those calculated with a more precise one by Ref. [8] differ by up to one order of magnitude.

In order to check the dependence of the cross sections on the continuum wave function, we have generated numerically a two-center molecular wave function. Following Richards and Larkins [13] we have solved numerically the Schrödinger equation for the continuum electron in the cylindrical symmetric field of the residual ion. This was done for all L, M combinations up to $L = 2$. Using the finite difference method on a 120×16 mesh we have obtained a system of linear equations with 1920 unknowns. For solving it we have used the computer code in Ref. [14]. The normalization of the wave function was done by matching the asymptotic part to the Coulomb wave function with the method of Burgess [15]. These two-center molecular wave functions have caused a stronger dependence of the cross sections on the orientation of the molecular axis.

Our calculations for the ionization plus excitation of the $2s\sigma_g$ state by the double collision and shake-up mechanisms, using the numerically generated continuum wave functions and for the ground state the basic configuration taken from Ref. [8], gave acceptable results [16]. But including the ground-state correlation mechanism, the energy dependence of the cross sections has become peculiar. As shown in Fig. 3, the cross section has a tendency to remain constant even at high energies. The ground-state correlation components of the cross sections

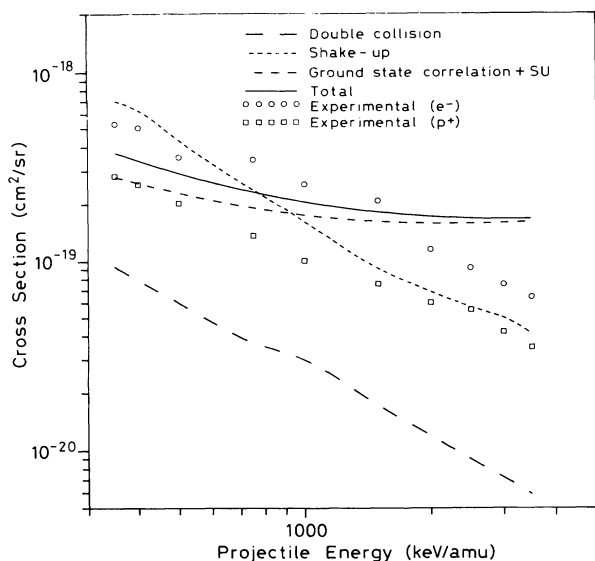


FIG. 3. Ionization plus excitation of the $2s\sigma_g$ cross sections of H_2 with the molecular axis oriented at 90° relative to the projectile motion as a function of projectile energy using the ground-state wave function from Ref. [8]. The experimental data were taken from Ref. [5].

for the ionization and excitation of the $2p\sigma_u$ and of the $2p\pi_u$ states express the same unacceptable behavior. We have realized that even if a ground-state wave function is proper in giving more or less precise dissociation energies, it is not necessarily good for the study of correlation effects in two-electron processes. It seems that the ground-state correlation is sensitive to such properties of the wave functions which do not have an essential effect on the position of the energy levels.

We have generated a ground-state wave function for the study of this problem. For configuration wave functions we have used the exact wave functions of the elec-

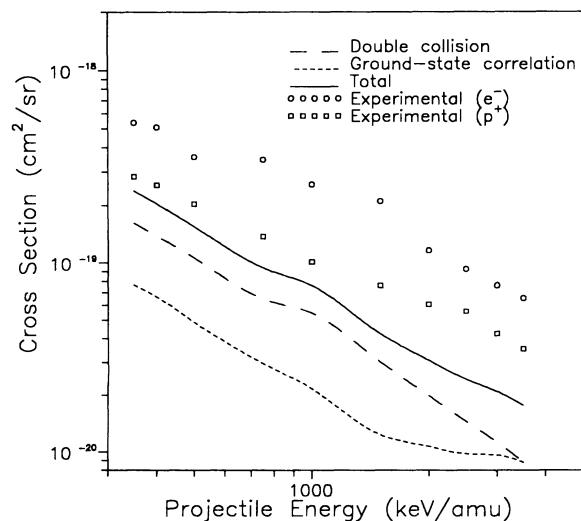


FIG. 4. Same as Fig. 3, but the ground-state wave function is constructed from the H_2^+ wave functions as in Eq. (37).

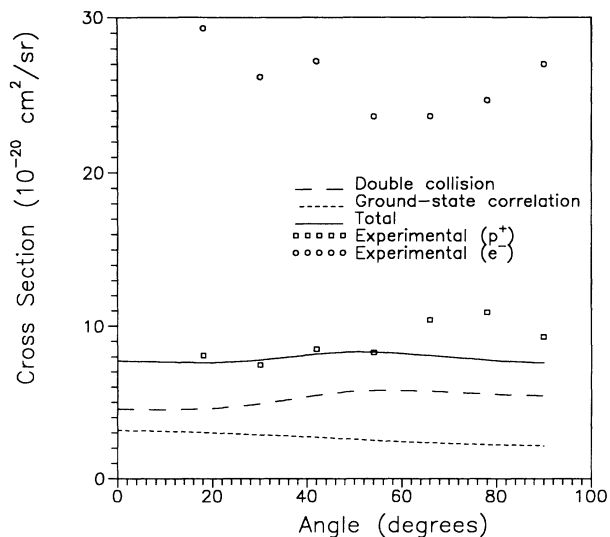


FIG. 5. Angular dependence of the ionization plus excitation of $2s\sigma_g$ cross section on the orientation of the molecular axis relative to the projectile motion at 1 MeV/amu projectile energy. The ground-state wave function is constructed from the H_2^+ wave functions as in Eq. (37). The experimental points are taken from Ref. [6].

tron in the H_2^+ molecular ion. By a variational method we have obtained the following ground-state wave function of the hydrogen molecule:

$$\psi_i = 0.993(1s\sigma_g)^2 - 0.107(2p\sigma_u)^2 - 0.028(2p\pi_u)^2 - 0.022(2s\sigma_g)^2. \quad (37)$$

The internuclear distance was taken at the experimental one $R_0 = 1.4$. The dissociation energy obtained with this

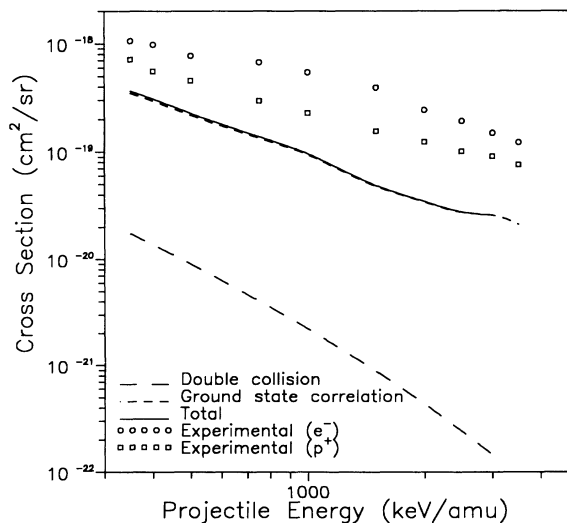


FIG. 6. Ionization plus excitation of the $2p\sigma_u$ cross sections of H_2 with the molecular axis oriented at 90° relative to the projectile motion as a function of projectile energy. The ground-state wave function is constructed from the H_2^+ wave functions as in Eq. (37). The experimental data were taken from Ref. [5].

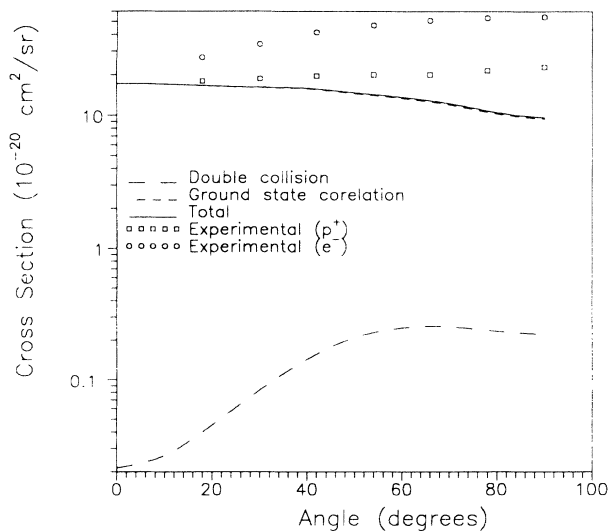


FIG. 7. Same as Fig. 5, but for the excitation of the $2p\sigma_u$ state.

wave function is 2.38 eV, far from the experimental value (4.74 eV).

Using the ground-state wave function (37) constructed from the H_2^+ wave functions, the results for the production of the $2s\sigma_g$ state of the H_2^+ molecular ion are plotted in Figs. 4 and 5. Now the contribution of the ground-state correlation mechanism gives better results. For this ground-state wave function the final excited state is orthogonal to the basic configuration and therefore the shake-up term is zero. The results are slightly lower than the experimental values. The double collision mechanism in this energy range is more important than the ground-state correlation. As Fig. 5 shows, the angular distribution fits well the proton data.

In the case of the excitation of the $2p\sigma_u$ the situation

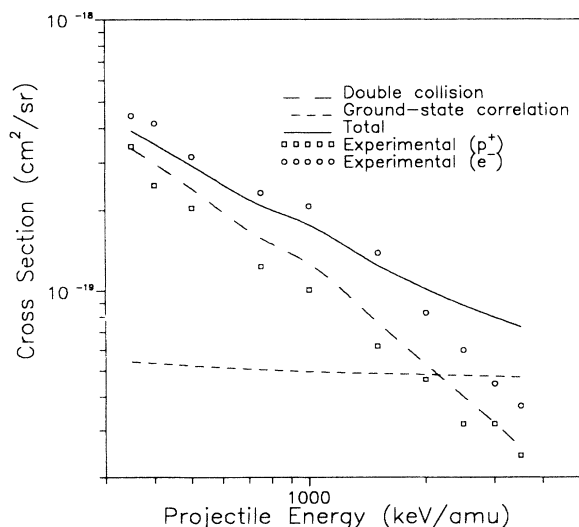


FIG. 8. Same as Fig. 6, but for the excitation of the $2p\pi_u$ state.

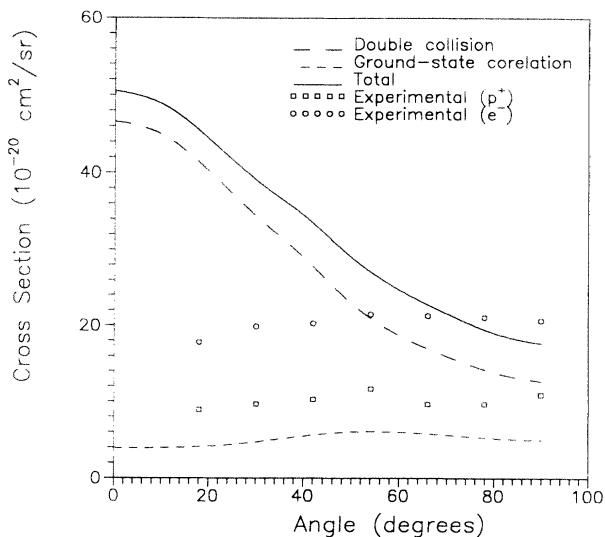


FIG. 9. Same as Fig. 5, but for the excitation of the $2p\pi_u$ state.

is reversed. The contribution of the ground-state correlation mechanism to the cross section is much more higher than that of the double collision; see Fig. 6. As for the molecular orientation dependence represented in Fig. 7, the dominant mechanism does not fit the tendency found in the experiment. Double collision would lead to a correct angular distribution, but its effect is negligible.

Finally in the case of the ionization plus excitation of the $2p\pi_u$ state the cross section due to the ground-state correlation has a peculiar behavior; it decreases only by 10% if the impact energy is increased from 350 to 3500 keV; see Fig. 8. The double collision mechanism dominates, but it does not fit the measured angular distribution; see Fig. 9.

IV. CONCLUSIONS

For the two-electron processes in the ionization of molecular hydrogen by proton impact, using the model of simple mechanisms, the calculated cross sections do not fit satisfactorily the experimental data. The most reliable results are for the double ionization. In this case we could tell something certain about the relative importance of the TS2 and the shake-off mechanism. As expected, the shake-off cross section is inversely proportional to the projectile velocity and the cross section due to the TS2 mechanism decreases as $1/v^2$.

In the case of the ionization plus excitation the relative importance of different mechanisms to the energy and angular dependence of the cross sections is strongly dependent on the applied ground-state wave functions. We can find ground-state wave functions which may lead to more or less acceptable total cross sections within the framework of our model. Since the time-ordering effects, which are relevant in our case, are not included, we cannot tell anything certain about the relative importance of the different mechanisms. We could select the most appropriate wave function only within a more complete

framework.

The inclusion of the TS1 mechanism in our calculation would not change essentially our results, especially at the higher energies. As McGuire has shown [4], the TS1 amplitude decreases with the inverse of the cube of the projectile's velocity and is not important until the velocity is relatively small.

The absence of the shake-off term in the cross section for the ionization and excitation of the $2s\sigma_g$ state using the ground-state wave function (37) constructed from the H_2^+ wave functions has an important effect on the total cross section. But the inclusion of the shake-off would not necessarily lead to the increase of the total cross section because the signs of the shake-off and ground-state correlation amplitudes could have opposite signs. The reason for using this ground-state wave function was to obtain an acceptable behavior of the ground-state corre-

lation cross sections.

Comparing the two dipole allowed excitations of the $2p\sigma_u$ and of the $2p\pi_u$ states, one can state the difference in the dominant mechanisms. One of the reasons is that in the wave function (37) of H_2 , constructed from the H_2^+ wave functions, the coefficient of the $(2p\sigma_u)^2$ configuration is about four times larger than that of the $(2p\pi_u)^2$, leading to a much more important ground-state correlation contribution in the excitation of the $2p\sigma_u$ state. The difference in the magnitude of the TS2 cross sections in these two cases could be explained by the different form of the excited-state wave functions.

ACKNOWLEDGMENT

This work was supported by the Hungarian OTKA Foundation under Contract No. 3011.

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