

LETTER TO THE EDITOR

Double excitation of the hydrogen molecule by fast charged particle impact

D Bodea and L Nagy

Faculty of Physics, Babeş-Bolyai University, str. Kogălniceanu nr. 1, 3400 Cluj, Romania

Received 7 October 1999, in final form 2 November 1999

Abstract. Theoretical calculation for the double excitation of the hydrogen molecule to the $(2p\sigma_u^2)^1\Sigma_g^+$ and $(2p\sigma_u2p\pi_u)^1\Pi_g$ states induced by fast charged particles are reported for the first time. Electron correlation and time-ordering are considered in order to reproduce the dependence of the cross sections on the sign of the projectile charge. We have also analysed the dependence of the cross sections on the angle between the molecular axes and the beam direction. Our theoretical results are compared with the experimental data.

The two-electron processes in atoms and molecules induced by fast charged projectiles have been studied intensively both theoretically and experimentally over the last decade. It has been made clear that taking into account the electron correlation is essential for a correct theoretical description of these transitions [1, 2].

The most studied target has been the simplest two-electron system, the helium atom. In the case of double ionization and ionization–excitation, experimental studies [3, 4] have revealed that negative projectiles (electrons and antiprotons) lead to larger cross sections by a factor of two than equivelocity protons over a wide velocity range. This behaviour has been explained theoretically [1], but an accurate quantitative agreement has been obtained only for double ionization [5]. As for the double excitation of helium, the dependence of the cross sections on the sign of the projectile charge depends on the specific doubly excited state, and the agreement between theory and experiment, because of experimental difficulties and the different results of the theoretical approaches is not conclusive [6].

The two-electron transitions in another two-electron target, the hydrogen molecule, have also been studied, by a group at the University of Georgia [7–9]. The doubly excited states of H_2 , the excited states of the H_2^+ ion, and certainly the doubly ionized hydrogen molecule are all dissociative states. The energy of the outgoing fragments give information on the produced state. Measuring the energy and direction of the outgoing protons, the experimental procedure of this group makes it possible to extract cross sections for each dissociative state as a function of the orientation of the molecular axes versus the projectile beam direction.

Similarly to the helium target, cross sections for proton projectiles have been obtained to be smaller by a factor of two than for equivelocity electrons [7]. This experimental finding has not been reproduced theoretically yet.

The theoretical calculations by one of us for double ionization and ionization–excitation of the hydrogen molecule [10, 11] gave the correct order of magnitude of the cross sections, but have not been able to reproduce the dependence of the cross sections on the sign of the

projectile charge. The reason for this lack of agreement is that we have not taken into account the time-ordering effects in those calculations [12].

In the present paper we have investigated the double excitation of the hydrogen molecule induced by fast charged particles. To our knowledge this is the first attempt to make theoretical calculations for these transitions. We have taken into account electron correlation and time-ordering, in order to reproduce the dependence of the cross sections on the sign of the projectile charge. We have also studied the dependence of the cross sections on the angle between the molecular axes and the beam direction.

The framework of our calculation is the impact parameter method, where the projectile moves on a classical straight-line trajectory.

For the study of the evolution of the two-electron system we have applied second-order time-dependent perturbation theory.

The first-order probability amplitude for the transition of the electrons can be written as

$$a^{(1)} = -i \int_{-\infty}^{+\infty} dt e^{i(E_f - E_i)t} \langle f | [V_1(t) + V_2(t)] | i \rangle. \quad (1)$$

Here $|i\rangle$ and $|f\rangle$ are the initial and final two-electron states, respectively, E_i and E_f are the energies of these states, while $V_1(t)$ and $V_2(t)$ denote the two time-dependent projectile-electron interactions.

The second-order amplitude is obtained to be

$$a^{(2)} = - \sum_k \int_{-\infty}^{+\infty} dt e^{i(E_f - E_k)t} \langle f | V_1(t) | k \rangle \int_{-\infty}^t dt' e^{i(E_k - E_i)t'} \langle k | V_2(t') | i \rangle \\ - \sum_k \int_{-\infty}^{+\infty} dt e^{i(E_f - E_k)t} \langle f | V_2(t) | k \rangle \int_{-\infty}^t dt' e^{i(E_k - E_i)t'} \langle k | V_1(t') | i \rangle. \quad (2)$$

Here we have to sum up over the intermediate states $|k\rangle$ with energies E_k , the infinite number of eigenstates of the two-electron unperturbed Hamiltonian.

For the description of the ground and doubly excited states we have used configuration-interaction (CI) wavefunctions, a linear combination of different two-electron configurations with the same symmetry

$$i(\mathbf{r}_1, \mathbf{r}_2) = \sum_m c_m \phi_m(\mathbf{r}_1) \phi_m(\mathbf{r}_2) \quad (3)$$

$$f(\mathbf{r}_1, \mathbf{r}_2) = \sum_n d_n \phi'_n(\mathbf{r}_1) \phi_n(\mathbf{r}_2). \quad (4)$$

The values of the coefficients c_m for the ground state and d_n for the different excited states have been obtained by a variational method. We have taken into account for the ground state and the doubly excited states with $^1\Sigma_g^+$ symmetry the $(1s\sigma_g)^2$, $2p\sigma_u^2$, $(2p\pi_u)^2$ and the $2s\sigma_g^2$ configurations. The one-electron molecular orbitals are linear combinations of atomic orbitals. We have obtained for the ground state the following CI wavefunction:

$$i = 0.9954(1s\sigma_g)^2 - 0.0741(2p\sigma_u)^2 - 0.0553(2p\pi_u)^2 - 0.0233(2s\sigma_g)^2 \quad (5)$$

and the doubly excited state with the lowest energy, the $(2p\sigma_u^2)^1\Sigma_g^+$, is described by

$$f = -0.0627(1s\sigma_g)^2 - 0.8714(2p\sigma_u)^2 - 0.4336(2p\pi_u)^2 + 0.2028(2s\sigma_g)^2. \quad (6)$$

In the case of the asymmetric excited state $(2p\sigma_u 2p\pi_u)^1\Pi_g$ we have taken into account only the basic $(2p\sigma_u 2p\pi_u)$ configuration, so it is a properly symmetrized product of one-electron wavefunctions

$$f = \frac{1}{\sqrt{2}}(2p\sigma_u 2p\pi_u + 2p\pi_u 2p\sigma_u). \quad (7)$$

The matrix element from the first-order amplitude (1) can be written in terms of one-electron wavefunctions using the expressions (3) and (4),

$$\begin{aligned}\langle i|V_1(t) + V_2(t)|f\rangle &= 2\langle i|V_1|f\rangle \\ &= 2\sum_{n,m} d_n^* c_m \langle \phi_n'(\mathbf{r}_1)|V_1(t)|\phi_m(\mathbf{r}_1)\rangle \langle \phi_n(\mathbf{r}_2)|\phi_m(\mathbf{r}_2)\rangle \\ &= 2\sum_n d_n^* c_n \langle \phi_n'(\mathbf{r}_1)|V_1(t)|\phi_n(\mathbf{r}_1)\rangle\end{aligned}\quad (8)$$

where we have used

$$\langle \phi_n(\mathbf{r}_2)|\phi_m(\mathbf{r}_2)\rangle = \delta_{nm} \quad (9)$$

because the initial and the final states are described by the same orthonormal basis sets.

The ϕ_n one-electron molecular orbitals depend on the direction of the \mathbf{R}_0 molecular axes. The linear combination of these orbitals from (8) is expanded into a Legendre series

$$\sum_n c_n d_n^* \phi_n^*(\mathbf{r}_1) \phi_n(\mathbf{r}_1) = \sum_l C_l(r_1) P_l(\cos \omega_1) \quad (10)$$

where ω_1 is the angle between vectors \mathbf{r}_1 and \mathbf{R}_0 . The expansion coefficients are defined as

$$C_l(r_1) = \frac{1}{2}(2l+1) \int_{-1}^{+1} d(\cos \omega_1) P_l(\cos \omega_1) \left[\sum_n c_n d_n^* \phi_n^*(\mathbf{r}_1, \mathbf{R}_0) \phi_n(\mathbf{r}_1, \mathbf{R}_0) \right]. \quad (11)$$

In order to separate the dependence of the amplitude on the direction of the molecular axes we express the Legendre polynomials in terms of products of spherical harmonics,

$$P_l(\cos \omega_1) = \frac{4\pi}{2l+1} \sum_m Y_{lm}(\hat{\mathbf{R}}_0) Y_{lm}^*(\hat{\mathbf{r}}_1). \quad (12)$$

In order to calculate the amplitudes, the projectile–electron Coulomb interaction is expanded into a partial-wave series

$$V_1(t) = \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} = \sum_{l_c} \frac{4\pi}{2l_c+1} \frac{r_{<}^{l_c}}{r_{>}^{l_c+1}} \sum_{m_c} Y_{l_c m_c}(\hat{\mathbf{R}}_1) Y_{l_c m_c}^*(\hat{\mathbf{r}}_1) \quad (13)$$

where \mathbf{R}_1 is the position vector of the projectile. Using expressions (10) and (13) the first-order amplitude becomes

$$a^{(1)} = \frac{2(4\pi)^2 Z_p}{v} \sum_l \sum_m A_{lm}(B) Y_{lm}(\hat{\mathbf{R}}_0) \quad (14)$$

where we have introduced

$$A_{lm}(b) = \int_{-\infty}^{+\infty} dz \exp\left(i\frac{\Delta E}{v} Z_p\right) Y_{lm}(\hat{\mathbf{R}}_1) \int_0^{+\infty} dr_1 r_1^2 \frac{r_{<}^l}{r_{>}^{l+1}} \frac{C_l(r_1)}{(2l+1)^2} \quad (15)$$

with b the impact parameter. In order to calculate the second-order amplitude, from the infinite number of intermediate states we keep only the most important ones. As described in [13], these are assumed to be those reachable from the initial and the final state by a single-electron transition. Simplified, in the considered intermediate states, one of the electrons is in its initial state and the other one has reached the final state. Performing similar expansions as for the first-order amplitude, (10) and (13), we can express the second-order amplitude (2) as

$$a^{(2)} = \frac{2(4\pi)^4}{v^2} \sum_{l_1, l_2} \sum_{m_1, m_2} B_{l_1 l_2 m_1 m_2}(b) Y_{l_1 m_1}^*(\hat{\mathbf{R}}_0) Y_{l_2 m_2}^*(\hat{\mathbf{R}}_0) \quad (16)$$

where

$$B_{l_1 l_2 m_1 m_2}(b) = \int_{-\infty}^{+\infty} dz_1 \exp\left(i \frac{\Delta E_1}{v} z_1\right) Y_{l_1 m_1}(\hat{\mathbf{R}}_1) \int_0^{+\infty} dr_1 r_1^2 \frac{r_{1<}^{l_1}}{r_{1>}^{l_1+1}} \frac{D_{l_1}(r_1)}{(2l_1+1)^2} \\ \times \int_{-\infty}^{z_1} dz_2 \exp\left(i \frac{\Delta E_2}{v} z_2\right) Y_{l_2 m_2}(\hat{\mathbf{R}}_2) \int_0^{+\infty} dr_2 r_2^2 \frac{r_{2<}^{l_2}}{r_{2>}^{l_2+1}} \frac{D_{l_2}(r_2)}{(2l_2+1)^2}. \quad (17)$$

The coefficients D_l are obtained similarly to C_l in the first-order amplitude (11),

$$D_{l_i}(r_i) = \frac{1}{2}(2l_i+1) \int_{-1}^{+1} d(\cos \omega_i) P_l(\cos \omega_i) \left[\sum_n c_n d_m^* \phi_m^*(\mathbf{r}_i, R_0) \phi_n(\mathbf{r}_i, R_0) \right]. \quad (18)$$

The cross section is obtained as the integral over the impact parameter of the square of the modulus of the transition amplitude,

$$\sigma(\hat{\mathbf{R}}_0) = \int db |a^{(1)} + a^{(2)}|^2. \quad (19)$$

Using the presented method first we have studied the dependence of the cross sections on the energy and charge sign of the projectile. In figures 1(a) and (b) we have represented the cross sections for the double excitation of the hydrogen molecule by proton and antiproton impact for the $(2p\sigma_u^2)^1\Sigma_g^+$ and the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ states, respectively, as a function of the projectile energy. Cross sections are calculated for 90° orientation of the molecular axes relative to the beam direction. We have also represented the contributions of the first- and second-order amplitudes to the cross section.

For the excitation of the $(2p\sigma_u^2)^1\Sigma_g^+$ state the first-order contribution to the cross section dominates over the entire energy range. This means that the main cause of the production of this doubly excited state is electron correlation. As for the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ state, the first-order mechanism is more important than the second-order one only above 1 MeV projectile energy. As a consequence of the interference between the first- and the second-order amplitudes, cross sections obtained for antiprotons are higher than those for protons for both states.

In the experiment of Edwards *et al* [7] the authors have extracted the cross sections for the double excitation of the hydrogen molecule, but their method did not permit them to distinguish between contributions from the different doubly excited states. Searching for the best fit of the theoretically predicted energy distributions of the resulting H^+ ions from the dissociating molecule on the experimental spectrum, the authors have concluded that mainly the $(2p\sigma_u^2)^1\Sigma_g^+$ and the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ states contribute to the double-excitation cross section. Consequently, we can assume that the cross sections for the double excitation of H_2 given by Edwards *et al* represent the sum of the cross sections for these two doubly excited states. In figure 2 we have represented along with the experimental cross sections of Edwards *et al* [7] the sum of our calculated cross sections for the excitation of the $(2p\sigma_u^2)^1\Sigma_g^+$ and the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ states of the H_2 molecule for proton and antiproton impact. Our calculated values are of the same order of magnitude as the experimental ones, but we have obtained a much smaller difference between cross sections obtained for positive and negative projectiles.

Figures 3(a)–(d) represent the dependence of the cross sections on the orientation of the molecular axes relative to the beam direction for protons and antiprotons of different energies. Full curves represent the results obtained with the expansion (10) up to $l = 8$, while the broken curves stand for this expansion taken up to $l = 2$. In figures 3(a) and (b) we have shown the angular dependence of the cross sections for the $(2p\sigma_u^2)^1\Sigma_g^+$ state. One can observe that, if we stop with the expansion at $l = 2$, the dependence of the cross sections on the orientation of the molecular axes is relatively weak. The contributions up to $l = 8$ are important, mainly

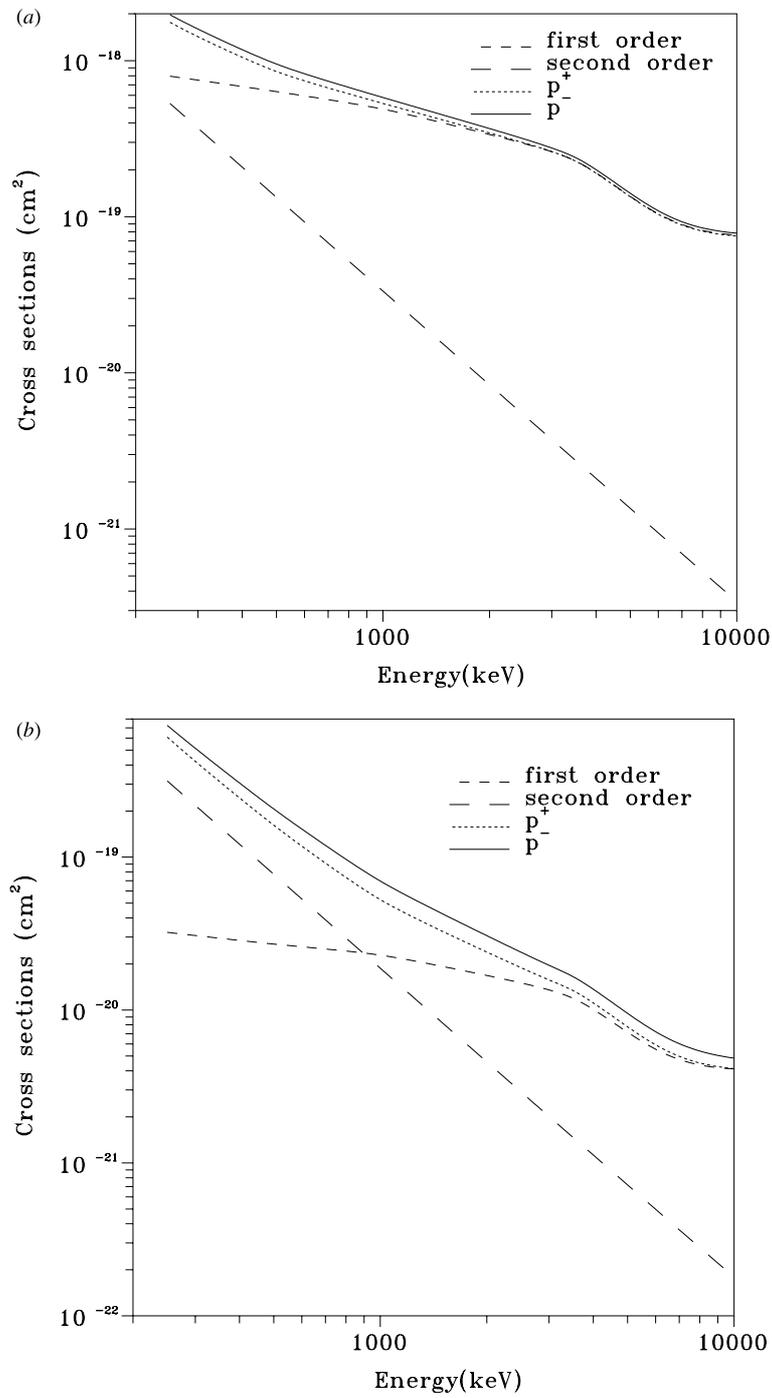


Figure 1. Cross sections for the double excitation of the hydrogen molecule by proton (dotted curve) and antiproton (full curve) impact for the (a) $(2p\sigma_u^2)^1\Sigma_g^+$ and (b) $(2p\sigma_u 2p\pi_u)^1\Pi_g$ states, respectively, as a function of the projectile energy. We have also represented the contributions of the first-order (short-broken curve) and second-order (long-broken curve) amplitudes to the cross section.

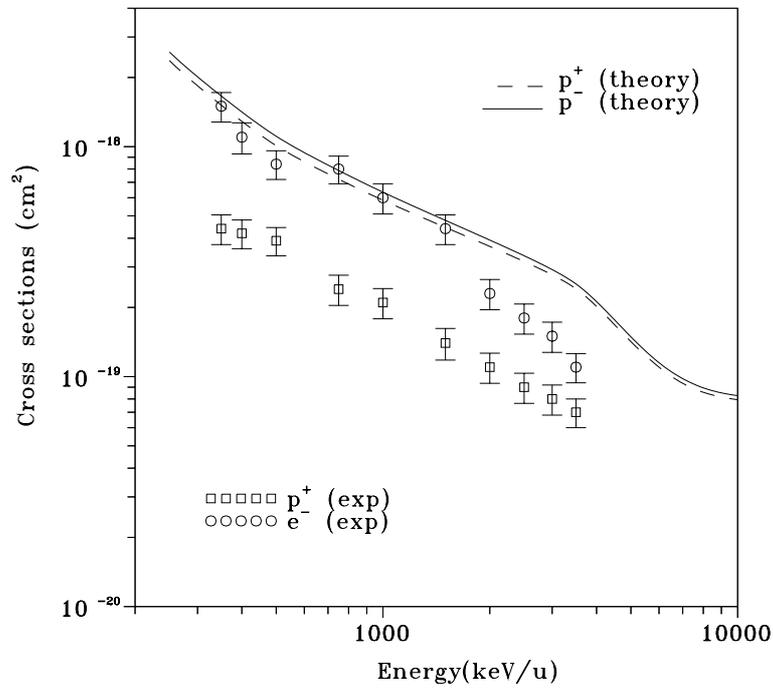


Figure 2. The sum of our calculated cross sections for the excitation of the $(2p\sigma_u^2)^1\Sigma_g^+$ and the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ states of the H_2 molecule for proton (broken curve) and antiproton (full curve) impact. Our theoretical data are compared with the experimental results of Edwards *et al* [7]. Squares denote proton impact, while circles denote equivelocity electron impact.

regarding the angular dependence. This importance of the $l > 2$ contributions is even more accentuated for the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ state, as shown in figures 3(c) and (d). For both states and both types of projectiles the cross sections have a maximum at around 60° between the molecular axes and the beam direction.

In figure 4 we have compared the angular dependence of the sum of the cross sections for the two doubly excited states considered with the experimental data of Edwards *et al* [8]. In the case of the proton projectiles our results are much higher than the experimental data. The angular dependence is also different, the experimental data have a maximum at 90° . The situation is much better for antiproton projectiles in comparison with the experimental data obtained with equivelocity electrons. Here the order of magnitude of the cross sections obtained is the same. The angular dependence for lower projectile energies (750 and 1000 keV u^{-1}) is different, the experimental data show an increase up to 90° , while we have obtained a maximum at 60° . At 2000 keV u^{-1} projectile energy the experimental data also show a maximum at 70° .

In conclusion, we have calculated for the first time cross sections for the double excitation of helium by proton and antiproton impact. The calculation includes static electron correlation in the initial and final states, and applies a perturbation expansion through second order. We do obtain higher cross sections for the negative projectile, in accordance with the experimental findings. However, there is not an accurate agreement between our results and the experimental data, neither for the absolute value of the cross sections nor for the angular dependence. The agreement is better in the case of the negative projectiles, probably because in this case dynamic correlation is less important. This is supported in the paper by Bronk *et al* [14] by the argument

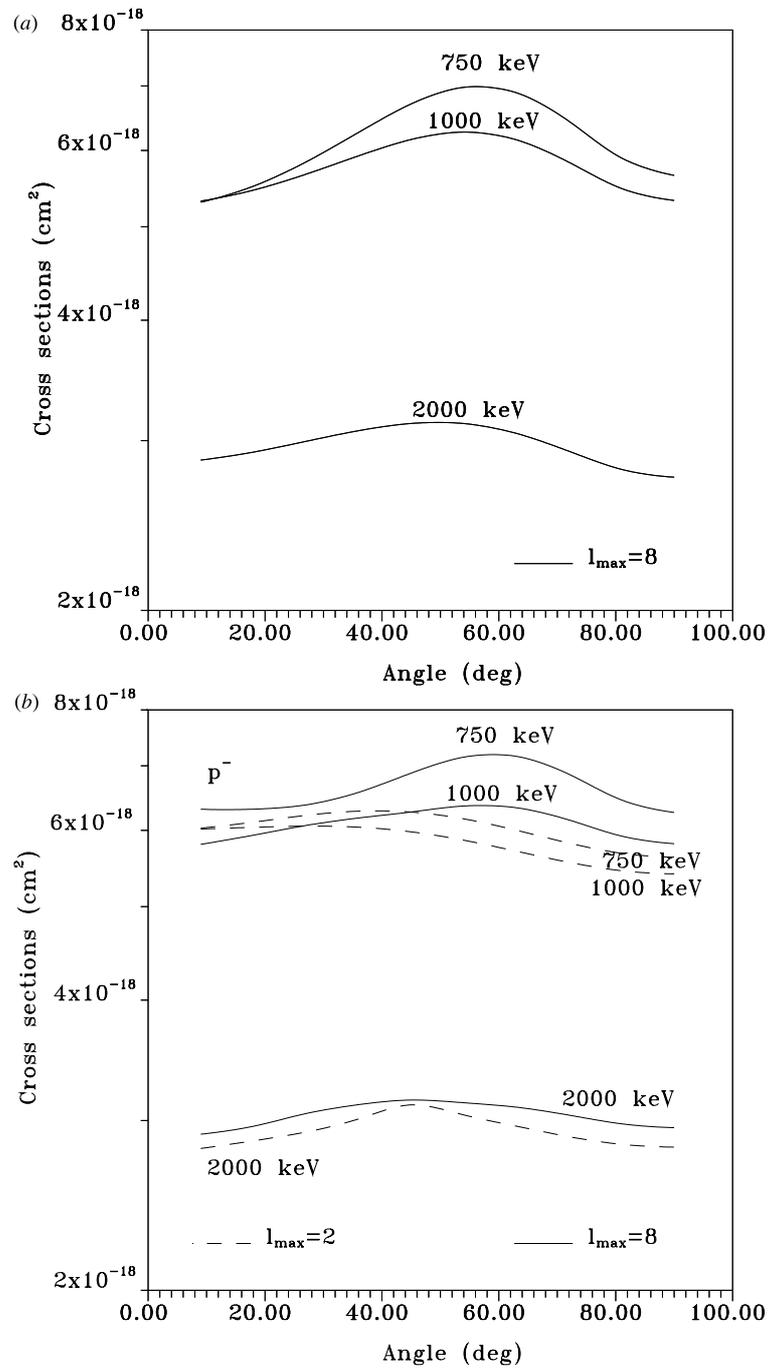


Figure 3. The dependence of the cross sections on the orientation of the molecular axes relative to the beam direction for protons and antiprotons of different energies. Full curves represent the results obtained with the expansion (10) up to $l = 8$, while the broken curves denote this expansion taken up to $l = 2$. Parts (a) and (b) contain the angular dependence of the cross sections for the $(2p\sigma_u^2)^1\Sigma_g^+$ state, while (c) and (d) are for the $(2p\sigma_u 2p\pi_u)^1\Pi_g$ state, respectively.

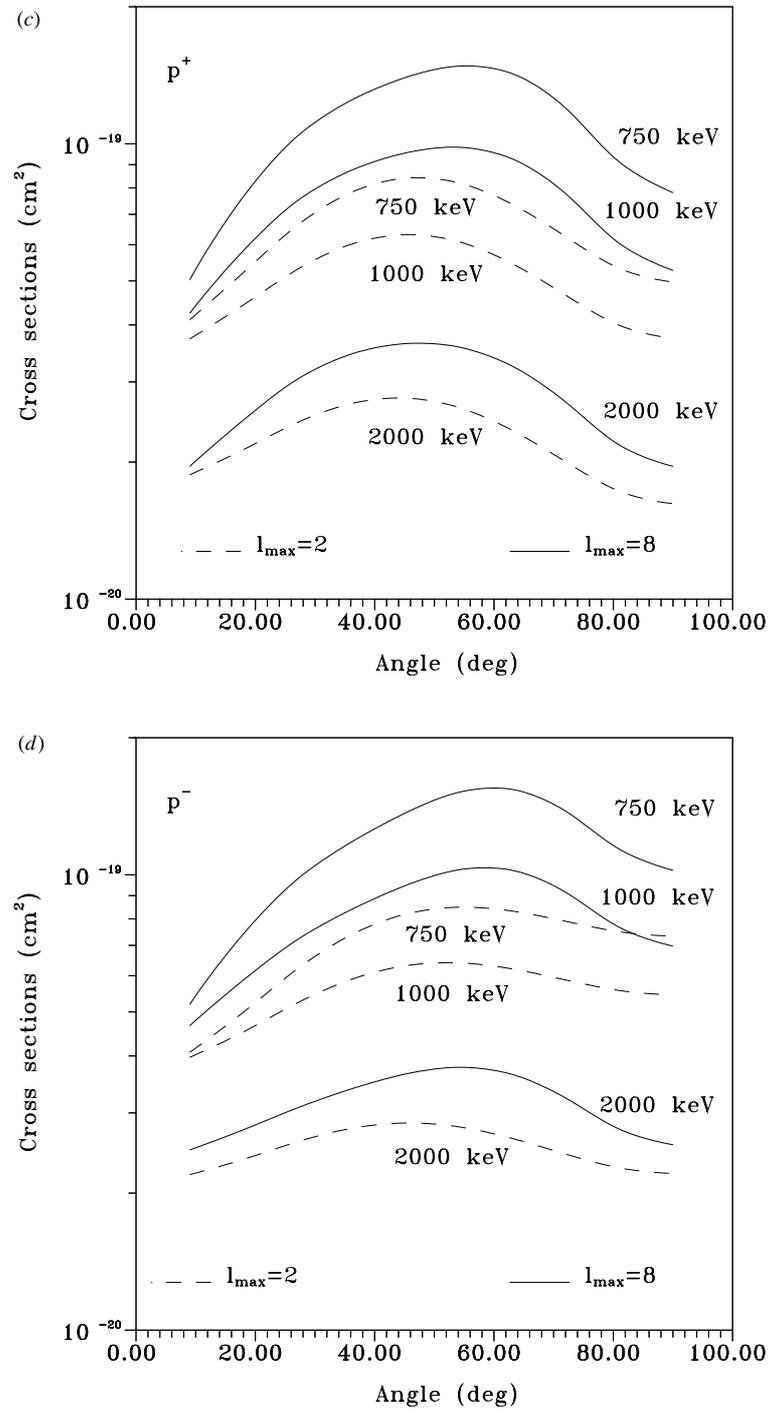


Figure 3. Continued.

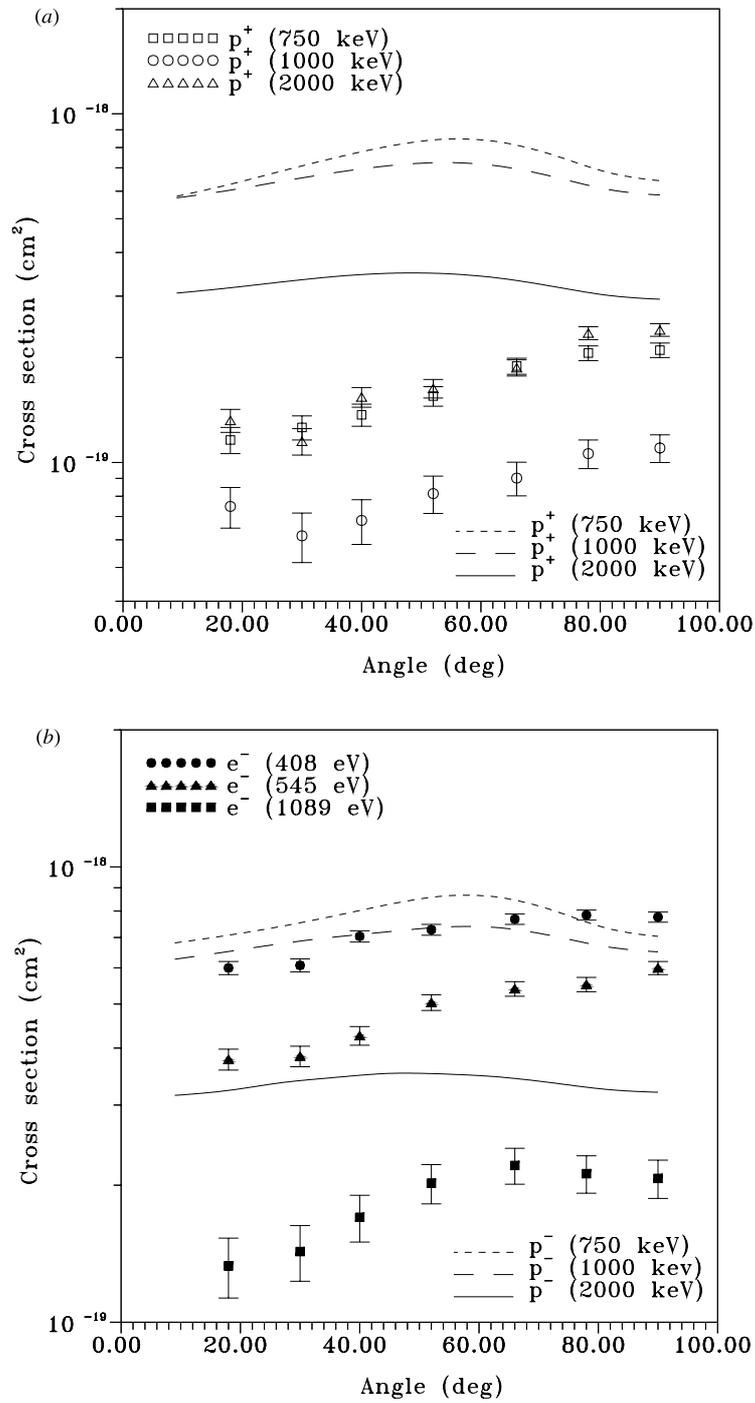


Figure 4. Angular dependence of the sum of the cross sections for the two doubly excited states considered, $(2p\sigma_u^2)^1\Sigma_g^+$ and $(2p\sigma_u 2p\pi_u)^1\Pi_g$, compared with the experimental data of Edwards *et al* [8].

that the collision system is more pliable for negative projectiles. Disagreement may be caused by the imperfections of our model (the neglect of the TS1 process, the dynamic electron correlation) and by the inaccuracies in the experimental data.

References

- [1] McGuire J H 1992 *J. Phys. B: At. Mol. Opt. Phys.* **29** 217
- [2] Martin F and Salin A 1996 *Phys. Rev. Lett.* **76** 1437
- [3] Andersen L H, Hvelplund P, Knudsen H, Møller S P, Sørensen A H, Elsner K, Rensfelt K G and Uggerhøj E 1987 *Phys. Rev. A* **36** 3612
- [4] Bayley M, Bruch R, Rausher E and Bliman S 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 2655
- [5] Ford A L and Reading J F 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 4215
- [6] Bodea D, Orban A, Ristoiu D and Nagy L 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L745
- [7] Edwards A K, Wood R M and Davis J L 1990 *Phys. Rev. A* **42** 1367
- [8] Edwards A K, Wood R M and Mangan M A 1992 *Phys. Rev. A* **46** 6970
- [9] Mangan M A, Wood R M and Edwards A K 1999 *Phys. Rev. A* **59** 358
- [10] Nagy L and Végh L 1992 *Phys. Rev. A* **46** 290
- [11] Nagy L and Végh L 1994 *Phys. Rev. A* **50** 3984
- [12] Nagy L, McGuire J H, Végh L, Sulik B and Stolterfoht N 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 1239
- [13] Nagy L 1999 *Nucl. Instrum. Methods B* **154** 123
- [14] Bronk T, Reading J F and Ford A L 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2477