

LETTER TO THE EDITOR

Theoretical studies of electron capture in $H^+ + H_2$ collisions

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Abstract. The differential electron capture probabilities at a laboratory scattering angle of 3° in $H^+ + H_2$ collisions have been calculated against scattering energies, using the orientation-dependent atomic model for charge transfer in ion-molecule collisions recently proposed by Shingal and Lin. The calculated oscillatory behaviour of the capture probabilities is found to be in good agreement with the experimental data of Lockwood and Everhart. The cross sections for capture to $2s$ and $2p$ states of the hydrogen atom have also been computed and found to be in reasonable agreement with the experimental data.

The differential charge transfer probabilities in $H^+ + H$ and $H^+ + H_2$ collisions at a 3° laboratory scattering angle were measured more than twenty-five years ago (Lockwood and Everhart 1962). Their results, reproduced in figure 1, showed that the charge

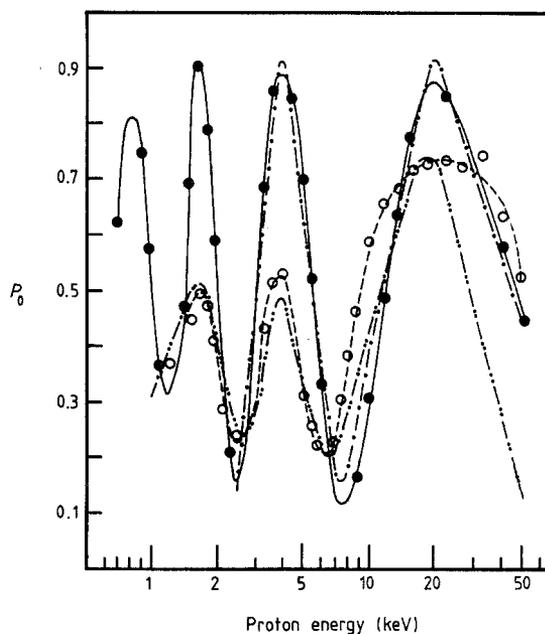


Figure 1. The total electron capture probability P_0 , at a laboratory scattering angle of 3° . The full and broken curves represent the experimental data of Lockwood and Everhart (1962) for $H^+ + H$ and $H^+ + H_2$ collision systems respectively. The chain and double-dotted chain curves are the corresponding theoretical curves (present calculation).

transfer probabilities oscillate as a function of scattering energies. These data have served as the basis for testing many theoretical models. For $H^+ + H$ system, the observed frequency of oscillation and the positions of maxima and minima have been successfully explained in three-state ($1s\sigma-2p\sigma-2p\pi$) or many-state molecular-orbital calculations (see, for example, McCarroll and Piacentini 1970, Ferguson 1961, Gaussorgues *et al* 1975). Similarly, calculations based on atomic-orbital expansions are also capable of reproducing the observed oscillation if pseudostates are included in the basis expansion (see, for example, Fritsch and Lin 1982, Lin *et al* 1982). On the other hand, to our knowledge, only two calculations (Piacentini and Salin 1978, Yenen *et al* 1984) have attempted to explain the experimental data in the more complex $H^+ + H_2$ collision, with varying degrees of success.

Examination of the measured electron transfer probability showed striking similarities for the two collision systems. The positions of the maxima and minima occur at about the same energies except that the oscillations are much more damped for the $H^+ + H_2$ system. These data suggest that the dominant feature of the electron transfer probability at 3° for $H^+ + H_2$ collisions is governed by the close collision between the proton and one of the hydrogen atoms in the H_2 molecule, with modifications due to averaging over the orientation of the molecule.

A simple model for describing electron transfer in ion-molecule collisions has been proposed recently by Shingal and Lin (1989). In this model the orientation of the molecule is assumed to be stationary during the collision. The electron-capture amplitude is expressed as a coherent sum of two single-electron-capture amplitudes $A(b)$ describing the collision between the projectile and the constituent atom of the target molecule, with the relative phase between the two amplitudes depending on the collision velocity v and the orientation (θ) of the molecule with respect to the incident projectile

$$A_{ji}(b, \theta, \varphi) = (1/\sqrt{2})\{A(b_1) + A(b_2) \exp[-i\rho \cos \theta(v/2 - \omega/v)]\}. \quad (1)$$

In equation (1) ω is the energy defect, ρ is the equilibrium distance between the two atoms in the target molecule and b_1 and b_2 are the impact parameters of the projectile with respect to the two atomic centres in the target. There are a number of assumptions (see Shingal and Lin 1989) used in the derivation of equation (1), including that perturbation theory and unitarised approximation were invoked. We note that this expression can also be obtained starting from the full wave treatment of the heavy particle motion (Tuan and Gerjuoy 1960) and applying the eikonal transformation from the scattering angles of the projectile to the impact parameters. However, in actual applications of this model, the amplitudes $A(b_1)$ and $A(b_2)$ are not treated perturbatively but are obtained from the standard two-centre multi-state atomic-orbital expansion method. To enable comparison with experimental results, the calculated electron transfer probability is averaged over all orientations of the molecule.

The experiment of Lockwood and Everhart (1962) measured the total charge transfer probability as a function of energy at a large scattering angle (3°). For such a close collision, it is safe to assume that the trajectory of the projectile is determined by the Rutherford scattering between the projectile and one of the target nuclei. (Diffraction effects from different impact parameters are not important at this large scattering angle; see McCarroll *et al* (1970).) Thus the impact parameter b_1 in (1) is identical to the impact parameter responsible for the 3° oscillations in $H^+ + H$ collisions. On the other hand, for $H^+ + H_2$ collisions, contributions from the other atom in the target molecule (the second term in equation (1)) have to be included and an average over the orientation of the molecule must be carried out.

The calculated differential charge transfer probabilities, as a function of impact energy, for both the $H^+ + H$ and $H^+ + H_2$ collision systems are shown in figure 1 along with the experimental data of Lockwood and Everhart (1962). The atomic basis functions given in table 1 of Shingal *et al* (1985) were placed on the two centres for studying the $H^+ + H$ system. Our results are in good agreement with experiment over the whole energy shown. For $H^+ + H_2$ collisions, the 'atomic' electron capture amplitudes $A(b_1)$ and $A(b_2)$ are obtained by assuming that the target hydrogen 'atom' has an effective charge of 1.09 and a binding energy of -0.599 au. A basis set consisting of 6s (with exponents 1.09, 0.547, 0.547, 0.368, 0.368 and 0.368), 5p (with exponents 0.547, 0.368, 0.368, 1.37 and 0.168) and 2d (with exponents 0.368 and 1.17) Slater-type orbitals was placed on the target atom. These basis functions had the same powers as assigned to the hydrogen atom basis set with the exception of the p-type orbitals which had the powers 1, 1, 2, 2, 3, respectively. The projectile (hydrogen atom) was represented by the same basis set used in the $H^+ + H$ atom collision. The results from this simple model, shown in figure 1, are in good agreement with the experimental data, not only in the positions of the maxima and minima, but also in the magnitude. Increasing discrepancy occurs only at the higher energies. We emphasise that the rotational coupling between the projectile and the target atom is included in our calculations. The rotational coupling is responsible for the non-zero minima in the capture probability for $H^+ + H$ collisions (the quantal interference effect is also responsible for non-zero minima at lower energies) and presumably also affects the minima in the H_2 target. We note that the rotational coupling has not been included in the calculations for the H_2 target so far (Piacentini and Salin 1978, Yenen *et al* 1984, Kimura 1985).

To illustrate the similarity between the atomic and the orientation-averaged molecular targets further, in figure 2, we show the total charge transfer probability

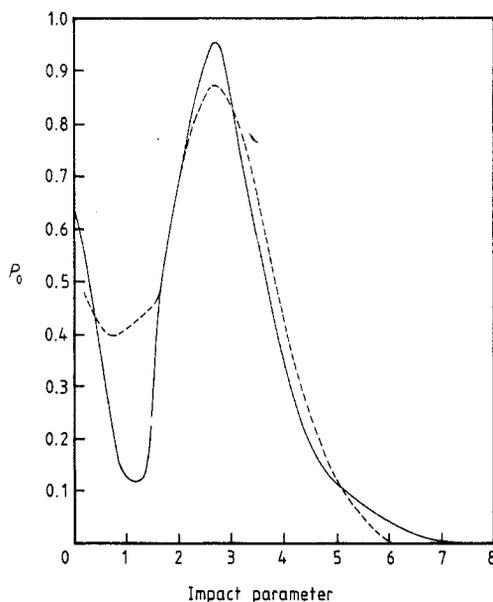


Figure 2. The calculated total electron capture probability P_0 for the $H^+ + H$ (full curve) and the $H^+ + H_2$ (broken curve) collisions at an impact energy of 5 keV.

against impact parameters for $H^+ + H$ and $H^+ + H_2$ at an impact energy of 5 keV. The capture probability also shows oscillatory behaviour for the H target. For the H_2 target, damped oscillations due to average over the molecular orientation are observed. We note that for the H_2 target the relation between the impact parameters and scattering angles for large b is more complicated and the results shown in figure 2 cannot be directly related to angular measurements.

The good agreement with experimental data in the differential charge transfer probabilities calculated here, together with our earlier work on the total electron transfer cross sections of H_2 by protons and α particles, suggests that the simple

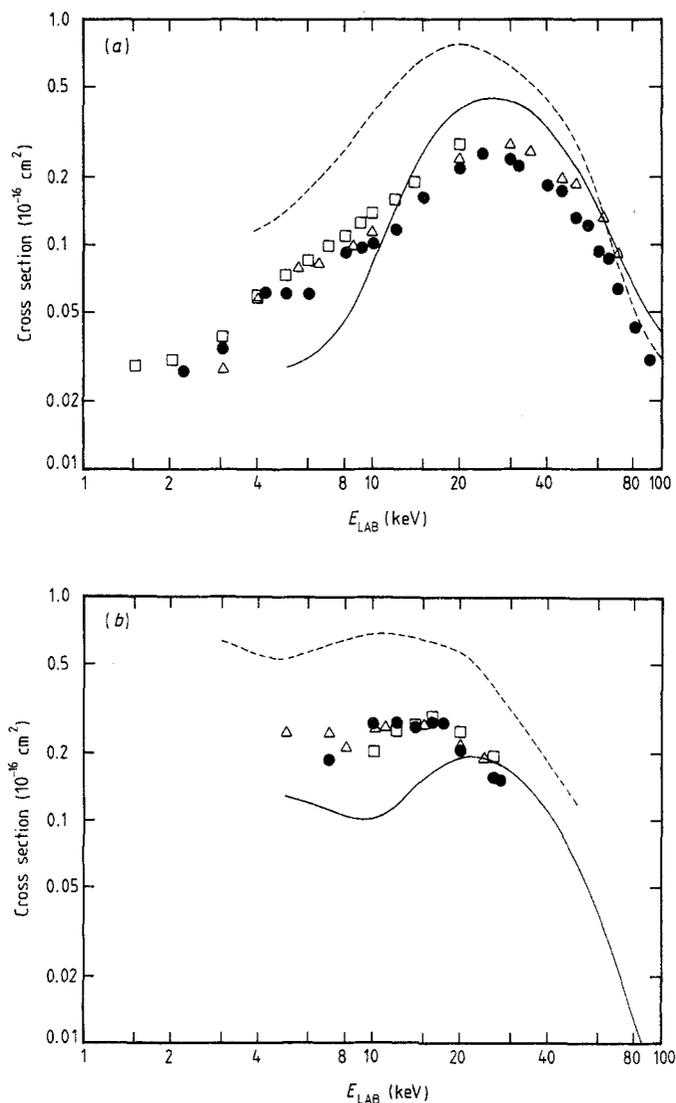


Figure 3. (a) The cross section for capture into H(2s) in the $H^+ + H_2$ collision. Theory: full curve, present results; Broken curve, twice the calculated cross section for the $H^+ + H$ system. Experiment: Δ , Bayfield (1969); \square , Hill *et al* (1979); \bullet , Morgan (1989). (b) The cross section for capture into H(2p) in the $H^+ + H_2$ collision. Theory: as in figure 3(a). Experiment: \square , Andreev *et al* (1967); Δ , Birley and McNeal (1972); \bullet , Morgan *et al* (1973).

orientation-dependent atomic model proposed by Shingal and Lin (1989) is capable of reproducing the major features of ion-molecule collisions. To explore whether the model also works for the smaller electron transfer channels, we have applied the model to study electron capture to 2s and 2p states by H^+ on H_2 targets. These computed cross sections are compared with the available experimental data in figure 3. A reasonable agreement with the experimental measurements has also been seen. For impact energies at and below 10 keV the computed 2s capture cross section lies below the experimental data, whereas at higher energies it overestimates the measurements. However, the shape of the experimental data is reasonably well reproduced for impact energies above 10 keV. For capture to 2p states, the calculated cross sections are compared with the experimental data in the 4–30 keV energy region. Our results in this energy region are not in very good agreement with the experiment. On the other hand, the distinct shoulder in the 2p capture cross section is consistent with the recent experimental data of van Zyl *et al* (1989) where the shoulder was observed at around 3 keV. For comparison, in each case we also show a curve which is twice the capture cross section from the atomic hydrogen target. These later results are obtained if one assumes that the two atoms in the target molecule are completely random in motion.

To summarise, the differential total charge transfer probability at a large laboratory scattering angle of 3° for $H^+ + H_2$ collision has been calculated using the recently proposed orientation-dependent atomic model for charge transfer in ion-molecule collisions. Excellent agreement between the theory and the measurements of Lockwood and Everhart (1962) has been found. The calculated cross section for capture to the 2s and 2p states of the hydrogen atom in proton- H_2 collisions have also been found to be in reasonable agreement with the available experimental data. The calculated partial capture cross section for the $H^+ + H_2$ collision has been found not to be equal to twice the corresponding capture cross section for the $H^+ + H$ collision.

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