PHYSICAL REVIEW A VOLUME 27, NUMBER 6 JUNE 1983

Coupled-state calculations for excitation, charge transfer, and ionization in 1–75-keV proton–hydrogen-atom collisions

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(Received 15 March 1983)

Coupled-state calculations based upon a two-center expansion in atomic orbitals and pseudostates have been performed for $H^+ + H$ in the 1–75-keV region. Cross sections for excitation and charge transfer to $n = 2$ states as well as total ionization cross sections are reported. It is shown that the calculated cross sections are not sensitive to the specific set of pseudostates included if the low-energy continuum states are reasonably well represented. The present results compare favorably with several sets of experimental data and with some large-scale calculations. The need for further experimental data in some areas is discussed.

The proton–hydrogen-atom collision system has been studied extensively within various theoretical models and in several experiments, but discrepancies among theoretical calculations and among experimental results are still quite large. In this Communication we report new results from coupled-state calculations for excitation, charge transfer, and ionization cross sections in the 1–75-keV region. We point out areas where experimental data are now well confirmed by theoretical calculations as well as areas where further theoretical and experimental investigations are still needed.

In the energy range mentioned, excitation, charge transfer, and ionization processes are strongly coupled in the geometrical interaction region and thus nonperturbative approaches are needed. Coupled-state calculations and direct numerical integration of the time-dependent Schrödinger equation (TDSE) are well established examples of nonperturbative approaches. In the low-energy regime ($E \leq 7$ keV), coupled-state calculations using traveling molecular base functions have been carried out recently by two groups.[1,2] In these studies, excitation and charge transfer to $2s$ and $2p$ orbitals were investigated with the same set of molecular orbitals but different electron translational factors (ETF's). Calculated cross sections from these two studies differ significantly for excitation and charge transfer to $2s$ orbitals. In recent work covering the 1–50-keV region, Lüdde and Dreizler[3] adopted an expansion of the electronic wave function in terms of a large basis set ($N = 120$) of Hylleraas-type functions. In another investigation, Terlecki, Grun, and Scheid[4] solved the TDSE numerically to obtain total charge transfer and ionization cross sections in the higher-energy region ($E \geq 30$ keV). In an earlier work, Shakeshaft[5] used scaled hydrogenic wave functions in a two-center expansion (35 functions on each center) to calculate excitation and charge transfer to $n = 2$ and $n = 3$ states, as well as ionization cross sections for $15 \leq E \leq 200$ keV.

In a recent article,[6(a)] we proposed a modified two-center atomic-orbital expansion method (AO+) for studying slow ion-atom collisions. This is a generalization of the conventional two-center atomic-orbital expansion method[7] in that, in addition to orbitals of the separated atoms, some united-atom orbitals are explicitly included into the expansion. It has been demonstrated in several studies[6] that the molecular correlation diagram of the collision system can be accurately reproduced with such AO+ expansion. It is this feature of the AO+ expansions which lends them as an alternative to molecular-orbital (MO) expansions for use in collision studies at low energies. It is noted that, since each atomic orbital is associated with one of the collision centers, there is no ambiguity in the choice of electron translational factors in the AO-type expansions. We have applied the AO+ description to study[6(c)] excitation and charge transfer to $2s$ and $2p$ states in $H^+ + H$ collisions for $E = 1$–20 keV. Partial cross sections from these calculations agree well with results from the MO calculations of Kimura and Thorson[2] for $E \leq 6$ keV. At higher energies, the AO+ results are still in good accord with experimental data while MO results show increasing deviations.

At energies above 15 keV, a gradual failure of the AO+ model has been observed. It has been argued that this failure originates from the lack of properly representing ionization channels in the AO+ expansion. While ionization is not significant at low collision energies, it does contribute considerably to inelastic processes at higher energies. In this Com-

TABLE I. Parameters for the hydrogenic basis function. For each nl hydrogenlike orbital, the effective charge Z is specified. The entries for E_i are the eigenenergies of atomic and pseudostates obtained from diagonalizing the hydrogenic Hamiltonian within the basis.

ns	Z	E_i (a.u.)	np	Z	E_i (a.u.)
$1s$	1.0	−0.5	$2p$	1.0	−0.125
$2s$	1.0	−0.125	$2p$	0.666	−0.0555
$1s$	0.5	−0.0555	$2p$	1.8	−0.0196
$3s$	1.0	−0.0129	$2p$	2.9	0.1309
$1s$	0.8	0.1342	$2p$	4.48	0.8299
$1s$	1.25	0.6117	$3p$	1.0	4.5760
$1s$	1.563	2.3372			
$1s$	2.441	13.1746			

munication we report new results for excitation and charge transfer to $n=2$ states, excitation to $n=3$ states, as well as total ionization cross sections in AO+-type calculations modified such that ionization channels are included in the expansion basis.

In the present study, the continuum states at target and projectile are represented in terms of square-integrable functions. Basically, these pseudostates are obtained by diagonalizing the hydrogenic Hamiltonian within a set of Slater orbitals. The precise form of the slater orbitals is not important except that there should be a few $(3\sim4)$ pseudostates within an energy band of $1\sim2$ a.u. above the ionization threshold such as to represent the low-energy continuum electron states of the ionization channels. In this respect we differ from other studies[5] where particular forms of pseudostates were often emphasized. In order to test this assumption, we have calculated ionization cross sections with different sets of pseudostates. A convenient check, e.g., consists of calculating direct Coulomb ionization cross sections using first-order perturbation theory and comparing the results to cross sections obtained from the semiclassical approximation (SCA), the latter involving exact continuum wave functions. In a later publication, details of this check will be shown. We only point out here that ionization cross sections thus computed from different sets (orbital angular momentum $l=0,1$) agree with each other and with exact SCA results[8] at all energies to better than 5%. When these sets were used in full coupled-state calculations, the agreement still remains to be within 10%.

The computer code used in the present calculation is conveniently modified from the program used earlier for the AO+ model. To minimize the modifications, we actually expressed our pseudostates in terms of linear combination of hydrogenic orbitals. Table I lists the quantum numbers nl and effective charges used in the basis (at each center) and the resulting energy spectrum after diagonalization of the atomic Hamiltonian. After the basis functions have been defined, the solution of the TDSE follows the standard procedure.[6] In terms of the basis functions listed in Table I, there are 20 atomic states on each center.

In Fig. 1, we show cross sections for excitations to $2s$ and $2p$ states for collision energies 1–75 keV. The present results, shown in solid lines, are in overall good accord with experimental data[9–12] over the energy range shown. Particularly, the experimental data

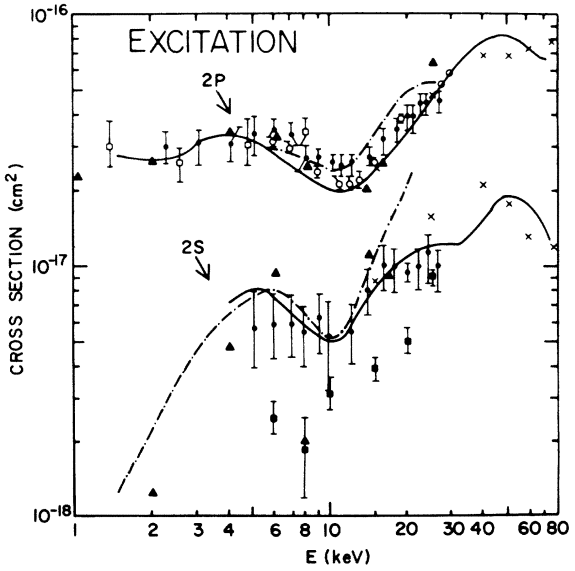

FIG. 1. Cross sections for excitation of atomic hydrogen to $2s$ and $2p$ levels by proton impact. Experimental: ●, Morgan *et al.* (Ref. 9); ⊞, Stebbings *et al.*, (Ref. 10); ⊕, Kondow *et al.* (Ref. 11); ■, Chong and Fite (Ref. 12). Theoretical: solid lines, present calculation; dash-dot curves, earlier 22AO+ calculations [Ref. 6(c)]; ×, Shakeshaft (Ref. 5); ▲, Lüdde and Dreizler (Ref. 3).

for excitation to $2p$ state from different laboratories are in reasonably good agreement among each other and they are well confirmed by the present calculation. For excitation to $2s$ state, there are only two measurements,[9,12] both in the 5–30-keV region. The results of Morgan, Geddes, and Gilbody[9] are in good agreement with our calculations, while the data by Chong and Fite[12] are much lower. At low energies, the present results do not differ from the earlier 22AO+ results[6(c)] (shown in dash-dot lines), but at higher energies, the effect of including ionization channels for improving excitation to $2s$ and $2p$ states is clearly seen. We also show the results of calculations by Lüdde and Dreizler.[3] While those cross sections are in rough agreement with the present ones, it appears that they scatter more around experimental data than the present results do. Comparisons with MO calculations at low energies can be found in Ref. 6(c) and will not be repeated here. The present resutls in the 30–75-keV region, while quite close to Shakeshaft's results,[5] do show a slightly different energy dependence.

In Fig. 2 we show cross sections for capture to $2s$ and $2p$ states. The present results (in solid lines) again show improvement over the earlier 22AO+ results (in dash-dot lines) and are in good agreement with experimental data.[9,13–15] We note that experimental data for capture to $2p$ state in the 3–9-keV region still differ among each other by 50% and that our results are in better agreement with the data by Morgan *et al.*[9] At higher energies, the experimental data for $2p$ state are consistently lower than our calculations, although our calculations are in good agreement with Shakeshaft's[5] results in this region.

In Fig. 3 we show the total excitation cross sections to $n=2$ and $n=3$ states in the 10–80-keV region measured by Park *et al.*[16] Theoretical calculations from the present work and from Shakeshaft[5] are also shown for comparison. We notice that the general agreement is quite good, although small deviations do still exist. In order to calculate excitation to $n=3$ states shown in Fig. 3, H $3d$ orbitals were added at each center in addition to those shown in Table I.

In Fig. 4 total ionization cross sections from the present work are shown in the 3–75-keV region. They are compared with the data by Shah and Gilbody[17] for $E \geq 34$ keV, by Park *et al.*[18] and by Fite *et al.*[19] at lower energies. Results of calculations by Shakeshaft[5] and by Terlecki *et al.*[4] are also shown. At higher energies, experimental data and theoretical results are in rough harmony although deviations among theoretical results amount to up to 70%. The present results agree with Shakeshaft's at 25 and 15 keV, and show the same slope as the data by Shah and Gilbody, while those by Terlecki *et al.* are larger. In checking the convergence of the present calculation, bound and continuum d orbitals should be included as they have been in Shakeshaft's study. In first calculations it turns out that the inclusion of hydrogenic $3d$ orbitals does not significantly alter the ionization results. Calculations including d continuum pseudostates are time consuming and have not been undertaken here. These states are likely to account for the difference between our results and

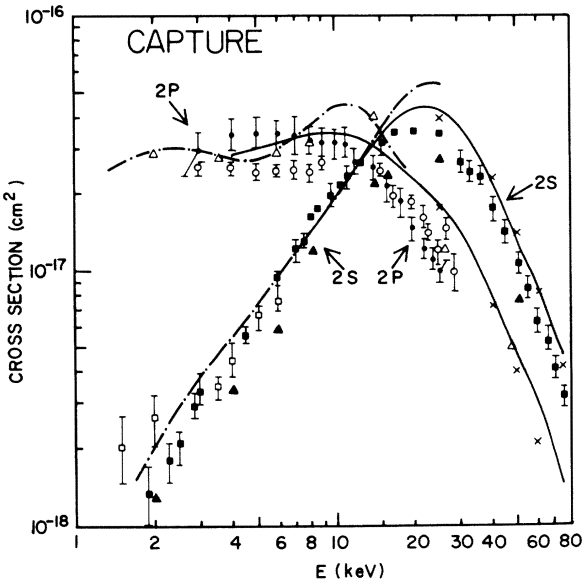

FIG. 2. Cross sections for charge transfer to $2s$ and $2p$ levels of atomic hydrogen by proton impact. Experimental: ⧳, Morgan *et al.* (Ref. 9); ⧲, Hill *et al.* (Ref. 13); ⧳, Morgan *et al.* (Ref. 14); ⧲, Kondow *et al.* (Ref. 15). Theoretical: solid curves, present results; —·—·, earlier AO+ calculations [Ref. 6(c)]; ▲ and Δ, $2s$ and $2p$, respectively, from Lüdde and Dreizler (Ref. 3); ×, Shakeshaft (Ref. 5).

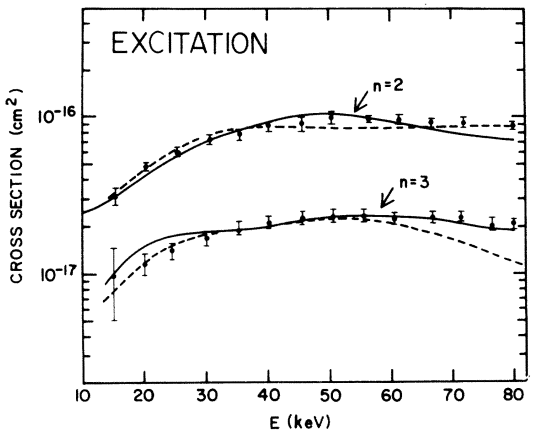

FIG. 3. Cross sections for excitation of atomic hydrogen to $n=2$ and $n=3$ states by proton impact. Experimental data from Park *et al.* (Ref. 16); solid lines from the present work and dashed lines from Shakeshaft (Ref. 5).

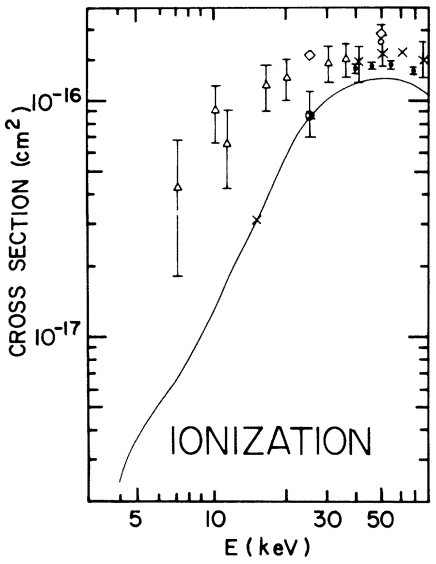

FIG. 4. Total ionization cross sections of atomic hydrogen by proton impact. Experimental: ●, Shah and Gilbody (Ref. 17); ⊕, Park *et al.* (Ref. 18); ⊼, Fite *et al.* (Ref. 19). Theoretical: solid curve, present 46AO+; ×, Shakeshaft (Ref. 5); ◇, TDSE (Ref. 4).

those of Shakeshaft in the higher-energy region. (It might as well be possible that orbitals with even higher angular momenta are needed to obtain converged results.) In the lower-energy region ($E < 30$ keV), it is desirable to have new experimental ionization cross sections with smaller error bars to check the accuracy of the present results.

In summary, results of coupled-state calculations for excitation, charge transfer, and ionization cross sections in $H^+ + H$ collisions are presented. We stress that continuum states can be reasonably well represented in terms of square-integrable functions. Calculated results appear to be insensitive to details of the choice of pseudostates. It is illustrated that excitation and charged transfer to $n = 2$ states can be accurately predicted for $E \geq 15$ keV only if ionization channels are included. The present results are in general agreement with experimental data. As for ionization cross sections, the situation is still not satisfactory and new data at low energies are desirable.

One of us (C.D.L.) acknowledges support from the U.S. Department of Energy, Division of Chemical Sciences, and from the Alfred P. Sloan Foundation.

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