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PROTON–HYDROGEN COLLISIONS: DIFFERENTIAL AND TOTAL CROSS SECTIONS FOR H(2s) AND H(2p) PRODUCTION IN THE 1–7 keV RANGE

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CONTENTS

A multistate molecular approach to the proton–hydrogen collision is formulated in terms of an impact parameter perturbed stationary-states approximation. Spurious long range couplings are avoided and Galilean invariance is enforced by the inclusion of momentum translation factors which are determined variationally within an Euler–Lagrange formalism (Crothers & Hughes 1978). Well defined radial and rotational coupling matrix elements are employed in the 1–7 keV impact energy range in a six-state ($1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $3p\sigma_u$, $3p\pi_u$, $4f\sigma_u$) calculation of elastic and inelastic differential scattering cross sections, charge exchange probabilities and both direct and exchange H(2p) production total cross sections. They are also employed in the same energy range in a ten-state ($1s\sigma_g$, $2p\sigma_u$, $3d\pi_g$, $2p\pi_u$, $2s\sigma_g$, $3p\sigma_u$, $3d\sigma_g$, $4f\sigma_u$, $4d\pi_g$, $3p\pi_u$) calculation of both direct and exchange H(2s) production total cross sections.

The results are in excellent accord with experimental data and show considerable improvement on previous molecular calculations. This success is attributed to the inclusion of both momentum translation factors and radial coupling matrix elements.

1. Introduction

Despite its simplicity, the proton–hydrogen atom collision continues to be a non-trivial prototype for homonuclear ion–atom collisions. Whether between theory and experiment or experiment and experiment, there remains disagreement which is more or less according to energy

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range, angle and final-state products as reviewed, for instance, by Bates (1962), Bates & McCarroll (1962), Mott & Massey (1965), Bransden (1970), McDowell & Coleman (1970), Mapleton (1972), Massey & Gilbody (1974), Gayet (1977) and Basu *et al.* 1978. To be concrete, we shall restrict our attention to elastic scattering, charge transfer and excitation at non-relativistic energies. We shall, however, not be concerned with very low energies ($\lesssim$ 200 eV), at which a number of quantal or semiquantal calculations has been performed (Dalgarno & Yadav 1953; Smith 1964, 1967; Crothers *et al.* 1968; Knudson & Thorson 1970; Kubach & Sidis 1975; Matveenko & Ponomarev 1975; Hunter & Kuriyan 1977*a*, *b*; Davis & Thorson 1978). In the last sixteen years there have been a number of experiments (Lockwood & Everhart 1962; Helbig & Everhart 1965; Stebbings *et al.* 1965; Ryding *et al.* 1966; Young *et al.* 1968; Bayfield 1969, 1970; Kauppila *et al.* 1970; Morgan *et al.* 1973; Houver *et al.* 1974; Park *et al.* 1975; Park *et al.* 1976; Chong & Fite 1977; Park *et al.* 1978). Theoretically, there are a considerable number of approaches, which are more likely to be valid at high energies ($\gtrsim$ 25 keV) but which are frequently quite accurate in the intermediate energy range, perhaps down to 10 keV. These include O.B.K., first, second and higher Born, distortion, distorted wave, Glauber, eikonal, impulse, continuum distorted wave, continuum intermediate states, Fadeev, second order potential, classical and refined-orthogonal close coupling of a linear combination of atomic orbitals (l.c.a.o.) as well as a variety of hybrids (see, for example, Thomas 1927; Oppenheimer 1928; Brinkman & Kramers 1930; Jackson & Schiff 1953; Bates & Dalgarno 1953; Bates & Griffing 1953; Bates 1958*b*; Bates 1959; McCarroll 1961; Mapleton 1962; Bransden & Cheshire 1963; McElroy 1963; Cheshire 1964; Lovell & McElroy 1965; Coleman & McDowell 1965, 1966; Wilets & Gallaher 1966; Cheshire & Sullivan 1967; Coleman 1968; Flannery 1969; Salin 1970; Shastry *et al.* 1970; Ghosh & Sil 1971; Franco & Thomas 1971; Chen & Hambro 1971; Chen & Kramer 1971, 1972; Shastry *et al.* 1972; Rapp & Dinwiddie 1972; Rapp *et al.* 1972; Bransden *et al.* 1972; Sullivan *et al.* 1972; Baye & Heenen 1973; Band 1973*a*, *b*, *c*; Joachain & Vanderpoorten 1973; Gryzinski 1973; Winter & Lin 1974; Demkov & Ostrovskii 1975; Sil *et al.* 1975; Saha *et al.* 1976; Belkic 1977; Glembocki & Halpern 1977; Fitchard *et al.* 1977; Dewangan 1977; Morrison & Öpik 1978; Tripathy & Rao 1978).

The remaining energy range (*ca.* 200 eV–10 keV), in which a molecular treatment would appear more appropriate, may be subdivided at approximately 1 keV. Above 1 keV, and following the pioneering work of Mott (1931), Massey & Smith (1933) and Bates *et al.* (1953), Bates & McCarroll (1958) formulated a satisfactory impact-parameter perturbed stationary-state (p.s.s.) treatment which avoided spurious long range couplings and enforced Galilean invariance through the inclusion of momentum translation factors. It was applied in the two state approximation by Ferguson (1961), and later, in the three state approximation and in the low velocity limit by Bates & Williams (1964), and McCarroll & Piacentini (1970). Later impact parameter multistate p.s.s. treatments (Rosenthal 1971; Chidichimo-Frank & Piacentini 1974; Schinke & Krüger 1976*b*) were unfortunately not Galilean invariant and did involve spurious long range couplings. Of course, other impact-parameter treatments have sought to simulate the molecular features of the collision at 1 keV, while still retaining the correct l.c.a.o. behaviour at higher energies and larger impact parameters. These include Sturmian states (Gallaher & Wilets 1968; Shakeshaft 1975, 1976), triple-centre approximation (Antal *et al.* 1975), Gaussian orbitals (Dose & Semini 1975), variational effective charge theory (Cheshire 1968; McCarroll *et al.* 1970) and notably pseudo-states (Cheshire *et al.* 1970).

Below 1 keV, and particularly for differential cross sections, classical-path p.s.s. models have been developed to exploit the semiclassical nature of the collision while permitting possibly substantial deviations from straight-line impact-parameter paths.[†] These include the models used by Chen & Watson (1969), Knudson & Thorson (1970), Bates & Sprevak (1970), Corrigall & Wallace (1971), Corrigall *et al.* (1971), Chen *et al.* (1972, 1973*a*), Chen *et al.* (1973*b*), Gaussorgues *et al.* (1975*a*, *b*), Hatton *et al.* (1975), Schinke & Krüger (1976*b*) and Cayford & Fimple (1976), although in our view none of these models applies a completely consistent, multistate, Galilean-invariant classical-path theory.

Recently, Crothers & Hughes (1978) have improved the impact parameter p.s.s. theory of Bates & McCarroll (1958) by determining the momentum translation factors variationally. They were thus able to provide an extremely accurate description of proton hydrogen close-capture collision spectroscopy. In particular the locations of the turning points in the curve of capture probability against energy for large-angle scattering were found to be in excellent agreement with experiment (Lockwood & Everhart 1962) and to compare more than favourably with previous extremely elaborate calculations (Gallaher & Wilets 1968; Cheshire *et al.* 1970). The purpose of this paper is to adapt the method of Crothers & Hughes to provide a multistate molecular description of the proton–hydrogen collision at energies not less than 1 keV.

In § 2, we compare our well defined radial and rotational couplings with the more prevalent spurious couplings of other authors. In § 3, we present elastic and inelastic (both direct and exchange) differential cross sections, together with total and fractional charge exchange probabilities. In § 4, we compare experiment with our total cross sections for 2s and 2p production, for both exchange and excitation.

2. Well defined radial and rotational couplings

The original version of the p.s.s. approximation was thought to tend to the first Born approximation in the high-velocity and weak-interaction limit. Thus, it was assumed that all transitions, except that from the initial state p to the final state q, may be ignored in treating slow heteronuclear collisions and it was deduced that the probability of charge exchange is given by

$$P_{pq} = \frac{1}{v^2}\left|\int_{-\infty}^{+\infty} \mathscr{M}_{qp}(\boldsymbol{R}) \exp\left\{-\frac{\mathrm{i}}{v}\int_0^Z (\epsilon_p(R)-\epsilon_q(R))\,\mathrm{d}Z'\right\}\mathrm{d}Z\right|^2 \tag{1}$$

where

$$\mathscr{M}_{qp}(\boldsymbol{R}) = \int \chi_q^{\mathrm{B}*}\left(\frac{\partial}{\partial Z_{r_{\mathrm{A}}}}\chi_p^{\mathrm{A}}\right)\exp(-\mathrm{i}vz)\,\mathrm{d}\boldsymbol{r}, \tag{2}$$

and where, as below, the notation of Crothers & Hughes 1978 (to be referred to as I) is followed, except that the molecular wavefunctions χ in (2) have, in addition to the state label as subscript, a superscript which denotes the nucleus to which the electron attaches in the separated-atoms limit.

This procedure is incorrect except in special cases (Bates 1957*a*, *b*, 1958*a*), the improper simplification being the omission of strong coupling terms introduced by the rotation of the polar axis of the basis functions, this being the internuclear line. The electronic motion cannot readily follow this rotation and this is manifested through there being a high probability of transitions occurring between states differing in the magnetic quantum number m. (This

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[†] This is not to say that curved impact-parameter paths are not required for large angle scattering at or above 1 keV (see § 3).

accounts for instance for the high probability of $2p\sigma_u$–$2p\pi_u$ transitions in very close proton–hydrogen collisions (Bates & Williams 1964; Bates & Sprevak 1970).) Consequently, states additional to the initial and final states must in general be taken into account.

On the other hand, and of direct relevance to this paper, the simplest homonuclear molecule H_2^+ possesses many states having potential energy surfaces in close proximity and within a relatively small energy interval from that of the first excited state. The inclusion of one of these states seemingly necessitates the inclusion of another and, as we proceed along the sequence to higher states, coupling becomes increasingly effective and the margin by which I(3) is satisfied diminishes (see Bates 1970). The purpose of this paper is to show that nevertheless quite accurate results may be obtained by sensibly truncating the infinite molecular basis set. In fact, we shall consider up to ten molecular states, namely:

$$\chi_0^+ \equiv |1s\sigma_g\rangle \rightarrow \tfrac{1}{\sqrt{2}}[\phi_{1s}^{A}(\boldsymbol{r}_A) + \phi_{1s}^{B}(\boldsymbol{r}_B)], \tag{3}$$

$$\chi_0^- \equiv |2p\sigma_u\rangle \rightarrow \tfrac{1}{\sqrt{2}}[\phi_{1s}^{A}(\boldsymbol{r}_A) - \phi_{1s}^{B}(\boldsymbol{r}_B)], \tag{4}$$

$$\chi_1^+ \equiv |3d\pi_g\rangle \rightarrow \tfrac{1}{\sqrt{2}}[\phi_{2p_{\pm1}}^{A}(\boldsymbol{r}_A) + \phi_{2p_{\pm1}}^{B}(\boldsymbol{r}_B)], \tag{5}$$

$$\chi_1^- \equiv |2p\pi_u\rangle \rightarrow \tfrac{1}{\sqrt{2}}[\phi_{2p_{\pm1}}^{A}(\boldsymbol{r}_A) - \phi_{2p_{\pm1}}^{B}(\boldsymbol{r}_B)], \tag{6}$$

$$\chi_2^+ \equiv |2s\sigma_g\rangle \rightarrow \tfrac{1}{2}[\phi_{2s}^{A}(\boldsymbol{r}_A) + \phi_{2s}^{B}(\boldsymbol{r}_B) - \phi_{2p_0}^{A}(\boldsymbol{r}_A) - \phi_{2p_0}^{B}(\boldsymbol{r}_B)], \tag{7}$$

$$\chi_2^- \equiv |3p\sigma_u\rangle \rightarrow \tfrac{1}{2}[\phi_{2s}^{A}(\boldsymbol{r}_A) - \phi_{2s}^{B}(\boldsymbol{r}_B) - \phi_{2p_0}^{A}(\boldsymbol{r}_A) + \phi_{2p_0}^{B}(\boldsymbol{r}_B)], \tag{8}$$

$$\chi_3^+ \equiv |3d\sigma_g\rangle \rightarrow \tfrac{1}{2}[\phi_{2s}^{A}(\boldsymbol{r}_A) + \phi_{2s}^{B}(\boldsymbol{r}_B) + \phi_{2p_0}^{A}(\boldsymbol{r}_A) + \phi_{2p_0}^{B}(\boldsymbol{r}_B)], \tag{9}$$

$$\chi_3^- \equiv |4f\sigma_u\rangle \rightarrow \tfrac{1}{2}[\phi_{2s}^{A}(\boldsymbol{r}_A) - \phi_{2s}^{B}(\boldsymbol{r}_B) + \phi_{2p_0}^{A}(\boldsymbol{r}_A) - \phi_{2p_0}^{B}(\boldsymbol{r}_B)], \tag{10}$$

$$\chi_4^+ \equiv |4d\pi_g\rangle \rightarrow \tfrac{1}{\sqrt{2}}[\phi_{3p_{\pm1}}^{A}(\boldsymbol{r}_A) + \phi_{3p_{\pm1}}^{B}(\boldsymbol{r}_B)], \tag{11}$$

$$\chi_4^- \equiv |3p\pi_u\rangle \rightarrow \tfrac{1}{\sqrt{2}}[\phi_{3p_{\pm1}}^{A}(\boldsymbol{r}_A) - \phi_{3p_{\pm1}}^{A}(\boldsymbol{r}_B)], \tag{12}$$

where the $\phi_{nl}^{A,B}$ denote the hydrogen-atom states, appropriate to the asymptotic separated-atoms limit. Thus, for example, the transition amplitude for H(2s) andH($2p_0$) direct and exchange excitation are formed from linear combinations of the amplitudes associated with the $2s\sigma_g$, $3p\sigma_u$, $3d\sigma_g$ and $4f\sigma_u$ states.

As a further guide to our studies, we may recall that for a collision between a proton and a hydrogen atom, the initial amplitude is equally divided between the $1s\sigma_g$ and $2p\sigma_u$ states and in the course of the collision, *gerade* and *ungerade* states are uncoupled. The $2p\sigma_u$ state is radially coupled to $3p\sigma_u$ and, at small internuclear separations, it is strongly coupled rotationally to $2p\pi_u$. In the asymptotic region the $2p\pi_u$ state is rotationally coupled to both the $3p\sigma_u$ and $4f\sigma_u$ states. The $3p\pi_u$ state goes asymptotically to the $n = 3$ level, but at small R it is strongly coupled rotationally to the $3p\sigma_u$ state. Its inclusion is therefore necessary, as for the $2p\pi_u$, to give expression to the great reluctance of the electronic motion to follow the rotation of the polar axis at small impact parameters. Coupling between gerade states is very weak in view of the large energy separations between the $1s\sigma_g$ state and even the lower excited gerade states. At comparatively higher energies ($E \gtrsim 5$ keV) however, radial coupling between $1s\sigma_g$, $2s\sigma_g$ and $3d\sigma_g$ becomes increasingly significant.

Substituting I(21) into I(24) gives, setting $s \equiv q$ and $k \equiv p$,

$$\mathrm{i}v \sum_q S_{pq}^{\pm\pm} \frac{\mathrm{d}c_q^{\pm}}{\mathrm{d}Z} = \sum_q F_{pq}^{\pm\pm} c_q^{\pm}, \tag{13}$$

where
$$S_{pq}^{\pm\pm} \equiv \int \Phi_p^{\pm *}\,\Phi_q^{\pm}\,\mathrm{d}\boldsymbol{r} \tag{14}$$
$$= \tfrac{1}{2}\exp\left\{-\frac{\mathrm{i}}{v}\int_0^Z \{\epsilon_p^{\pm}(R)-\epsilon_q^{\pm}(R)\}\,\mathrm{d}Z'\right\}\int \mathrm{d}\boldsymbol{r}\,[(\chi_p^+\,\chi_q^+ - \chi_p^-\,\chi_q^-)$$
$$\pm\{(\chi_p^+\,\chi_q^+ - \chi_p^-\,\chi_q^-)\cos(vfz) - \mathrm{i}(\chi_p^+\,\chi_q^- - \chi_p^-\,\chi_q^+)\sin(vfz)\}] \tag{15}$$

and
$$F_{pq}^{\pm\pm} \equiv \int \Phi_p^{\pm *}\left\{H_e - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t_r}\right\}\Phi_q^{\pm}\,\mathrm{d}\boldsymbol{r} \tag{16}$$
$$= (\mathrm{i}\alpha_{pq}^{\pm} + \beta_{pq}^{\pm})\exp\left\{-\frac{\mathrm{i}}{v}\int_0^Z (\epsilon_p^{\pm}(R) - \epsilon_q^{\pm}(R)\}\,\mathrm{d}Z'\right\}, \tag{17}$$

in which
$$\alpha_{pq}^{\pm} = \tfrac{1}{2}\{\epsilon_q^{\mp}(R) - \epsilon_q^{\pm}(R)\}\int \chi_p^{\pm}\,\chi_q^{\mp}\sin(vfz)\,\mathrm{d}\boldsymbol{r}$$
$$+\tfrac{1}{2}vf\int\left\{\chi_p^{\mp}\frac{\partial\chi_q^{\pm}}{\partial z}\sin^2(\tfrac{1}{2}vfz) + \chi_p^{\pm}\frac{\partial\chi_q^{\mp}}{\partial z}\cos^2(\tfrac{1}{2}vfz)\right\}\mathrm{d}\boldsymbol{r}$$
$$-v\int\left\{\chi_p^{\pm}\frac{\partial\chi_q^{\pm}}{\partial Z_r}\cos^2(\tfrac{1}{2}vfz) + \chi_p^{\mp}\frac{\partial\chi_q^{\mp}}{\partial Z_r}\sin^2(\tfrac{1}{2}vfz)\right\}\mathrm{d}\boldsymbol{r}$$
$$+\tfrac{1}{4}v^2\frac{\mathrm{d}f}{\mathrm{d}Z}\int\{\chi_p^{\pm}\,z\chi_q^{\pm} - \chi_p^{\mp}\,z\chi_q^{\mp}\}\sin(vfz)\,\mathrm{d}\boldsymbol{r} \tag{18}$$

and
$$\beta_{pq}^{\pm} = \{\epsilon_q^{\mp}(R) - \epsilon_q^{\pm}(R)\}\int \chi_p^{\mp}\,\chi_q^{\mp}\sin^2(\tfrac{1}{2}vfz)\,\mathrm{d}\boldsymbol{r}$$
$$+\tfrac{1}{4}vf\int\left\{\chi_p^{\pm}\frac{\partial\chi_q^{\pm}}{\partial z} - \chi_p^{\mp}\frac{\partial\chi_q^{\mp}}{\partial z}\right\}\sin(vfz)\,\mathrm{d}\boldsymbol{r} + \tfrac{1}{2}v\int\left\{\chi_p^{\mp}\frac{\partial\chi_q^{\pm}}{\partial Z_r} + \chi_p^{\pm}\frac{\partial\chi_q^{\mp}}{\partial Z_r}\right\}\sin(vfz)\,\mathrm{d}\boldsymbol{r}$$
$$-\tfrac{1}{2}v^2\frac{\mathrm{d}f}{\mathrm{d}Z}\int\{\chi_p^{\mp}\,z\chi_q^{\pm}\sin^2(\tfrac{1}{2}vfz) + \chi_p^{\pm}\,z\chi_q^{\mp}\cos^2(\tfrac{1}{2}vfz)\}\,\mathrm{d}\boldsymbol{r}. \tag{19}$$

As in I, we expand $S_{pq}^{\pm\pm}$ and $F_{pq}^{\pm\pm}$ as power series in v and retain just sufficient terms to give the coefficients in the coupled equations (13) correct to the second power. Separating the derivatives from each other by rearrangement, we then obtain
$$\mathrm{i}v\frac{\mathrm{d}c_p^{\pm}}{\mathrm{d}Z} = \sum_q\{F_{pq}^{\pm\pm} - \sum_{r\neq p,\,q} S_{pr}^{\pm\pm}\,F_{rq}^{\pm\pm}\}\,c_q^{\pm}, \tag{20}$$

where, to the approximation indicated, we have
$$S_{pq}^{\pm\pm} = \pm\tfrac{1}{2}\exp\left\{-\frac{\mathrm{i}}{v}\int_0^Z\{\epsilon_p^{\pm}(R) - \epsilon_q^{\pm}(R)\}\,\mathrm{d}Z'\right\}[\mathrm{i}vf(\mathscr{I}_{pq}^{-+} + \mathscr{I}_{pq}^{+-}) + \tfrac{1}{2}v^2f^2(\mathscr{Q}_{pq}^{--} - \mathscr{Q}_{pq}^{++})] \tag{21}$$
and
$$F_{pq}^{\pm\pm} = \tfrac{1}{2}\exp\left\{-\frac{\mathrm{i}}{v}\int_0^Z\{\epsilon_p^{\pm}(R) - \epsilon_q^{\pm}(R)\}\,\mathrm{d}Z'\right\}[\mathrm{i}v\{f(\epsilon_q^{\pm} - \epsilon_p^{\pm})\,\mathscr{I}_{pq}^{\pm\mp} - 2\mathscr{R}_{pq}^{\pm\pm}\}$$
$$+\tfrac{1}{4}v^2\{f^2(\epsilon_q^{\mp} + \epsilon_p^{\mp} - 2\epsilon_q^{\pm})\,\mathscr{Q}_{pq}^{\mp\mp} + f^2(\epsilon_q^{\pm} - \epsilon_p^{\pm})\,\mathscr{Q}_{pq}^{\pm\pm} \pm 4f(\mathscr{S}_{pq}^{-+} - \mathscr{S}_{pq}^{+-}) - 4(\mathrm{d}f/\mathrm{d}Z)\,\mathscr{I}_{pq}^{\pm\mp}\}], \tag{22}$$

with
$$\mathscr{I}_{pq}^{\pm\mp} \equiv \int \chi_p^{\pm *}\,z\chi_q^{\mp}\,\mathrm{d}\boldsymbol{r}, \tag{23}$$
$$\mathscr{Q}_{pq}^{\pm\pm} \equiv \int \chi_p^{\pm *}\,z^2\chi_q^{\pm}\,\mathrm{d}\boldsymbol{r}, \tag{24}$$
$$\mathscr{R}_{pq}^{\pm\pm} \equiv \int \chi_p^{\pm *}\frac{\partial\chi_q^{\pm}}{\partial Z_r}\,\mathrm{d}\boldsymbol{r}, \tag{25}$$
$$\mathscr{S}_{pq}^{\pm\mp} \equiv \int \chi_p^{\pm *}\,z\frac{\partial\chi_q^{\mp}}{\partial Z_r}\,\mathrm{d}\boldsymbol{r}. \tag{26}$$

Actually, we solve (20) in the form

$$\frac{\mathrm{d}c_p^{\pm}}{\mathrm{d}Z} = -\sum_q A_{pq}^{\pm\pm} c_q^{\pm} \exp\left\{-\frac{\mathrm{i}}{v}\int_0^Z \{\epsilon_q^{\pm}(R)-\epsilon_p^{\pm}(R)\}\,\mathrm{d}Z'\right\}, \tag{27}$$

but with $A_{pq}^{\pm\pm}$ and $A_{qp}^{\pm\pm *}$ replaced by their arithmetic average, as may be justified (Crothers 1979) by a variation–perturbation treatment using orthogonalized bases:

$$\Phi_q^{\pm\prime} = \Phi_q^{\pm} - \tfrac{1}{2} \sum_{p\neq q} S_{pq}^{\pm\pm}\,\Phi_p^{\pm}. \tag{28}$$

In practice, the numerical integration of the system of coupled equations (27) is, by now, a routine matter with the use of the method of Bulirsch & Stoer (1966) as programmed by Gaussorgues *et al.* (1975). It is worth mentioning, however, that, particularly in our problem, great care is required in evaluating phases at large internuclear separations where both Coulomb and inverse-square potentials assume great importance (cf. Bates & Reid 1968). Details are given by Hughes (1978), concerning the combinations of the $c_p^{\pm}$ required to express the transition amplitudes of the various direct and exchange processes.

But perhaps the most significant aspect of the problem is the behaviour of the matrix elements $A_{pq}^{\pm\pm}$ of equation (27). In many recent theoretical investigations of low proton–hydrogen collisions, the translation factors in the basis functions I(22) are neglected *a priori*; that is, $f(R)$ is set equal to zero (cf. Rosenthal 1971; Chidichimo-Frank & Piacentini 1974; Gaussorgues *et al.* 1975*a*, *b*; Schinke & Krüger 1976*a*, *b*; Cayford & Fimple 1976). This procedure leads to a set of differential equations for the expansion coefficients of the form (27) but with

$$A_{pq}^{ii} = A_{qp}^{ii*} = \mathscr{R}_{pq}^{ii} \quad (i \equiv \pm). \tag{29}$$

By contrast, our theory yields coupling matrix elements which, to *first* order in velocity, may be written

$$A_{pq}^{ii} = A_{qp}^{ii*} = \mathscr{R}_{pq}^{ii} - \tfrac{1}{4} f(R)\,\{\epsilon_q^{i}(R)-\epsilon_p^{i}(R)\}\,\{\mathscr{I}_{pq}^{ij}+\mathscr{I}_{pq}^{ji}\}. \tag{30}$$

Here the superscript j is ± according as i is ∓. Formula (30) generalizes the 2pσ–2pπ formula given by equation (18) of Bates & Williams (1964); the only difference is that their f is unity at all separations, which is the asymptotic classical choice of Bates & McCarroll (1958). The essence of our formulation is that Galilean invariance is guaranteed as a result of our variational determination of f in I. Galilean invariance is also guaranteed in the work of Taulbjerg *et al.* (1975) and Fritsch & Wille (1977), but is based on a non-variational choice of $f(\boldsymbol{r}, R)$. The important issue is that the more prevalent choice of $f = 0$ leads to spurious, ill-defined radial and rotational couplings, as we now demonstrate.

The matrix elements $\mathscr{R}_{pq}^{ii}$ may be divided into radial and rotational contributions according to

$$\mathscr{R}_{pq}^{ii} = \frac{Z}{R} D_{pq}^{ii} + \frac{\rho}{R^2} P_{pq}^{ii}, \tag{31}$$

where

$$D_{pq}^{ii} \equiv \left\langle \chi_p^{i} \left| \frac{\mathrm{d}}{\mathrm{d}R_r} \right| \chi_q^{i} \right\rangle \tag{32}$$

and

$$P_{pq}^{ii} \equiv \langle \chi_p^{i} \,|\mathrm{i}L_y|\, \chi_q^{i} \rangle, \tag{33}$$

where L_y is the component of the electronic orbital angular momentum along a direction perpendicular to the collision plane. The standard rotational matrix elements P_{pq}^{ii} couple states whose magnetic quantum numbers differ by ±1, while the standard radial matrix elements

D^{ii}_{pq} couple states with the same magnetic quantum number. In our theory, the radial coupling matrix elements are, to first order in velocity, given by

$$D^{ii'}_{pq} = \left\langle \chi^i_p \middle| \frac{\mathrm{d}}{\mathrm{d}R_r} \middle| \chi^i_q \right\rangle - \tfrac{1}{4} f(R)\,(\epsilon^i_q - \epsilon^i_p)\,\{\langle \chi^i_p \,| r\cos\theta |\, \chi^j_q \rangle + \langle \chi^j_p \,| r\cos\theta |\, \chi^i_q \rangle\}, \tag{34}$$

while the rotational matrix elements are given by

$$P^{ii'}_{pq} = \langle \chi^i_p \,| iL_y |\, \chi^i_q \rangle - \tfrac{1}{4} R f(R)\,(\epsilon^i_q - \epsilon^i_p)\,\{\langle \chi^i_p \,| r\sin\theta\cos\phi |\, \chi^j_q \rangle + \langle \chi^j_p \,| r\sin\theta\cos\phi |\, \chi^i_q \rangle\}. \tag{35}$$

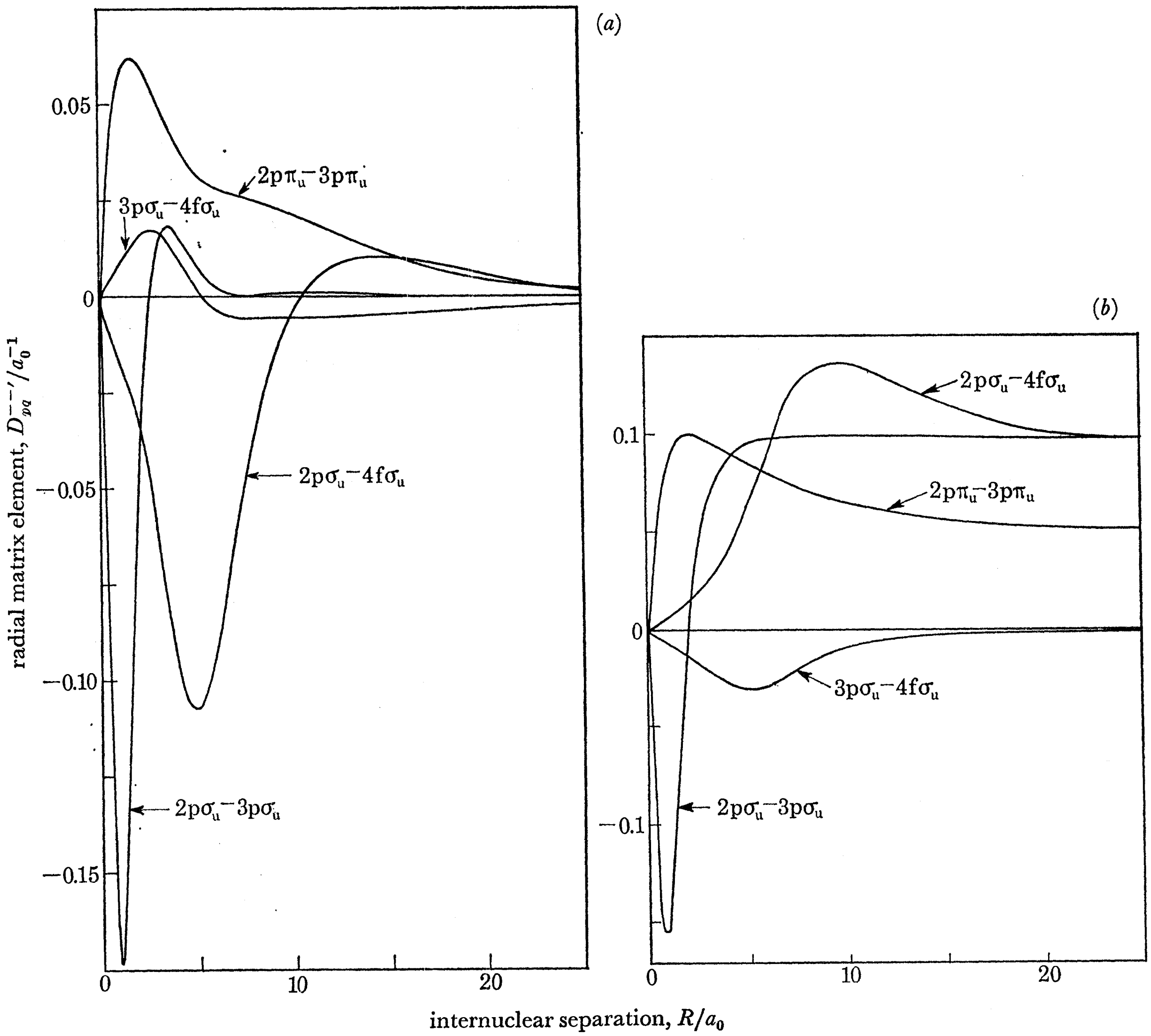

FIGURE 1. (*a*) The radial matrix elements $D^{--'}_{pq}$ of text. (*b*) The radial elements D^{--}_{pq} of text. The values of p and q are given by the curve labels.

We have already outlined in I our methods for calculating matrix elements such as these and so we shall omit further details. In any case, Salin (1978) has recently published routines to calculate expressions (32) and (33). We merely mention in passing that one of us (Hughes 1979) has developed a more compact manner for performing the angular integrations by using Clebsch–Gordan coefficients and that, unlike Salin, the sign of our wavefunction is not arbitrary, being dictated by consideration of translation factors in the asymptotic limit.

Our well-defined matrix elements $D^{ii'}_{pq}$ and $P^{ii'}_{pq}$ are illustrated in figures 1 (*a*), 2 (*a*), 3 (*a*) and 4 (*a*), and are contrasted with the standard matrix elements D^{ii}_{pq} and P^{ii}_{pq} which are illustrated in 1 (*b*), 2 (*b*), 3 (*b*) and 4 (*b*) and which may be compared with figures 4 and 5 of Hatton *et al.* (1975). It is clear that, in general, both D^{ii}_{pq} and P^{ii}_{pq} have physically spurious asymptotic behaviour, either tending to constants or, in the case of some rotational couplings, diverging as $R \to \infty$. It is equally clear that the inclusion of variationally determined translation factors in $D^{ii'}_{pq}$ and $P^{ii'}_{pq}$ eliminates this spurious behaviour. For the specific cases of rotational coupling between the pairs of states (3dσg, 3dπg), (4fσu, 2pπu), (2sσg, 3dπg) and (3pσu, 2pπu), long range interactions are present which are generated by the asymptotic rotational coupling between the H(2p$_0$) and H(2p$_{\pm 1}$) atomic states (cf. expressions (5)–(10)). These interactions may only be removed by the use of space-fixed atomic basis sets (Hatton *et al.* 1975).

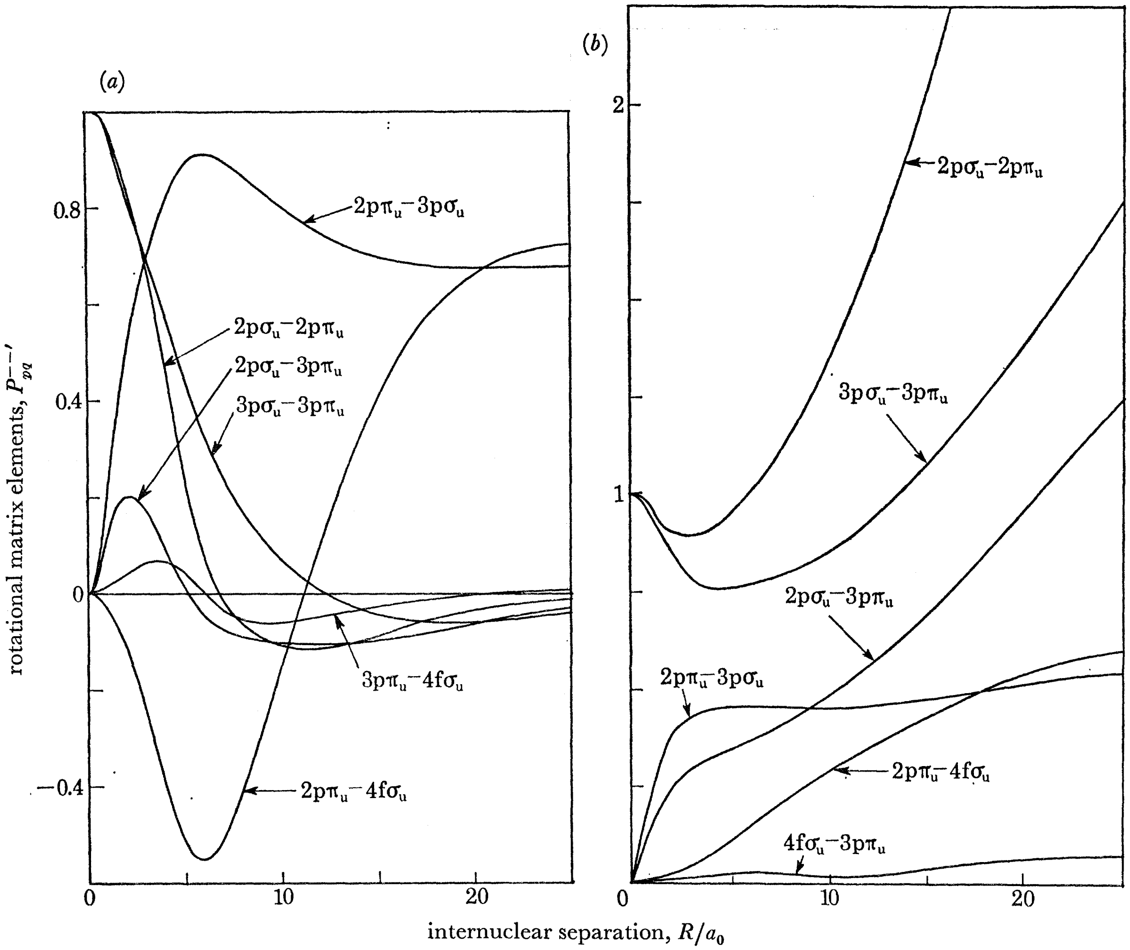

FIGURE 2. (*a*) The rotational matrix elements $P^{--\prime}_{pq}$ of text. (*b*) The rotational matrix elements P^{--}_{pq} of text. Labels as in figure 1.

If the energy is very low ($E \lesssim 1$ keV) and only rotational couplings are taken into account, the spurious asymptotic behaviour of the P^{ii}_{pq} has little affect on the solution of the coupled equations since, due to the action of the operator

$$\dot{\theta} = \rho/R^2, \tag{36}$$

only the near united-atoms form of the matrix elements are of importance (Bates & Sprevak 1971). At higher energies however, or when spurious radial coupling matrix elements are included, some of the transition amplitudes will oscillate indefinitely and the attainment of convergence for the integrated solution becomes impossible.

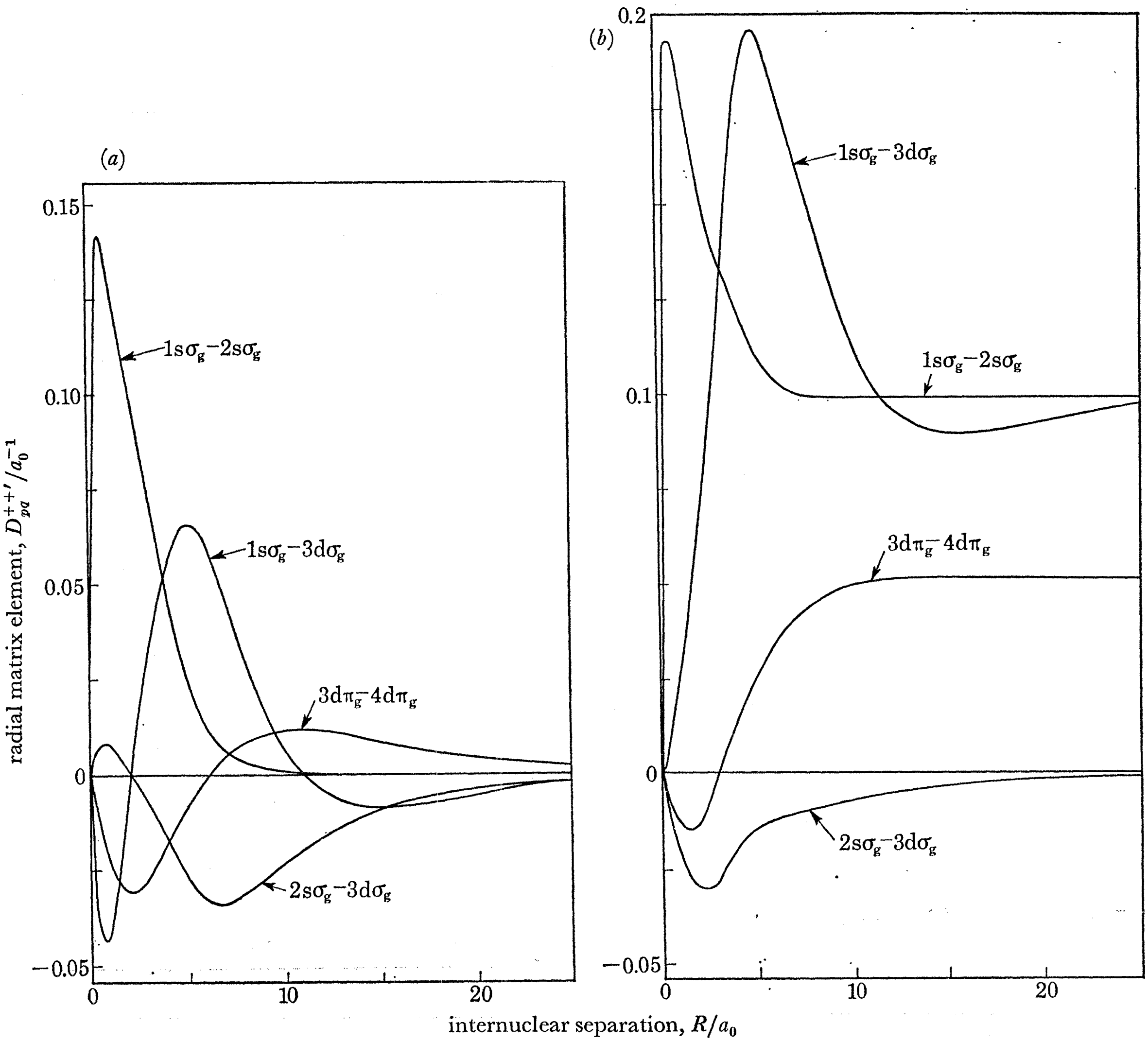

FIGURE 3. (*a*) The radial matrix elements $D_{pq}^{++'}$ of text. (*b*) The radial matrix elements D_{pq}^{++} of text. Labels as in figure 1.

Several authors (Chidichimo-Frank & Piacentini 1974; Schinke & Krüger 1976*b*) have chosen to avoid this difficulty by neglecting radial couplings, with the assertion that these are much weaker than rotational couplings. However, in line with the conclusions of Cayford & Fimple (1976), our calculations show that this neglect is unjustified even at energies as low as 2 keV and particularly in close collisions (large-angle scattering). Thus in figure 5 we compare the transition probabilities for $2p_{\pm 1}$, $2s+2p_0$ and $3p_{\pm 1}$ excitation, obtained from our multistate expansion (cf. § 3), with those of Schinke & Krüger (1976*b*) who neglected translation factors and radial couplings. The much larger probability which we obtain for $2s+2p_0$ excitation is due mainly to our inclusion of the $2p\sigma_u$–$3p\sigma_u$ radial coupling matrix element, which of course has the correct asymptotic behaviour. The importance of this coupling in close collisions was originally predicted by Bates & Williams (1964) to explain in part the heavy damping observed in the oscillations of the curve of the total charge exchange probability against energy at large scattering angles. As we shall see in § 3, it has a considerable affect on differential cross sections for H(2s) and H(2p$_0$) direct and exchange excitation.

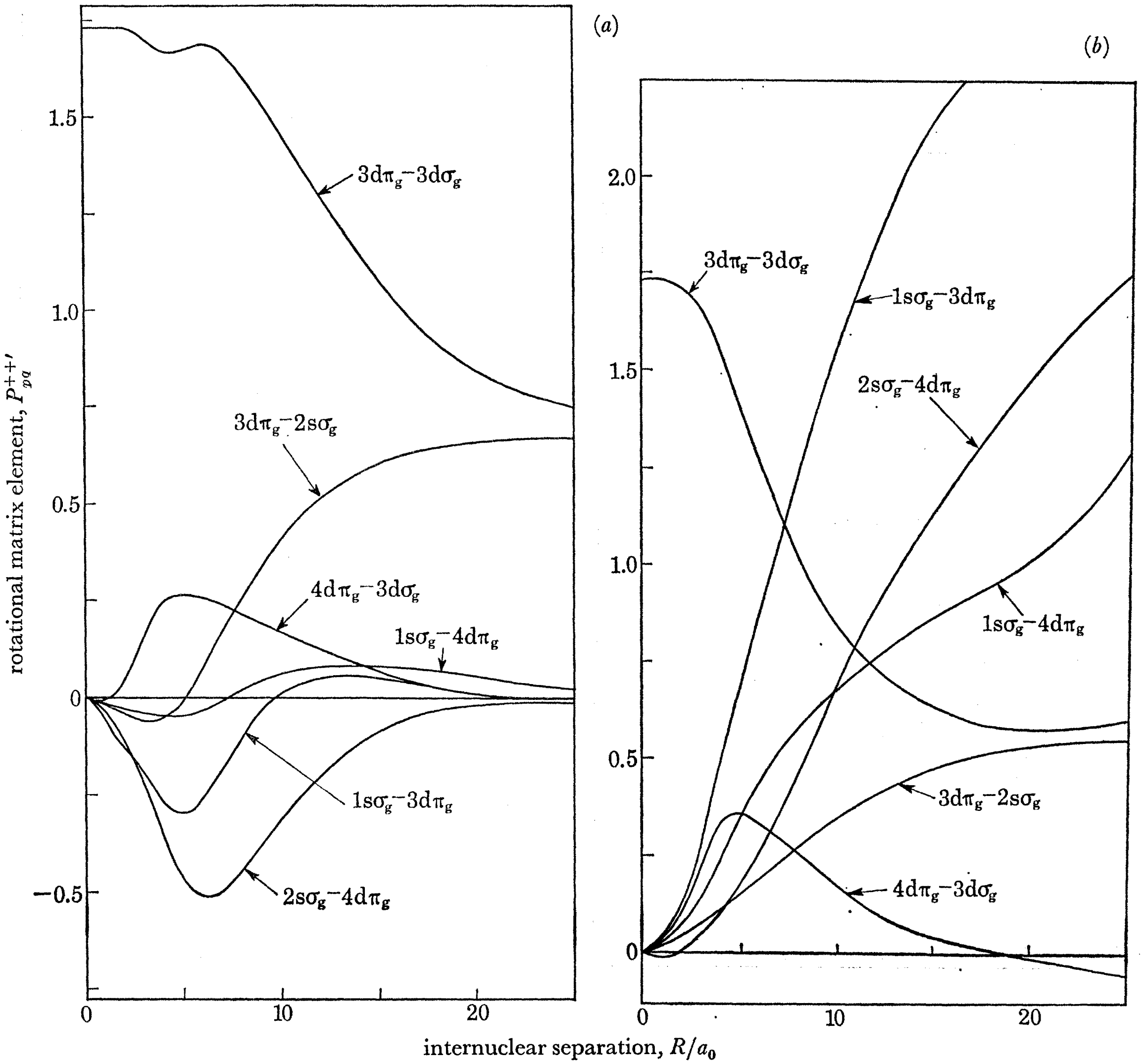

Figure 4. (*a*) The rotational matrix elements $P_{pq}^{++\prime}$ of text. (*b*) The rotational matrix elements P_{pq}^{++} of text. Labels as in figure 1.

Albat & Gruen (1976), following Rosenthal (1971), remove the spurious asymptotic radial coupling on an ad hoc basis by means of a unitary transformation of the molecular states χ_p^i to a new basis set ψ_p^i defined by

$$\psi_p^i = \sum_q U_{pq}\,\chi_q^i, \tag{37}$$

where the unitary matrix $\boldsymbol{U}$ is chosen in order to diagonalize the relevant two-state coupling matrix at infinity, for instance:

$$\begin{pmatrix} \epsilon_p^i(\infty) & -\mathrm{i}ZD_{pq}^{ii}/R \\ \mathrm{i}ZD_{pq}^{ii}/R & \epsilon_q^i(\infty) \end{pmatrix}. \tag{38}$$

Though the new basis ψ_p^i is slightly velocity dependent, this procedure is not equivalent to the inclusion of translation factors. Indeed, the validity of this approach has recently been questioned by Riera & Salin (1977) who show that it may yield transition amplitudes which are physically meaningless.

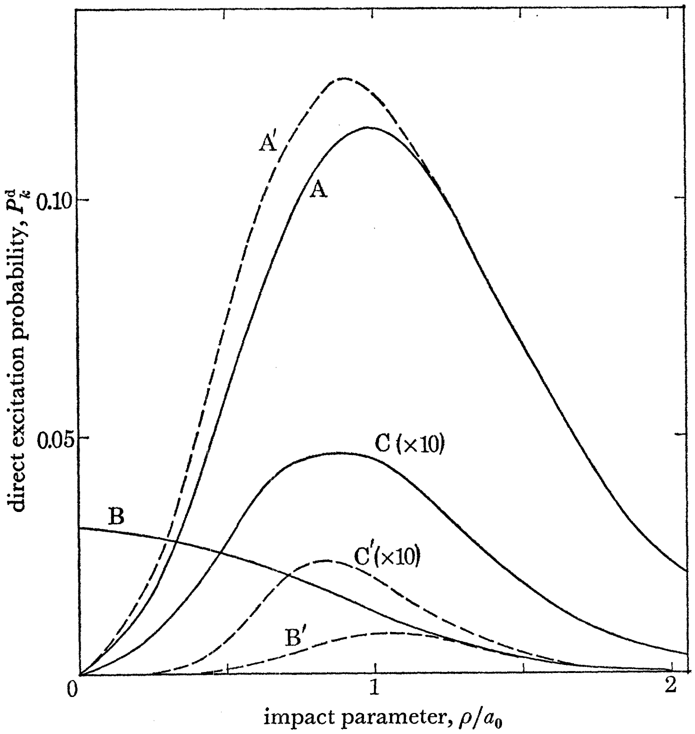

FIGURE 5. Direct excitation probabilities P_k^{d} plotted against impact parameter ρ for an incident proton energy of 2 keV. ——, This work; – – –, Schinke & Krüger (1976*b*); A, A′, $2p_{\pm 1}$ excitation; B, B′, $2s+2p_0$ excitation; C, C′, $3p_{\pm 1}$ excitation.

It is also clear from figures 1–4 that the pragmatic removal of spurious long-range couplings by subtracting off the asymptotic values (Chen *et al.* 1973*b*; Hatton *et al.* 1975) leads to considerable error at finite separations, as may be seen by comparing figures 1 (*a*) to 4 (*a*) with figures 6 and 8 of Hatton *et al.* (1975).

In the following, we use the well defined couplings of this section to calculate differential cross sections (§ 3) and total cross sections (§ 4).

3. ELASTIC AND INELASTIC DIFFERENTIAL CROSS SECTIONS

For H$^+$ on H collisions, the first experimental investigation of inelastic differential processes (Bayfield 1970) concerned electron capture into the 2s state. Previously, Everhart and his co-workers (Lockwood & Everhart 1962; Helbig & Everhart 1965) measured the total charge exchange probability for large scattering angles ($\theta_{\text{lab}} \gtrsim \frac{1}{2}^\circ$), observing damped oscillations. More recently, Houver *et al.* (1974) have made extensive differential measurements on elastic, charge exchange and direct excitation processes for proton energies in the range 250 eV–2 keV. Their results for the total charge exchange probability are in generally good agreement with the Everhart data, and, moreover, provide strong evidence for the exclusive excitation of the

$n = 2$ levels as confirmed by the absence of $n \geqslant 3$ energy losses in their spectra. This is a specific feature of the molecular approach at low energies, in which $n \geqslant 3$ excitations are conveyed via weak multistep coupling mechanisms (e.g. $2\mathrm{p}\sigma_u$–$2\mathrm{p}\pi_u$–$3\mathrm{p}\sigma_u$–$3\mathrm{p}\pi_u$).

Low-energy elastic and inelastic processes have also received extensive theoretical investigation. Within the p.s.s. framework, differential calculations have been carried out by several authors, notably McCarroll & Piacentini (1970), Chidichimo-Frank & Piacentini (1974), Gaussorgues *et al.* (1975 *b*), Schinke & Krüger (1976 *b*) and Cayford & Fimple (1976). However, none of these authors has satisfactorily included both radial and translational effects, both of which influence differential cross sections depending on angle and energy. We have therefore been encouraged to apply our well defined coupling theory of § 2, with terms up to order v^2 included.

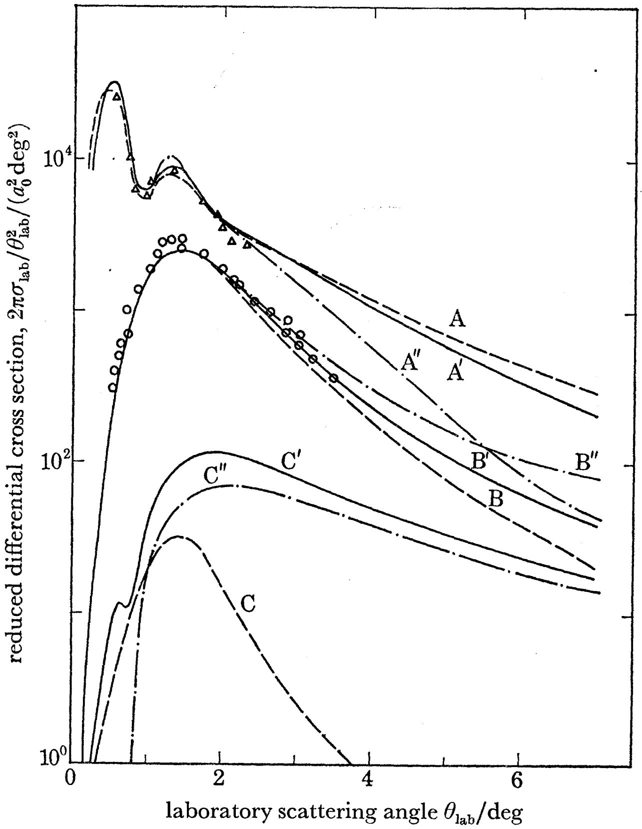

FIGURE 6. Reduced differential cross sections $2\pi\sigma_{\rm lab}\,\theta^2_{\rm lab}$ plotted against laboratory scattering angle $\theta_{\rm lab}$ for an incident proton energy of 1 keV. ——, This work (straight-line trajectory); - · -, this work (Coulomb trajectory); - - -, Schinke & Krüger (1976 *b*); △, ○, Houver *et al.* (1974). A, A′, A″, △, elastic scattering; B, B′, B″, ○, total ($n = 2$) direct excitation; C, C′, C″, $2\mathrm{s}+2\mathrm{p}_0$ direct excitation.

In our detailed calculations we have made use of the subroutine EIKON of Piacentini & Salin (1977) which, given the transition amplitude for each state, evaluates the scattering amplitude for the various processes within the eikonal approximation (McCarroll & Salin 1968; Wilets & Wallace 1968; Chen & Watson 1968; McCarroll & Piacentini 1970, 1971). In principle, the semi-classical partial wave method (Mott & Massey 1965; Bates & Sprevak 1970; Gaussorgues *et al.* 1975 *a*) is superior; however, for large angle scattering ($\theta \gtrsim 1/l$) the asymptotic properties of the Legendre polynomials and the Bessel function are such that only an irrelevant phase difference occurs upon making the stationary phase approximation (Smith 1964).

The most extended basis we have employed (cf. § 4) is that containing all ten states specified in § 2. However, at energies lower than about 5 keV, a six-state expansion, incorporating the $1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $3p\sigma_u$, $3p\pi_u$ and $4f\sigma_u$ states, is entirely adequate, the amplitudes associated with all other states being negligibly small. In figures 6 and 7 we present reduced differential cross sections for elastic scattering, $2s+2p_0$ excitation and total ($n = 2$) excitation, for incident proton energies of 1 and 2 keV respectively. Both straight-line and Coulomb trajectories (Bates & Boyd 1962) have been employed, and these two approaches are shown to yield significantly different results, particularly for elastic scattering at large angles. This is to be expected on physical grounds, since the Coulomb repulsion between the colliding nuclei is largely responsible for the scattering of the heavy particles for large values of θE (product of scattering angle and incident energy). Unfortunately, experimental results for differential cross sections are available only for small angles ($\theta_{lab} \lesssim 3°$), where the results obtained from straight-line and Coulomb trajectories effectively coincide. In common with Schinke & Krüger (1976*b*), we find excellent agreement between theory and experiment for elastic scattering and total ($n = 2$) excitation in this angular range.

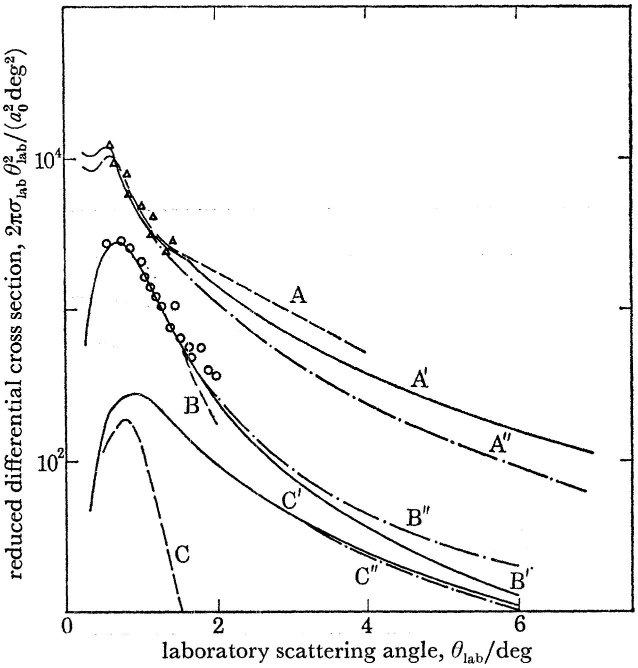

FIGURE 7. Reduced differential cross sections $2\pi\sigma_{lab}\theta^2_{lab}$ plotted against laboratory scattering angle θ_{lab} for an incident proton energy of 2 keV. Same labels as for figure 6.

Close examination of our results shows that the $2p\pi_u$ channel is the dominant inelastic component for $\theta E \lesssim 3$ deg keV, and that the inclusion of states other than $1s\sigma_g$, $2p\sigma_u$ and $2p\pi_u$ does not significantly affect the elastic, the resonance charge exchange or the $2p_{\pm 1}$ excitation cross sections in this range. However, differential cross sections for $2s+2p_0$ excitation are considerably increased by our inclusion of radial couplings. This is especially evident at large scattering angles where our results differ markedly from those of other authors (cf. Schinke & Krüger 1976*b*) who only took account of rotational couplings. Hence it appears that in close collisions, $2s+2p_0$ excitation is induced mainly via radial coupling between the $2p\sigma_u$ and $3p\sigma_u$

molecular states rather than by the relatively weak process of two-step rotational couplings ($2p\sigma_u$–$2p\pi_u$–$3p\sigma_u$, $4f\sigma_u$), which have been considered by other authors (Chidichimo-Frank & Piacentini 1974; Houver *et al.* 1974). This might have been expected since coupling in the united-atoms limit plays a fundamental role in large-angle scattering processes and since the $2p\sigma_u$–$3p\sigma_u$ non-adiabatic radial coupling matrix element, with or without momentum translation factor,

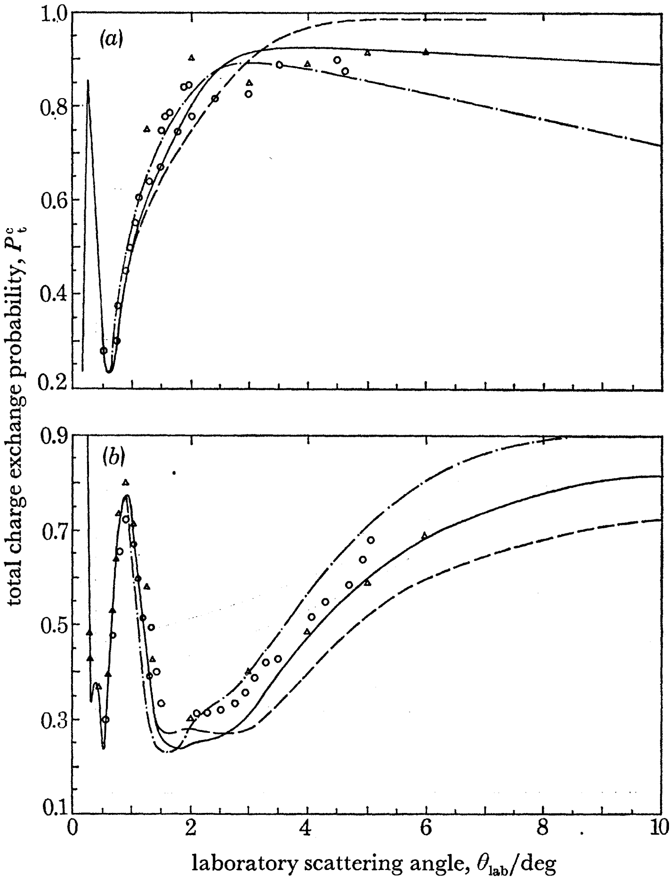

FIGURE 8. Total charge exchange probability P_t^c plotted against laboratory scattering angle θ_{lab} for incident proton energies of (*a*) 1.6 keV and (*b*) 1 keV. ——,This work (straight-line trajectory); –·–, this work (Coulomb trajectory); – – –, McCarroll & Piacentini (1970); ○, Houver *et al.* (1974); △, Helbig & Everhart (1965).

is stationary at the comparatively small internuclear distance of 1 a.u. (see figure 1*a*, *b*), where in fact the $2p\sigma_u$–$3p\sigma_u$ energy separation is not very large. Unfortunately, no direct experimental evidence regarding $2s+2p_0$ excitation is yet available for comparison. Nevertheless, our neglect of gerade coupling leads to identical cross sections for direct and exchange excitation, a prediction which is confirmed by experiment in this energy range, at least for total cross sections (Morgan *et al.* 1973). This might be expected since although the $1s\sigma_g$–$2s\sigma_g$ non-adiabatic radial coupling matrix element is stationary near the united-atoms limit, the $1s\sigma_g$–$2s\sigma_g$ energy separation is rather large. Although these arguments are not conclusive, nevertheless in the light of our own experience we wonder if the affects of the $2s\sigma_g$ and $3d\sigma_g$ states on the charge-exchange probability, found by Cayford & Fimple (1976), are not due to the spurious long range behaviour of their couplings.

In fact, the angular dependence of the total charge exchange probability $P_t^c(\theta)$, as measured by Helbig & Everhart (1965) and Houver *et al.* (1974), provides a further comparison between theory and experiment. This quantity may be calculated from the expression

$$P_{\mathrm{t}}^{\mathrm{c}}(\theta) = \frac{\sum\limits_i \sigma_i^{\mathrm{c}}(\theta)}{\sum\limits_i \{\sigma_i^{\mathrm{d}}(\theta) + \sigma_i^{\mathrm{c}}(\theta)\}}, \tag{39}$$

which, being a ratio of differential cross sections (d, c denote direct-excitation and charge-exchange respectively), provides a more definitive test of experimental data, since it avoids the difficulties associated with the latter's normalization.

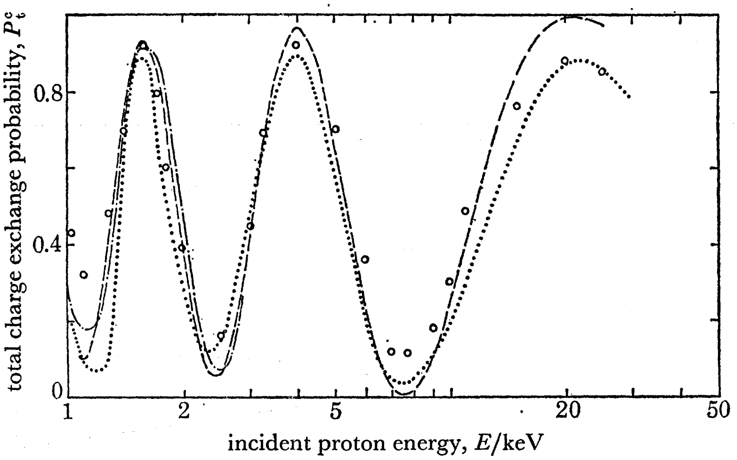

FIGURE 9. Total charge exchange probability $P_{\mathrm{t}}^{\mathrm{c}}$ plotted against incident proton energy E for a laboratory scattering angle of 3°. – – –, This work (six states, straight-line trajectory); –·–, this work (six states, Coulomb trajectory) · · ·, Cheshire *et al.* (1970); o, Lockwood & Everhart (1962).

In figure 8*a*, *b*, we compare our results for $P_{\mathrm{t}}^{\mathrm{c}}(\theta)$ with experiment and with some other theoretical predictions for incident proton energies of 1.6 and 1 keV respectively. For scattering angles less than about 2°, capture occurs principally into the 1s and $2\mathrm{p}_{\pm 1}$ states and our values effectively coincide with the three-state results of McCarroll & Piacentini (1970). Agreement with experiment in this angular range is excellent.

However, as the scattering angle increases our straight-line results show a marked improvement on those of McCarroll & Piacentini. This is due not only to our inclusion of radial couplings, but also to our retention of the terms of order v^2 in the coupled equations. We find that the diagonal matrix elements $A_{00}^{\pm\pm}$ of equation (27) have a sufficient influence on the phases of the $1\mathrm{s}\sigma_{\mathrm{g}}$ and $2\mathrm{p}\sigma_{\mathrm{u}}$ coefficients to significantly affect the transition amplitudes for elastic scattering and resonant charge exchange even at these relatively low energies. This is consistent with our results in I.

As in the case of differential cross sections we find that taking account of the Coulomb repulsion of the nuclei has a considerable affect on the total charge exchange probability at large angles. This is consistent with the work of Gaussorgues *et al.* (1975*b*) whose three-state Coulomb results at 1 keV are only slightly less than our six-state straight-line results and have therefore been omitted for clarity. Nor have we drawn in figure 8*b* Cayford & Fimple's seven-state results given in their figure 6, since they had convergence difficulties due to spurious couplings and since they had problems at the lower angles in relating angles and impact parameters. Nevertheless, at $\theta_{\mathrm{lab}} = 4°$ and 5° there is fair agreement between their results and ours.

In figure 9 we present our six-state results for $P^c_t(3°)$ as a function of incident proton energy. We compare with the well known experimental data of Lockwood & Everhart (1962) and with the seven-state (four hydrogenic, three pseudo-states) close-coupling l.c.a.o. calculations of Cheshire *et al.* (1970). In I we evaluated this quantity within a three-state straight-line approximation and found that the use of our variationally optimized switching function $f(R)$ gave remarkably close agreement with experiment, with regard to the phase of the oscillations. However, little damping was predicted. In figure 9 we see that the inclusion of other states in the basis set and allowance for the Coulomb repulsion increased the damping, though insufficiently particularly at the higher energies in comparison with experiment. The likely cause of this latter short-fall is the failure to allow for coupling to the continuum, whereas the $\overline{3\text{s}}$ pseudo-state of Cheshire *et al.* (1970) lies almost entirely in the continuum.

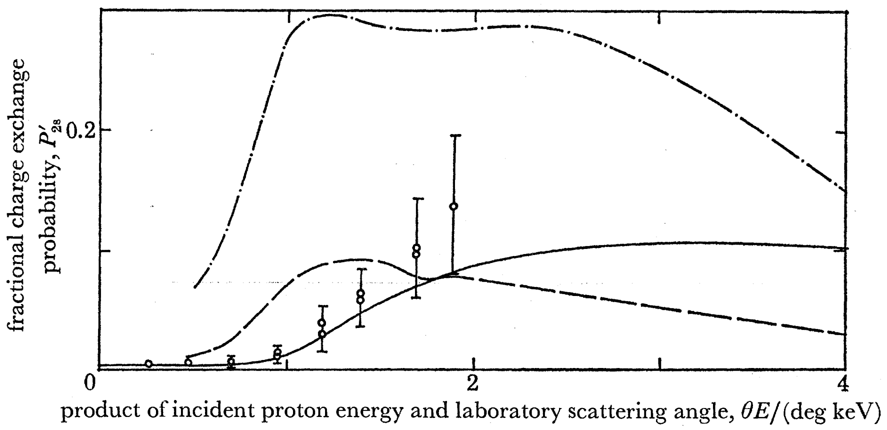

FIGURE 10. Fractional charge exchange probability P'_{2s} of the 2s state of hydrogen plotted against the product of incident proton energy (6 keV) and the laboratory scattering angle θ_{lab}. ——, This work; –·–, Gaussorgues *et al.* (1970); – – –, Chidichimo-Frank & Piacentini (1974); ○, Bayfield (1970).

A further acid test of our theory is made possible by the measurements of Bayfield (1970) on the fractional charge exchange probability $P'_{2s}(\theta)$ for H(2s) production, which is given by

$$P'_{2s}(\theta) = \frac{\sigma^c_{2s}(\theta)}{\sum\limits_i \sigma^c_i(\theta)}. \tag{40}$$

In figure 10 we compare our six-state results at 6 keV with Bayfield. In fact our ten-state results are virtually identical since *gerade* coupling is unimportant in the relevant impact parameter range. Also, allowance for the Coulomb repulsion does not affect the results for this range of θE. Our agreement with Bayfield is excellent.

The results of Gaussorgues *et al.* (1970) in this instance are an average of values obtained from the three-state molecular approach of McCarroll & Piacentini (1970) and the four-state l.c.a.o. treatment of Gaussorgues & Salin (1971). Both theories neglect translation factors and in the molecular calculation the amplitude associated with the 2s asymptotic state is chosen to be half that associated with the $2\text{p}\pi_\text{u}$ state. This is a very poor assumption and accordingly agreement with experiment is very poor. The five-state molecular theory of Chidichimo-Frank & Piacentini (1974) gives the correct order of magnitude in comparison with Bayfield and ourselves. However, even this should be considered fortuitous in our view, since the neglect by these authors of both translation factors and radial couplings is particularly unjustifiable at 6 keV. A similar assessment is appropriate to figure 5 of Schinke & Krüger (1976*b*), while of course, Cayford & Fimple (1976) were limited to 1 keV and below.

Unfortunately, apart from Bayfield's measurement, there have been no other differential measurements above 2 keV, where the full significance of our approach might be adequately assessed. We are fairly confident, however, that our approach, based on a molecular p.s.s. treatment, the velocity perturbations of which are determined variationally, is valid well into the keV range, and so we shall consider total cross sections for both direct and exchange 2s and 2p production in the energy range 1–7 keV in the following section.

4. Total cross sections for H(2s) and H(2p) production

Total cross sections for the four reactions

$$H^+ + H(1s) \rightarrow H(2s \text{ or } 2p) + H^+ \qquad (41)$$

and

$$H^+ + H(1s) \rightarrow H^+ + H(2s \text{ or } 2p) \qquad (42)$$

have been the subject of considerable experimental and theoretical investigation. However, in spite of the relative simplicity of the H_2^+ system, there is considerable variation in the results of the numerous theoretical descriptions. Moreover, experimental studies have been hampered by the practical difficulties associated with the production and handling of free hydrogen atoms, so that reliable measurements have become available only comparatively recently.

The earliest experimental measurements, made by Ryding *et al.* (1966), were on total cross sections for capture into the 2s state in the proton energy-range 40–200 keV with the beam furnace-gas-target method. This was followed by the experiment of Bayfield (1969) for 3–70 keV protons, while Stebbings *et al.* (1965) (revised by Young *et al.* (1968)) obtained cross sections for both capture and direct excitation into the 2p state for 0.5–30 keV protons.

More sophisticated modulated cross-beam techniques were then applied by Morgan *et al.* (1973) to obtain cross sections for all four processes in the energy range 2–26 keV. Using similar techniques but somewhat dissimilar normalization procedures, Chong & Fite (1977) have recently obtained cross sections for direct and exchange excitation to the 2s state for 6–25 keV protons. While their respective charge transfer cross sections are in satisfactory agreement, their 2s direct-excitation cross sections differ in both shape and magnitude.

The earliest theoretical treatment of reactions (41) and (42) was based on the first Born approximation (Bates & Griffing 1953; Bates & Dalgarno 1953) and, not surprisingly, the results were in poor accord with experiment below approximately 100 keV. Since then, many close coupling impact parameter calculations have been performed (Lovell & McElroy 1965; Wilets & Gallaher 1966; Cheshire & Sullivan 1967; Gallaher & Wilets 1968; Flannery 1969; Cheshire *et al.* 1970; Sullivan *et al.* 1972; Bransden *et al.* 1972; Rapp *et al.* 1972; Rapp & Dinwiddie 1972; Baye & Heenen 1973; Morrison & Öpik 1978). However, although the seven-hydrogenic state calculations of Rapp & Dinwiddie are impressive, the best agreement with experiment below 25 keV appears to be the seven (four-hydrogenic and three-pseudo-) state calculations of Cheshire *et al.* (1970). As we have already seen in § 3, the success of the latter lies in the simulation of molecular features at small internuclear separations. In particular, inclusion of the $\overline{3s}$ and $\overline{3p_m}$ pseudo-states gives 99% overlap with the united-atoms $He^+(1s)$ state, whereas the complete hydrogenic basis set gives a mere 76%. This dovetails with the philosophy of the current paper, which concentrates exclusive attention upon the molecular formulation. Moreover, unlike the pseudo-state approach, our molecular approach is fully variational and as such, may be generalized.

This is not to say that molecular calculations have been ignored. The pioneering three-state calculations of Bates & Williams (1964) are reliable below approximately 1 keV. Above 1 keV, however, momentum translation factors and radial couplings become increasingly important, so that the results of Chidichimo-Frank & Piacentini (1974) and Schinke & Krüger (1976*b*) must be considered to be of limited value. That the five-state ($1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $3p\sigma_u$, $3p\pi_u$) results of Rosenthal (1971) for 2p excitation are in reasonable accord with experiment below approximately 7 keV, must in our view be considered fortuitous in view of the remarks of Albat & Gruen (1976) (see § 2) and Riera & Salin (1977), who cast doubt on the validity of a diagonalization procedure in Rosenthal's paper, and since momentum translation factors were effectively omitted.

Most certainly, at energies below approximately 7 keV the experimental data of Morgan *et al.* (1973) exhibit a number of features which are consistent with a molecular description of the collision. In particular, they show that direct and exchange excitation are equally probable, which is consistent with our molecular model of § 3, since coupling between *gerade* states is very weak. Moreover, the experimental results show that the ratio of H(2p) to H(2s) production at low energies is much greater than unity. This is also consistent with the molecular model in which rotational coupling from the $2p\sigma_u$ to the $2p\pi_u$ channel (which dissociates to give $H(2p_{\pm 1})$) is the dominant inelastic component, while H(2s) production is enhanced mainly via $2p\sigma_u$–$3p\sigma_u$ radial coupling which is of importance only in close encounters. However, as the energy increases from 1 to 7 keV, the probability of $2p_0$ production increases while that of $2p_{\pm 1}$ declines, and the probability of 2s production is increasingly reinforced by large-impact parameter contributions (see Hughes 1978). The former may be explained in terms of long-range rotational coupling between the $2p\pi_u$ and $4f\sigma_u$ states which cross near $16a_0$ due to the linear Stark effect. The latter, which results in a double-peaked structure, is due to long-range radial coupling between the $2p\sigma_u$, $3p\sigma_u$ and $4f\sigma_u$ states.

Although *gerade* coupling, especially the $1s\sigma_g$–$3d\sigma_g$ radial coupling, becomes significant for H(2s) production as the energy increases above 1 keV, it has little affect on the total 2p cross section below 7 keV, so that the six-state basis set ($1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $3p\sigma_u$, $3p\pi_u$, $4f\sigma_u$) suffices. In figure 11 we present our results for $Q^d(2p)$† $= Q^c(2p)$ and compare with the $Q^d(2p)$ of other authors. The experimental results for $Q^c(2p)$ are almost identical to those shown for $Q^d(2p)$. Equally well the theoretical results for $Q^c(2p)$ are little different from the corresponding $Q^d(2p)$. Our results are in good agreement with experiment out to 6 keV and compare very favourably with previous elaborate close-coupling calculations. Comparing with Bates & Williams (1964) we see that our inclusion of translation factors has a significant influence on the total cross sections even at the lower energies in the 1–7 keV range. In this connection it is important to note that translation factors have considerably more influence on total cross sections than on differential cross sections at large scattering angles (cf. § 3). This is because the latter are governed primarily by non-adiabatic effects at small internuclear separations, where our switching function f is small. For completeness, we include in figure 11 the results of Gaussorgues & Salin (1971) who used a four-state atomic expansion as well as omitting momentum translation factors. Their curve clearly shows the importance of adopting a molecular model and of including momentum translation factors.

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† The superscripts d and c on Q denote direct excitation and charge exchange respectively.

The breakdown of our approach above 7 keV is partly due to our perturbation treatment of the matrix elements, neglecting terms higher than those of order v^2, and partly due to the ultimate inadequacy of our truncated molecular basis set. The first difficulty could clearly be rectified by greater computational effort (cf. reference 29 of Winter & Lane 1978); the second difficulty however is not easily amenable to progress. At energies higher than 7 keV, coupling to highly excited states becomes increasingly significant and a small number of discrete molecular states is unable to take account of the large number of relevant coupling processes. Thus for example, if significant coupling between $2p\sigma_u$ and $4f\sigma_u$ takes place on the inward trajectory, the final amplitude of the $4f\sigma_u$ state will be seriously in error unless account is taken of the large number of states which are strongly coupled to $4f\sigma_u$ at small internuclear separations. A similar situation arises among the gerade states where the main coupling is between $1s\sigma_g$ and $3d\sigma_g$. The inclusion of $3d\sigma_g$ in the basis set however, seemingly necessitates the inclusion of (at least) $2s\sigma_g$, $3d\pi_g$, $3s\sigma_g$ and $3d\sigma_g$. Unfortunately, economy of computer time limits the basis set to a small number of molecular states, particularly when translation factors are included, as indeed they must be. Moreover, in contrast to the pseudo-state approach (Cheshire *et al.* 1970), no coupling to the continuum is included.

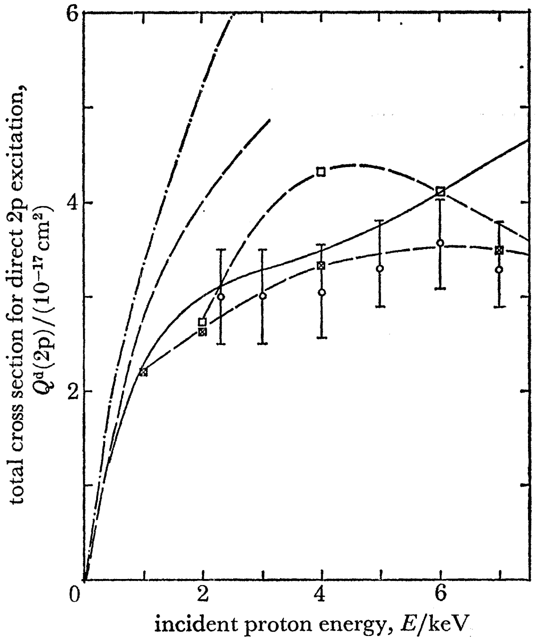

FIGURE 11. Total cross sections $Q^d(2p)$, for direct excitation in proton collisions with atomic hydrogen against incident proton energy E. *Experiment*: ○, Morgan *et al.* (1973). *Theory*: ——, this work (six states); –□–, Rapp & Dinwiddie (1972); –⊠–, Cheshire *et al.* (1970); – – –, Bates & Williams (1964); –·–, Gaussorgues & Salin (1971).

The *gerade* basis set of § 2 is adequate below 7 keV since coupling to $3d\sigma_g$ is rather weak and is significant only at large impact parameters. Thus the above arguments need not apply since in distant encounters the strong coupling region is not reached.

In figures 12 and 13 we present our ten-state results for 2s direct and exchange excitation. For these processes there are large variations in the theoretical† and experimental results of other

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† In particular the omission of the $4f\sigma_u$ state causes the cross sections, in common with previous molecular calculations (Chidichimo-Frank & Piacentini 1974; Schinke & Krüger 1976), to fall off much too rapidly at low energies in comparison with experiment.

authors. Nevertheless the overall agreement between our theoretical results and experiment is quite satisfactory; there is also considerable similarity to the seven-state l.c.a.o. close-coupling calculations of Rapp & Dinwiddie (1972). In common with these authors our cross sections exhibit a trough between 3 and 4 keV, though ours is not as pronounced as theirs. The charge transfer cross sections of Bayfield (1969), who provides the only experimental data below 5 keV, also exhibit a minimum in this energy region, in close accord with our results.

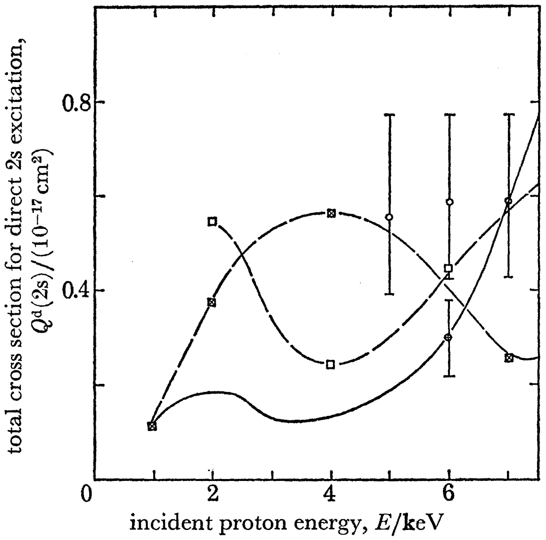

FIGURE 12. Total cross sections $Q^d(2s)$, for direct excitation in proton collisions with atomic hydrogen, against incident proton energy E. *Experiment*: o, Morgan *et al.* (1973); ⊕ Chong & Fite (1977). *Theory*: ——, this work (ten states); –□– Rapp & Dinwiddie (1972); –⊠–, Cheshire *et al.* (1970).

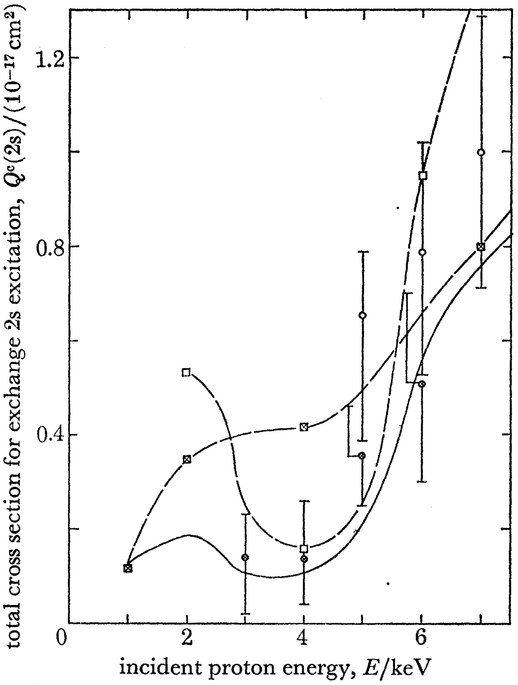

FIGURE 13. Total cross sections $Q^c(2s)$, for charge transfer in proton collisions with atomic hydrogen, against incident proton energy E. ⊗, Bayfield (1969) (experiment). Other labels as for figure 12.

Above 5 keV our charge transfer cross sections lie well above those for direct excitation, a prediction which is confirmed by the experimental data. Unfortunately, for reasons already described, the ten-state basis set is inadequate to determine these cross sections accurately above 7 keV.

The polarization Π of the emitted Lyman-α radiation for direct excitation has been measured by Kauppila *et al.* (1970), We have calculated this quantity from the formula

$$\Pi = \frac{Q^d(2p_0) - Q^d(2p_{\pm 1})}{aQ^d(2p_0) + bQ^d(2p_{\pm 1})}, \tag{43}$$

in which $a = 2.375$ and $b = 3.749$ (Percival & Seaton 1958). The results are presented in figure 14 along with other theoretical predictions. Once again there is close accord with Rapp & Dinwiddie at the lower energies but agreement with experiment is rather poor. However, there is some doubt as to the accuracy of the experimental values (see Gaussorgues & Salin 1971) and certainly, a positive or nearly zero polarization value in the 1–3 keV range is at variance with the molecular model which predicts a value of -0.267 in the low energy limit.

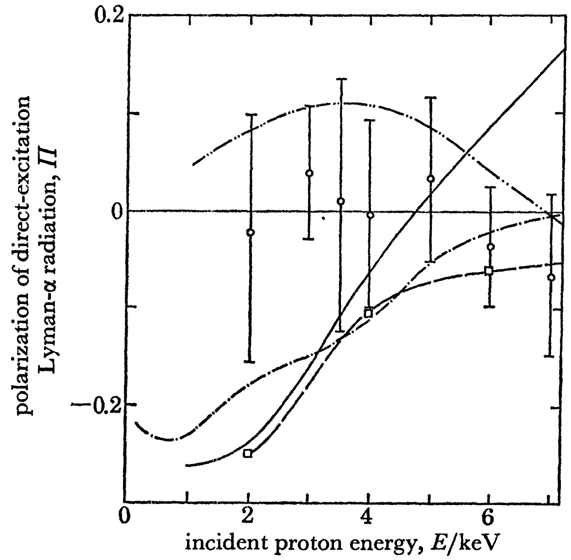

FIGURE 14. The polarization Π of the Lyman-α radiation, produced by direct excitation of hydrogen atoms by proton-impact, against incident proton energy E. o, Experimental values of Kauppila *et al.* (1970); ——, this work (six states); –·–, Gaussorgues & Salin (1971); –□–, Rapp & Dinwiddie (1972); –··–, Gallaher & Wilets (1968).

5. CONCLUSIONS

We conclude that the molecular p.s.s. approach to low energy homonuclear ion–atom collisions now appears to be a practical proposition and that valuable theoretical evidence may be adduced provided both rotational and radial couplings and momentum translation factors are included.

We also conclude that it is necessary to determine specific momentum translation factors variationally (Crothers & Hughes 1978), rather than merely to assume their existence, whether explicitly (Thorson & Delos 1978*a*) or implicitly (Thorson & Delos 1978*b*).

In particular, our results for proton–hydrogen collisions in the 1–7 keV energy range are in excellent accord with experiment, including elastic and inelastic differential cross sections, fractional and total charge exchange probabilities, and direct and exchange total H(2s) and H(2p) production cross sections.

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