Triple-center treatment of electron transfer and excitation in p-H collisions

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Cross sections have been calculated for electron transfer into the $1s$, $2s$, and $2p$ states and for excitation into the $2s$ and $2p$ states in collisions between 1.5—15-keV protons and hydrogen atoms. The triple-center, coupled-state method of Anderson, Antal, and McElroy has been used: Bound atomic states are centered on each nucleus and on a third center (the center of charge) in order to simulate the molecular character of slow collisions. Convergence of cross sections (and molecular potential-energy curves) with respect to the size of the basis has been studied; the present basis includes up to 36 states (16 gerade, 20 ungerade states). The $1s$ capture cross section is estimated to be converged, and the $2p$ and $2s$ cross sections are estimated to be converged to about 10% and 20%, respectively. Dips are observed in the $2s$ and $2p$ excitation cross sections at about 10 keV and in the $2p$ capture cross section at about 5 keV. Results have been compared with atomic-state, pseudostate, and molecular-state results, as well as with experimental results. The results agree fairly closely with the related AO+ pseudostate results of Fritsch and Lin at the lowest calculated energy, although there are differences at higher energies. There are differences from some of the many experimental results, but overall there is agreement within the experimental error limits.

I. INTRODUCTION

Electron transfer and, to a lesser extent, excitation in collisions between fully stripped ions and hydrogen atoms have been of considerable interest in the last thirty years. In most of the earlier work, the proton was taken to be the projectile, but in recent years theoretical and experimental interest has, to some extent, shifted to more highly charged ions. However, work continues to be done on collisions with both types of projectiles, and this is desirable since proton-hydrogen collisions are fundamentally different from those in which the projectile's charge is unequal to that of the target's nucleus: In the former case, the nuclear symmetry exactly decouples the gerade and ungerade parts of the time-dependent electronic wave function during the collision; the nuclear symmetry, to a lesser extent, also affects the character of the molecular energies and wave functions, which are important in a molecular-state treatment.

Both for symmetric and asymmetric collisions, many studies have focused on the intermediate-energy range in which the projectile's speed is not very different from the speed of the orbital electron in the target. Roughly speaking, the studies have used either atomic-state or molecular-state approaches. What follows is a summary of theoretical studies for the proton-hydrogen collision of interest here.

In the lower part of the energy range, various coupled-molecular-state calculations have been carried out. There, electron transfer may be dominated by the approximately decoupled molecular state $1s\sigma_g$ and the rotationally coupled states $2p\sigma_u$ and $2p\pi_u$.[1,2] (The states $1s\sigma_g$ and $2p\sigma_u$ correlate, respectively, to gerade and ungerade combinations of the initial states $1s_A$ and the resonant electron-transfer state $1s_B$ in the separated-atoms limit; the state $2p\pi_u$ correlates to an ungerade linear combination of the states $2p_{1A}$ and $2p_{1B}$.) In symmetric collisions, these three states may be expected to dominate electron transfer to the ground state, as well as electron transfer and excitation to the $2p$ state. (This contrasts with electron transfer in, for example, the asymmetric He^{2+}-H collision, which is dominated by the three states $2p\sigma$, $2p\pi$, and $3d\sigma$.[3]) Several pioneering molecular-state calculations have been carried out with two or three of these states.[1,2,4–6] However, additional states are certainly needed in order to test the convergence of these dominant cross sections with respect to the size of the molecular basis, and in order to extract the more sensitive $2s$ excitation and transfer cross sections. (The energy curves for molecular states correlating to separated-atoms states with principal quantum number up to two[7] are shown in Fig. 1. The states $2s\sigma_g$, $3d\sigma_g$, $3p\sigma_u$, and $4f\sigma_u$ correlate to combinations of the states $2s_A$ and $2s_B$, as well as $2p_{0A}$ and $2p_{0B}$, in the separated-atoms limit.[8]) Some, or all, of these states, and others, have been included in perturbed-stationary-state calculations.[9–11] Coupled-molecular-state calculations have more recently been carried out by Crothers and Hughes[12(a),12(b)] and Kimura and Thorson[13] using two different sets of optimized translational factors. Unlike the perturbed-stationary-state calculations, these two calculations are independent of the choice of origin of electronic coordinates. There are no large calculations using the plane-wave-factor molecular-state method of Bates and McCarroll,[14] which has, however, been applied to other systems.

In the upper part of the intermediate-energy range (and

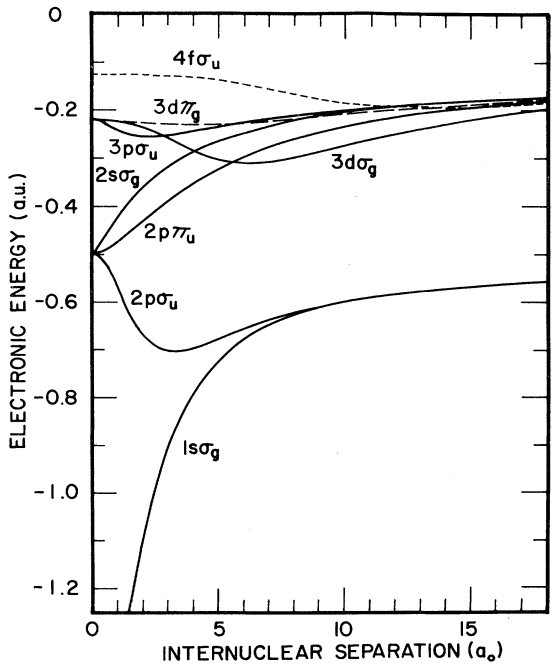

FIG. 1. Electronic energies of states of the H_2^+ molecule correlating to states of principal quantum number one or two in the separated-atoms limit (Ref. 7, and present results).

even in the lower part), the plane-wave-factor, atomic-state method of Bates[15] has been applied using various bases.[16–19] There are no recent large bound-atomic-state calculations for this system.

It may be feasible to extend each type of calculation beyond its "normal energy range." Shipsey, Green, and Browne[20] have argued recently that it may be possible to extend molecular-state calculations to energies somewhat above 25 keV (25 keV corresponding to 1 a.u. of velocity) if a sufficiently large basis is used.

Alternatively, atomic-state calculations may offer promise for extending into the "molecular-state energy range" below 25 keV. However, to do this it may be necessary to improve the atomic-state representation of molecular wave functions at small internuclear separations when these separations are important. To do this (and also to represent the continuum), Gallaher and Wilets[21] and Shakeshaft[22] used a Sturmian basis (a basis of up to 24 s and p functions); Cheshire, Gallaher, and Taylor[18] used an atomic basis augmented by six pseudostates; and Shakeshaft[23] used a scaled-hydrogenic basis (a large basis of 70 s, p, and d functions) which is closely related to the Sturmian basis. The Sturmian and scaled-hydrogenic bases are, in principle, complete. However, the Sturmian basis was truncated too soon to test the covergence of the $2s$ and $2p$ cross sections; the pseudostate basis of Cheshire *et al.* was also too small for a test of convergence. Direct convergence tests for the scaled-hydrogenic basis were not reported.

An interesting alternative, proposed by Anderson, Antal, and McElroy,[24] is to augment the atomic-state basis with atomic states placed on a third center. In this triple-center method, the third center C is normally chosen to be the center of nuclear charge, and the third-center atomic states are taken to be bound atomic states of a fictitious atom having nuclear charge which is the sum of the charges of the projectile and the target's nucleus. Aside from the question of translational factors, these third-center states are thus exact bound-molecular states in the united-atoms limit. A plane-wave translational factor is also attached to these third-center states in the manner described by Bates.[15] If the origin is chosen to be the midpoint of the internuclear line (the center of charge) then the plane-wave factor for the third-center states is unity since center C is then stationary; the matrix elements are, of course, independent of the choice of origin. Anderson *et al.* have noted that *in the united-atoms limit,* the third-center state $1s_C$ has a 24% overlap with the continuum of states centered on either nucleus, and that the first three third-center states have an 85% overlap with this continuum. (This ignores the different translational factors associated with the different centers.) Thus, the triple-center basis may be nearly complete in the united-atoms limit. Unlike the Sturmian and scaled-hydrogenic bases, however, the basis is not, in principle, complete at all internuclear separations. Thus, while an internal test of convergence with respect to the size of basis is very important, the final test must be an external one: a comparison with experimental results. Anderson *et al.* calculated ground-state electron-transfer probabilities (essentially at zero impact parameter) and a few total cross sections using a limited basis (the states $1s_A$, $2s_A$, $1s_B$, $2s_B$, $1s_C$); these calculations were recently checked by Lin, Winter, and Fritsch[25] using a very limited basis ($1s_A$, $1s_B$, $1s_C$). What will be presented here are the results of a much larger calculation using a basis of up to 36 states ($1s_\alpha$, $2s_\alpha$, . . . , $3d_{0,1,2\alpha}$, $\alpha=A, B, C$, $4p_{0,1C}$, $4f_{0,1,2,3C}$), as well as larger test bases. This basis is sufficiently large so that cross sections for electron transfer and excitation to the lower-lying excited states ($2s$,$2p$), as well as electron transfer to the ground state, may be tested for convergence with respect to the size of the triple-center basis.

When this method was first examined by us, it appeared to be too difficult and time-consuming for large calculations. A related method was therefore developed by Fritsch and Lin,[26] which they called "the AO + method." This method has been very successfully applied by them to several asymmetric collisions and the symmetric proton-hydrogen collision.[27] It is the double-center counterpart of the triple-center method in which, in addition to the normal bound atomic states centered on each nucleus, a set of united-atoms states is placed on each nucleus. The AO + basis, like the triple-center basis, is translationally invariant. Further, the *spatial* characters of the AO + and triple-center bases are similar in the united-atoms limit. However, the *phases* are different since the additional states in the triple-center method move with the center C, whereas the additional states in the AO + method move with the nuclei. Furthermore, for nonzero internuclear separations, even the *spatial* characters of the additional states are very different for the two methods. Which is preferable is questionable: For small internuclear separations it may, for some states at low speeds, be preferable to allow probability to build up at the center of

charge, as in the triple-center method, but in different circumstances, this buildup may be unphysical if the basis is not complete. The additional AO+ functions clearly play the role of continuum functions since, after orthogonalizing them to the normal bound-state functions already included, they give eigenvalues of the atomic Hamiltonian which lie in the continuum. (Presumably the triple-center functions also do this to some extent.) In the present paper, we will compare triple-center results with the AO+ results (using the 22 states $1s_A$, $2s_A$, $2p_{0,1A}$, $1s_B$, $2s_B$, $2p_{0,1B}$, $1\bar{s}_A$, $2\bar{s}_A$, $2\bar{p}_{0,1A}$, $3\bar{d}_{0,1,2A}$, $1\bar{s}_B$, $2\bar{s}_B$, $2\bar{p}_{0,1B}$, $3\bar{d}_{0,1,2B}$, where the overlined states here refer to "united-atoms states").

Two additional pseudostate calculations have recently been reported. First, a very large pseudostate calculation has recently been carried out by Lüdde and Dreizler.[28] The pseudostates are functions of spheroidal coordinates without translational factors.

Second, Fritsch and Lin have recently extended the AO+ model to include ionization channels by using additional pseudostates.[29] For these calculations, the pseudostates were obtained by diagonalizing the atomic Hamiltonian in a basis of hydrogenic orbitals of arbitrary effective charge. These orbitals were chosen in order to have more lower-lying continuum eigenvalues than were present with the AO+ basis. Specifically, they were designed to remedy what was viewed as a failure of the AO+ method to account for the important ionization channels above 15 keV. There also may have been some effect of neglecting higher-lying conventional atomic states. The intent of the present triple-center calculation is to extend the atomic-state calculation *downward* into the molecular-state region. Presumably, in the higher-energy region, except for possible "flux trapping,"[23] both AO+ and triple-center bases are superior to a conventional atomic-state basis containing the *same* atomic states.

Finally, Terlecki, Grün, and Scheid[30] have solved the time-dependent Schrödinger equation numerically. However, they do not present individual-state cross sections.

In addition to comparing our results with the other theoretical results, we will compare them with experimental results. There are no experimental cross sections for electron transfer to the ground state alone. We will compare our cross section for transfer into all (bound) states with the experimental cross section of McClure.[31] There are numerous experimental results for electron excitation and electron transfer to the $2s$ and $2p$ states. The more recent ones are the following: Morgan, Geddes, and Gilbody[32] for all four processes; Kondow, Girnius, Chong, and Fite[33] for transfer and excitation to the $2p$ states; Chong and Fite[34] for transfer and excitation to the $2s$ states; Young, Stebbings, and McGowan[35] for direct excitation of the $2p$ state; and Bayfield,[36] Hill, Geddes, and Gilbody,[37] and Morgan, Stone, and Mayo[38] for transfer to the $2s$ state.

The outline of the paper is as follows. In Sec. II, the coupled equations for the coefficients of the expansion of the electronic wave function will be reviewed, the method of calculation of triple-center matrix elements will be summarized, and tests of numerical accuracy will be presented. In Sec. III, convergence studies will be presented; triple-center approximations of molecular energies, probabilities times impact parameter, and total cross sections will be presented and compared with corresponding AO+ results; and total cross sections will be compared with other theoretical and with experimental results. Unless otherwise indicated, Hartree's atomic units are used throughout.

II. THEORY

A. Coupled equations

Following Anderson, Antal, and McElroy,[24] the time-dependent electronic wave function $\Psi(\vec{r},t)$ is expanded in a triple-center basis of traveling atomic orbitals $f_{k\alpha}(\vec{r},t)$:

$$\Psi(\vec{r},t)=\sum_{k,\alpha} a_{k\alpha}(t) f_{k\alpha}(\vec{r},t) , \tag{1}$$

where

$$f_{k\alpha}(\vec{r},t)=\psi_{k\alpha}(\vec{r}_\alpha(\vec{r},t)) \times \exp(-iE_{k\alpha}t+iq_\alpha \vec{v}\cdot\vec{r}-\tfrac{1}{2}iq_\alpha^2 v^2 t) , \tag{2}$$

$$q_\alpha=\begin{cases} -\frac{1}{2}, & \alpha=A \\ +\frac{1}{2}, & \alpha=B \\ p-\frac{1}{2}, & \alpha=C \end{cases} \tag{3}$$

each $\psi_{k\alpha}$ being a bound-state atomic wave function centered on nucleus α (where α denotes the target nucleus $A=H^+$, projectile $B=H^+$ or "virtual nucleus" C) with corresponding eigenvalue $E_{k\alpha}$ of the Hamiltonian

$$H_\alpha=-\tfrac{1}{2}\nabla^2-Z_\alpha/r_\alpha \tag{4}$$

(Z_α being the nuclear charge). The center C is an arbitrary point between A and B defined by $\overline{AC}/\overline{BC}=p/(1-p)$. This point will be taken to be the center of nuclear charge, in which case $p=Z_B/(Z_A+Z_B)$. The vectors $\vec{r}_\alpha$ and $\vec{r}$ are the position vectors of the electron relative to the nucleus α and the midpoint O of the internuclear line, respectively. Based on the formalism of Bates,[15] the origin of coordinates is arbitrary, although it has for definiteness been placed on the midpoint O; the matrix elements do not depend on this choice of origin if the velocity $\vec{v}$ of nucleus B relative to nucleus A is constant.

If the nuclei A and B are identical, then the points O and C coincide. For this symmetric case, one should, of course, separate the wave function Ψ into gerade and ungerade parts and solve for each part separately in order to elucidate the reaction paths and to reduce computing time; this has, in fact, been done. However, it seems preferable here to present a procedure which also applies to the asymmetric case. The notation and computational procedure follow the Sturmian paper of Winter[39] (for He^{2+}-H and He^+-H^+ collisions) more closely than the paper of Anderson *et al.*

Substituting the expansion for $\Psi(\vec{r},t)$ given by Eq. (1) into its time-dependent Schrödinger equation, multiplying

by $f^*_{k\alpha}$, and integrating over all space, one obtains coupled equations for the $a_{k\alpha}$'s. In vector form

$$\underline{S}'(t)\frac{d\vec{a}(t)}{dt}=-i\underline{G}'(t)\vec{a}(t)\ , \tag{5}$$

where

$$S'_{k\alpha k'\beta}(t)=\langle f_{k\alpha}\,|\,f_{k'\beta}\rangle=S_{k\alpha k'\beta}(t)P_{k\alpha k'\beta}(t)\ , \tag{6}$$

$$G'_{k\alpha k'\beta}(t)=\left\langle f_{k\alpha}\left|\left[H-i\frac{\partial}{\partial t}\right]\right|f_{k'\beta}\right\rangle$$

$$=G_{k\alpha k'\beta}(t)P_{k\alpha k'\beta}(t)\ , \tag{7}$$

$$P_{k\alpha k'\beta}(t)=\exp[\tfrac{1}{2}i(q_\alpha^2-q_\beta^2)v^2t+i(E_{k\alpha}-E_{k'\beta})t]\ . \tag{8}$$

The overlap and coupling matrix elements $S_{k\alpha k'\beta}$ and $G_{k\alpha k'\beta}$ take two different forms. If $\alpha=\beta$, then they are called "direct" matrix elements:

$$S_{k\alpha k'\alpha}(t)=\delta_{kk'}\ , \tag{9}$$

$$G_{k\alpha k'\alpha}(t)=\langle\psi_{k\alpha}(\vec{r}_\alpha)\,|\,\mathscr{V}_\alpha\,|\,\psi_{k'\alpha}(\vec{r}_\alpha)\rangle\ , \tag{10}$$

where

$$\mathscr{V}_\alpha=\begin{cases}-Z_B/r_B, & \alpha=A\\ -Z_A/r_A, & \alpha=B\\ -Z_A/r_A-Z_B/r_B+Z_C/r_C, & \alpha=C\ .\end{cases} \tag{11}$$

If $\alpha\neq\beta$, then they are called "charge-exchange" matrix elements:

$$S_{k\alpha k'\beta}(t)=\langle\psi_{k\alpha}(\vec{r}_\alpha)\,|\,\exp[i(-q_\alpha+q_\beta)\vec{v}\cdot\vec{r}]\,|\,\psi_{k'\beta}(\vec{r}_\beta)\rangle\ , \tag{12}$$

$$G_{k\alpha k'\beta}(t)$$

$$=\langle\psi_{k\alpha}(\vec{r}_\alpha)\,|\,\exp[i(-q_\alpha+q_\beta)\vec{v}\cdot\vec{r}]\mathscr{V}_\beta\,|\,\psi_{k'\beta}(\vec{r}_\beta)\rangle\ . \tag{13}$$

The evaluation of the direct and charge-exchange matrix elements will be summarized in Sec. II B.

If the electron is assumed to be initially in a state $k\alpha=1s_A$, then the initial condition for which the coupled Eqs. (5) are to be solved is

$$a_{k'\beta}(-\infty)=\delta_{1sA,k'\beta}\ . \tag{14}$$

The probability for electron transfer into a state $k''\gamma$ is

$$P_{k''\gamma}(\rho)=|\,a_{k''\gamma}(\infty)\,|^2 \tag{15}$$

for a given impact parameter ρ, where $\gamma=A$ for direct excitation and $\gamma=B$ for electron transfer.

As in previous work, the coupled equations have been integrated numerically with respect to the alternate variable $z=vt$ using Hamming's method.[39] The accuracy of the integration of the coupled equations and the accuracy of the non-Hermitian parts of the charge-exchange matrix elements were sufficient to keep the summed probability at unity to within 6×10^{-5}.

Each integration over the variable z was automatically done in four stages: (1) From $z=-500$ to -84 (or -64), only the direct states $1s_A$, $2s_A$, $2p_{0,1A}$ were coupled; (2) from $z=-84$ (or -64) to $+84$ (or $+64$), all gerade states were separately coupled and all ungerade states were separately coupled; (3) from $z=+84$ (or $+64$) to $+500$, the direct states $1s_A$, $2s_A$, $2p_{0,1A}$ were coupled and the direct states $1s_B$, $2s_B$, $2p_{0,1B}$ were coupled; and (4) from $z=+500$ to $+10000$, the direct states $2s_A$, $2p_{0,1A}$ were coupled and the direct states $2s_B$, $2p_{0,1B}$ were coupled. Each range was determined by means of 12-state ($1s_\alpha$, $2s_\alpha$, $2p_{0,1\alpha}$, $\alpha=A$, B, C) or 18-state (12-state plus $3s_C$, $3p_{0,1C}$, $3d_{0,1,2C}$) test calculations at projectile energies of 1.563, 5.11, and 11.11 keV for one to three impact parameters at each energy.

Range (4) was determined by comparing values of $P_{k\alpha}(\rho)$, $k\alpha=2s_A$, $2p_{0,1A}$, $2s_B$, $2p_{0,1B}$ using $z_{\max}=10000$ and using $z_{\max}$ an order of magnitude larger; the differences are at most one unit in the third digit (two units in the fifth decimal place). Integration over this degenerate-coupling region takes very little computing time: Since the retained matrix elements do not oscillate, a large z step size (of the order of 100) can be used. Ranges (1), (2), and (3) were also found to be large enough for at least three-digit accuracy.

States on center C lie between those on centers A and B. Thus, charge-exchange coupling persists to larger values of $|z|$ than when only states centered on A and B are included; the double-center range (2) might have only extended from about -40 to $+40$ rather than from -64 to $+64$. Another way to monitor the required range is to note how closely the probabilities at a given large z sum to unity: They will sum to unity only when $S'_{k\alpha k'\beta}(t)=\delta_{k\alpha k'\beta}$ in Eq. (6), i.e., when charge-exchange coupling is negligible. If more highly excited states are included, then the range of this coupling will increase: In the final 36-state calculations (with the states $1s_\alpha$, $2s_\alpha,\ldots,3d_{0,1,2\alpha}$, $\alpha=A$, B, C, $4p_{0,1C}$, $4f_{0,1,2,3C}$) the range was extended to be from -84 to $+84$ to keep the summed probability at unity to within the previously quoted amount. The range might have been reduced by the more complicated procedure of projecting states centered on C onto states centered on A and B when overlap was still not negligible (the states being partially redundant due to nonorthogonality), but we have not done this.

The total cross section for electron excitation or transfer into the state $k\alpha$ is obtained by integrating ρ times $P_{k\alpha}(\rho)$ [given by Eq. (15)]:

$$Q_{k\alpha}=2\pi\int_0^\infty d\rho\,\rho P_{k\alpha}(\rho)\ . \tag{16}$$

Simpson's rule has been used to an estimated accuracy of about 1 unit in the third digit. Values of $P_{k\alpha}(\rho)$ and $Q_{k\alpha}$ for p-H collisions are presented in Sec. III.

B. Matrix elements

1. *Direct matrix elements*

The direct coupling matrix elements, given by Eq. (10), may be expressed as

$$G_{kAk'A} = -Z_B g^B_{kk'A} , \tag{17a}$$

$$G_{kBk'B} = -Z_A g^A_{kk'B} , \tag{17b}$$

$$G_{kCk'C} = -Z_A g^A_{kk'C} - Z_B g^B_{kk'C} + Z_C g^C_{kk'C} , \tag{17c}$$

where

$$g^\beta_{kk'\alpha} = \left\langle \psi_{k\alpha}(\vec{r}_\alpha) \left| \frac{1}{r_\beta} \right| \psi_{k'\alpha}(\vec{r}_\alpha) \right\rangle . \tag{18}$$

The matrix elements $g^\beta_{kk'\alpha}$ for $\alpha\beta = AB$, BA are those encountered in a normal double-center treatment; those for $\alpha\beta = CA$, CB are also double-center integrals of a similar functional form; and those for $\alpha\beta = CC$ are single-center integrals.

The evaluation of the double-center integrals is similar to that described in the Sturmian paper of Winter:[39] The required radial integrals ${}_0f_{nln'l'L}(Z_\alpha, \overline{\alpha\beta})$ [defined by Eq. (34) of Ref. 39] are now integrals of hydrogenic radial wave functions,[40] and the integrals are now evaluated explicitly rather than by recurrence relations.[41]

For symmetric collisions, one can show

$$g^A_{kk'B} = (-1)^{l+l'} g^B_{kk'A} , \tag{19a}$$

$$g^A_{kk'C} = (-1)^{l+l'} g^B_{kk'C} , \tag{19b}$$

so only half as many double-center integrals need be evaluated for these cases.

2. *Charge-exchange matrix elements*

The (Hermitian) charge-exchange overlap matrix elements $S_{ka k'\beta} (\alpha \neq \beta)$ are given by Eq. (12). The charge-exchange coupling matrix elements $G_{ka k'\beta} (\alpha \neq \beta)$, given by Eq. (13), may be expressed as

$$G_{kAk'B} = -Z_A g^A_{kAk'B} , \tag{20a}$$

$$G_{k'BkA} = -Z_B (g^B_{kAk'B})^* , \tag{20b}$$

$$G_{kAk'C} = -Z_A g^A_{kAk'C} - Z_B g^B_{kAk'C} + Z_C g^C_{kAk'C} , \tag{20c}$$

$$G_{k'CkA} = -Z_B (g^B_{kAk'C})^* , \tag{20d}$$

$$G_{kCk'B} = -Z_A g^A_{kCk'B} , \tag{20e}$$

$$G_{k'BkC} = -Z_A (g^A_{kCk'B})^* - Z_B (g^B_{kCk'B})^* + Z_C (g^C_{kCk'B})^* , \tag{20f}$$

where

$$g^\gamma_{ka k'\beta} = \left\langle \psi_{k\alpha}(\vec{r}_\alpha) \left| \exp[i(-q_\alpha + q_\beta)\vec{v}\cdot\vec{r}] \frac{1}{r_\gamma} \right| \psi_{k'\beta}(\vec{r}_\beta) \right\rangle . \tag{21}$$

The matrix elements $g^\gamma_{ka k'\beta}$ for $\alpha\beta\gamma = ABA$, ABB and $S_{ka k'\beta}$ for $\alpha\beta = AB$ are those encountered in a normal double-center treatment; the matrix elements $g^\gamma_{ka k'\beta}$ for $\alpha\beta\gamma = ACA$, ACC, CBB, CBC and $S_{ka k'\beta}$ for $\alpha\beta = AC$, CB are also double-center charge-exchange integrals of a similar form; but the matrix elements $g^\gamma_{ka k'\beta}$ for $\alpha\beta\gamma = ACB$, CBA are true triple-center charge-exchange integrals.

The first step is the same for all the integrals. Proceeding as described more fully in Ref. 39, we express the modified spherical harmonics $\mathcal{Y}_{lm}(\hat{r}_\alpha)$, $m \geq 0$, in terms of those in the rotating (molecular) frame $\mathcal{Y}_{lm}(\hat{r}'_\alpha)$ by introducing rotation matrices $D^{(l)}_{mm'}$ as defined by Rose and stated by Gottfried[42] and modified rotation matrices $\tilde{d}^{(l)}_{mm'}$ defined[39] for $m \geq 0$. If the $+z_\alpha$ axes are along $\vec{v}$ and the y_α axes are perpendicular to the collision plane, then the Euler angles (π, Θ, π) specify the orientation of the rotated axes with respect to the space-fixed axes.

It can then be shown that

$$S_{ka k'\beta} = \sum_{m_1, m'_1 \geq 0} (-1)^\mu \tilde{d}^{(l)}_{mm_1}(\Theta) \tilde{d}^{(l')}_{m'm'_1}(\Theta) \times t_{k_1 \alpha k'_1 \beta}(q_\alpha, q_\beta, v, \rho, z) , \tag{22}$$

$$g^\gamma_{ka k'\beta} = \sum_{m_1, m'_1 \geq 0} (-1)^\mu \tilde{d}^{(l)}_{mm_1}(\Theta) \tilde{d}^{(l')}_{m'm'_1}(\Theta) \times h^\gamma_{k_1 \alpha k'_1 \beta}(q_\alpha, q_\beta, v, \rho, z) , \tag{23}$$

where[43] q_α is given by Eq. (3), $\mu = m + m_1 + m' + m'_1$, and

$$t_{k_1 \alpha k'_1 \beta}(q_\alpha, q_\beta, v, \rho, z) = \int d\vec{r}\,' R_{nl}(Z_\alpha, r'_\alpha) \mathcal{Y}_{lm_1}(\hat{r}'_\alpha) \times R_{n'l'}(Z_\beta, r'_\beta) \mathcal{Y}_{l'm'_1}(\hat{r}'_\beta) \times \exp[i(-q_\alpha + q_\beta)\vec{v}\cdot\vec{r}] , \tag{24}$$

and $h^\gamma_{k_1 \alpha k'_1 \beta}$ is the same except for a factor of r_γ^{-1} in the integrand.

All of these integrals are evaluated by introducing prolate spheroidal coordinates λ, μ, ϕ, as in Ref. 39. For the double-center integrals, the foci of this coordinate system are placed at the two atomic-state centers. For the triple-center integrals, however, one of the two foci is placed instead at the singularity of the potential energy in order to avoid a numerical singularity at this point. For example, in the triple-center integral for which $\alpha\beta\gamma = ACB$, one sets

$$r'_A = (\lambda + \mu)\frac{R}{2}, \quad \cos\theta'_A = \frac{\lambda\mu + 1}{\lambda + \mu} , \tag{25}$$

$$r'_B = (\lambda - \mu)\frac{R}{2} , \tag{26}$$

$$r'_C = [\lambda^2 + \mu^2 - 2(2p-1)\lambda\mu - 4p(1-p)]^{1/2}\frac{R}{2} ,$$

$$\cos\theta'_C = (\lambda\mu - 2p + 1)\frac{R}{2r'_C} . \tag{27}$$

The velocity-dependent phase in Eq. (24) is also expressible in spheroidal coordinates, and the integral over ϕ is evaluated analytically as in Ref. 39. The real and imaginary parts of the resulting double integrals over λ and μ have been evaluated numerically by Gauss-Laguerre integration over a variable depending on λ and Gauss-Legendre integration over μ. Tests carried out at projectile energies of 1.563, 5.16, and 11.11 keV show that the errors in $P_{k\alpha}(\rho)$ for $k\alpha = 2s_A$, $2p_A$, $2s_B$, $2p_B$ are probably no more than six units in the fourth digit (six units in the fifth decimal place) using 12, 16, and 24 λ points, respec-

tively, and using 16 μ points at all energies. Since the charge-exchange matrix elements are not Hermitian, the conservation of probability noted in Sec. II A is also a good check on their correctness.

Anderson, Antal, and McElroy[24] have also used spheroidal coordinates to reduce the triple-center integrals to integrals over two dimensions using a modified Laguerre quadrature scheme at a few internuclear separations, followed by a 1g-magnitude phase interpolation to reduce what they found to be an otherwise prohibitively large computing time. We have stored the matrix elements for about 100 values of R and interpolated them as needed during the integration of the coupled Eqs. (5). We have found that, at lower energies, the computing time to calculate the matrix elements is not the major part of the total time which is, rather, the time to integrate the coupled equations with their small z step sizes and long-range z range, both due to the presence of the third-center states.

The triple-center integral appearing in a three-state ($1s_\alpha$, $\alpha=A$, B, C) calculation for p-H collisions has also been evaluated by Lin, Winter, and Fritsch[25] using a Gaussian-type-orbital (GTO) expansion of the 1s atomic orbitals as well as the method described in the present paper. In the Gaussian method, the triple-center GTO integral is expressed in terms of a double-center integral, where the centers are the center C and the "Gaussian center" D. Elementary methods reduce this integral to a sum of one-dimensional integrals over GTO's and spherical Bessel functions. Matrix elements calculated using the two different methods in the three-state approximation agree closely.

For symmetric collisions, only about half as many charge-exchange integrals need be evaluated since, for example,

$$g^A_{kCk'B}=(-1)^{l+l'}(g^B_{k'AkC})^* \ . \tag{28}$$

Finally, one can show that for all collisions

$$G_{k\alpha k'\beta}(-t)=(-1)^{l+l'+m+m'}[G_{k\alpha k'\beta}(t)]^* \ , \tag{29}$$

(and similarly for $S_{k\alpha k'\beta}$) reducing the required number of integrals by about an additional factor of 2.

III. RESULTS

A. Approximate molecular energies

Approximate molecular energies have been calculated as functions of the internuclear separation R using various triple-center bases as well as conventional double-center atomic-state bases. Differences ΔE of these energies from exact energies are given in Table I for the "lowest" five states $1s\sigma_g$, $2s\sigma_g$, $3d\sigma_g$, $2p\sigma_u$, and $2p\pi_u$ along with ΔE's for the AO + basis of Fritsch and Lin;[27] exact energies are also given, and these and the remaining three lowest energies are graphed in Fig. 1. The approximate double- and triple-center energies have been obtained by diagonalizing the electronic Hamiltonian in the $v=0$ limit using the matrix elements calculated as in Sec. II B. The small differences ΔE when suitably large bases are used offer further support for the belief that the calculation of matrix elements for the dynamic processes is correct as described in Sec. II B. In the discussion to follow, it should be kept in mind that ΔE's ~ 0.005 would be barely visible on the scale of Fig. 1.

Consider first ΔE's for the $1s\sigma_g$ state. This state is important for describing electron transfer to the ground state at all projectile energies and electron transfer and direct excitation at higher projectile energies. It is seen that for $R \leq 1$, $\Delta E \geq 0.1$ using all two-center bases—unacceptably large differences. Inclusion of even a single third-center function ($1s_C$) dramatically reduces ΔE. Using 30 ($n \leq 3$) triple-center states, we have $\Delta E \leq 0.007$ for all R, and even 12 ($n \leq 2$) such states ensures a small $\Delta E \leq 0.005$ for $R \geq 2$. The 15-state, triple-center basis—"analogous" to the 22-state AO + basis—gives somewhat larger ΔE's than does this AO + basis at all R; however, although the two methods use states labeled by the same quantum numbers, they are certainly not identical, and the AO + basis is larger; the 30-state triple-center and 22-state AO + ΔE's are fairly comparable at all R.

Consider secondly ΔE's for the $2s\sigma_g$ and $3d\sigma_g$ states, both of which may be important for describing direct and electron-transfer excitation to the 2s state. Neither state is defined by the two-state, two-center basis, and the $2s\sigma_g$ state is poorly represented at small R for any of the two-center bases. The addition of a single third-center state does not help significantly (or at all). However, using 12 triple-center states gives $\Delta E \leq 0.002$ for $R \leq 1$, ≥ 10 for the $2s\sigma_g$ state and only somewhat larger ΔE's for the $3d\sigma_g$ state; differences near the $2s\sigma_g$-$3d\sigma_g$ crossing point at $R=4$ are larger. For the $2s\sigma_g$ state, ΔE using the 15-state triple-center basis is somewhat larger than that using the analogous 22-state AO + basis at all R, but is comparable for the $3d\sigma_g$ state; on the other hand, the 30-state triple-center basis gives smaller ΔE's than does the AO + basis except for the $2s\sigma_g$ state at the smallest R.

Consider thirdly ΔE's for the $2p\sigma_u$ state, which is the primary incident channel at most projectile energies. The two-state two-center basis gives large differences $\Delta E \geq 0.1$ for small $R \leq 1$, but the eight-state and certainly the 20-state two-center bases are probably adequate for all R. Since the $1s_C$ state is gerade, the three-state triple-center E's are identical to two-state two-center values. The 12-state triple-center basis gives very small ΔE's ≤ 0.003 for all R. The AO + ΔE's are smaller than the already small values using the analogous 15-state triple-center basis; they are marginally smaller than those using the 30-state triple-center basis.

Consider finally ΔE's for the $2p\pi_u$ state. Due to $2p\sigma_u$-$2p\pi_u$ rotational coupling, the $2p\pi_u$ state is important both for direct and electron-transfer excitation, and probably for electron transfer to the ground state. The two-center two-state basis has no π_u component. The larger two-center bases give $\Delta E \geq 0.1$ for $R \leq 1$ and may not be acceptable except for large R. The three-state triple-center basis also has no π_u component. Triple-center bases of at least 12 states give quite small ΔE's except possibly at intermediate values of R. For all values of R, the 30-state triple-center ΔE's are comparable to, or smaller than, values using the AO + basis.

Overall, the conventional two-center atomic-state basis

TABLE I. Differences of approximate energies of the H_2^+ molecular ion from exact values (in a.u.) for the lowest five states using various double-center and triple-center atomic-state bases, and an AO + atomic-state basis. The exact energies are also given.

State	Basis[a]	$R=0.2$	$R=1$	$R=2$	$R=4$	$R=6$	$R=10$
$1s\sigma_g$	2 double-center	0.445	0.1634	0.0489	0.0092	0.0029	0.0003
	8 double-center	0.395	0.1362	0.0387	0.0061	0.0014	0.0001
	20 double-center	0.380	0.1289	0.0349	0.0039	0.0008	0.0001
	3 triple-center	0.013	0.0888	0.0384	0.0080	0.0027	0.0003
	12 triple-center	0.010	0.0193	0.0043	0.0050	0.0011	0.0001
	15 triple-center	0.009_5	0.0193	0.0030	0.0045	0.0011	0.0001
	30 triple-center	0.007_5	0.0067	0.0014	0.0015	0.0003	0.0000
	22 AO +	0.0004	0.0054	0.0025	0.0005	0.0002	0.0000
	Exact	−1.9286	−1.4518	−1.1026	−0.7961	−0.6786	−0.6006
$2s\sigma_g$	2 double-center						
	8 double-center	0.1431	0.0889	0.0494	0.0260	0.0107	0.0031
	20 double-center	0.1280	0.0750	0.0371	0.0149	0.0052	0.0019
	3 triple-center	0.2546	1.3573	1.9903			
	12 triple-center	0.0009	0.0017	0.0125	0.0240	0.0097	0.0024
	15 triple-center	0.0009	0.0017	0.0113	0.0240	0.0097	0.0022
	30 triple-center	0.0008	0.0007	0.0015	0.0075	0.0024	0.0005
	22 AO +	0.0000	0.0011	0.0042	0.0071	0.0044	0.0016
	Exact	−0.4910	−0.4229	−0.3609	−0.2885	−0.2476	−0.2047
$3d\sigma_g$	2 double-center						
	8 double-center	0.0126	0.0182	0.0178	0.0046	0.0124	0.0065
	20 double-center	0.0069	0.0102	0.0130	0.0023	0.0058	0.0034
	3 triple-center				1.7525	1.7459	1.8760
	12 triple-center	0.0037	0.0148	0.0092	0.0042	0.0075	0.0022
	15 triple-center	0.0000	0.0001	0.0012	0.0035	0.0074	0.0021
	30 triple-center	0.0000	0.0001	0.0006	0.0005	0.0009	0.0008
	22 AO +	0.0000	0.0001	0.0014	0.0026	0.0026	0.0021
	Exact	−0.2223	−0.2252	−0.2358	−0.2857	−0.3125	−0.2731
$2p\sigma_u$	2 double-center	0.668	0.1102	0.00667	0.00066	0.00062	0.00020
	8 double-center	0.010	0.0086	0.00212	0.00022	0.00019	0.00006
	20 double-center	0.003	0.0026	0.00085	0.00016	0.00012	0.00004
	3 triple-center	0.668	0.1102	0.00667	0.00066	0.00062	0.00020
	12 triple-center	0.00001	0.0027	0.00176	0.00009	0.00014	0.00006
	15 triple-center	0.00001	0.0027	0.00176	0.00009	0.00014	0.00006
	30 triple-center	0.00001	0.0008	0.00057	0.00006	0.00006	0.00003
	22 AO +	0.00001	0.00007	0.00012	0.00002	0.00001	0.00001
	Exact	−0.50268	−0.56481	−0.66753	−0.69555	−0.65731	−0.59990
$2p\pi_u$	2 double-center						
	8 double-center	0.1239	0.1049	0.0740	0.0339	0.0711	0.0062
	20 double-center	0.1064	0.0885	0.0601	0.0254	0.0115	0.0035
	3 triple-center						
	12 triple-center	0.00001	0.0035	0.0158	0.0201	0.0126	0.0055
	15 triple-center	0.00001	0.0035	0.0158	0.0201	0.0126	0.0055
	30 triple-center	0.00000	0.0009	0.0012	0.0069	0.0081	0.0018
	22 AO +	0.00001	0.0008	0.0045	0.0085	0.0056	0.0020
	Exact	−0.49869	−0.4741	−0.4288	−0.3508	−0.2970	−0.2327

[a]The 2, 8, and 20 double-center states are all $n=1$, ≤ 2, and ≤ 3 states on each center, respectively; the 3, 12, and 30 triple-center states include triple-center states of the same respective quantum numbers as above, but on all three centers. The 15 triple-center states are all $n \leq 2$ states on each center, plus the states $3d_{0,1,2C}$; the 22 AO + states include the same $n \leq 2$ states on centers A and B as in the 15-state triple-center basis, plus states on A and B of the same nuclear charge and quantum numbers as for the states on C in the triple-center basis.

inadequately represents the molecular energies for small internuclear separations $R \leq 1$. The 12- or 15-state, triple-center bases have differences $\Delta E \leq 0.02$ for all R, while the 30-state triple-center and 22-state AO + bases have $\Delta E \leq 0.008$. As far as molecular energies are concerned, the 22-state AO + basis is superior to the analogous 15-state triple-center basis. The situation for the dynamic collision process is of course not necessarily the

same. Based on studies of convergence of cross sections (to be reported in Sec. III B), it was decided to include also the $4p_{0,1C}$ and $4f_{0,1,2,3C}$ states in the triple-center basis, although these states were not included in the molecular-energy calculations. The $4f_C$ states, as well as the previously included $3p_C$ states, may be important for representing the additional three states $3p\sigma_u$, $3d\pi_g$, and $4f\sigma_u$ which correlate to states of principal quantum number up to two in the separated-atoms limit. The united-atoms states corresponding to $3p\sigma_u$ and $4f\sigma_u$ were not included in the 22-state AO + basis.

B. Probabilities, cross sections, and their convergence

In this section, probabilities $P_{k\alpha}(\rho)$ versus impact parameter ρ and total cross sections $Q_{k\alpha}$ will be presented for electron transfer to the states $k\alpha=1s_B$, $2s_B$, and $2p_B$ and direct excitation to the states $2s_A$ and $2p_A$ in 1.5—15-keV p-H collisions using various triple-center bases. Their convergence with respect to the size of the bases will be described and a comparison will be made with the corresponding AO + results of Fritsch and Lin.[27]

Values of $\rho P_{k\alpha}(\rho)$, $k=2s$, $2p$, $\alpha=A$, B, and $P_{1sB}(\rho)$ are graphed in Figs. 2—7 for projectile energies of 1.563, 5.16, and 11.11 keV using 15-state and 36- or 28-state triple-center bases. Also shown are the graphs for the 22-state, AO + basis which is analogous to the 15-state triple-center basis. The 15-state basis includes all the states $1s_\alpha$, $2s_\alpha$, $2p_{0,1\alpha}$, $\alpha=A$, B, C and $3d_{0,1,2C}$; and the 36-state basis includes all the states $1s_\alpha, \ldots, 3d_{0,1,2\alpha}$, $\alpha=A$, B, C, and $4p_{0,1C}$, $4f_{0,1,2,3C}$. (The 28-state basis is the 36-state basis with the states $3d_{0,1,2\alpha}$, $\alpha=A$, B and $4p_{0,1C}$ removed.) The corresponding total cross sections are given in Table II. For later comparison in Secs. III C and III D with other theoretical and with experimental results, the excited state cross sections are also graphed in Figs. 8—11.

Before considering the present results in detail, it is worthwhile to review and emphasize the main features of the cross sections which have previously been pointed out by others and which are evident in the present results. First, ground-state capture dominates at low energies and is largely due to the two decoupled states $1s\sigma_g$ and $2p\sigma_u$,

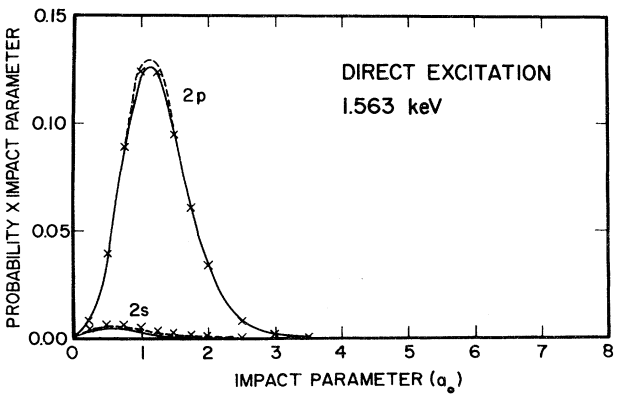

FIG. 2. Probability times impact parameter ρ vs ρ for electron excitation to the $2s$ and $2p$ states in 1.563-keV p-H collisions using 15-state (dashed curve) and 28-state (solid curve) triple-center bases and a 22-state AO + basis (crosses) (Ref. 27).

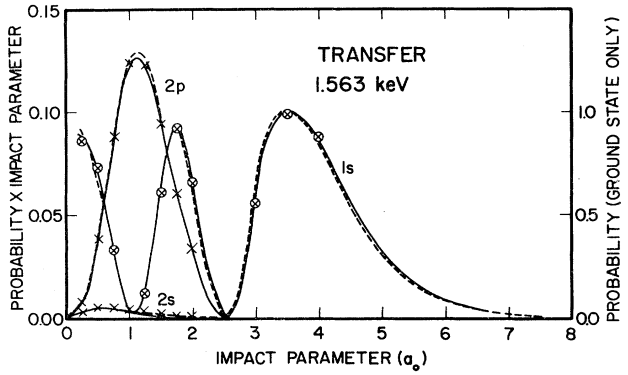

FIG. 3. Probability times impact parameter ρ vs ρ for electron transfer to the $2s$ and $2p$ states (left scale) and probability vs ρ for electron transfer to the ground state (right scale) in 1.563-keV p-H collisions using 15-state (dashed curve) and 28-state (solid curve) triple-center bases and a 22-state AO + basis (crosses) (Ref. 27).

the latter being coupled to the $2p\pi_u$ state. Secondly, the direct and transfer cross sections at low energies are nearly equal ($Q_{kA}\cong Q_{kB}$), since the gerade states are inaccessible from the ground state $1s\sigma_g$. (It may be mentioned here that Kimura and Thorson[13] note trajectory effects to be unimportant above 1 keV, so these effects need not be considered here.) Thirdly, in a molecular-state treatment, a minimal basis may be one which includes all states correlating to $n=2$ levels in the separated-atoms limit (see Fig. 1); the role of these and other states would have to be tested in actual calculations. Finally, the excited-state cross sections *may* display dips and peaks at lower energies due to the oscillations in the ground-state probability $P_{1sB}(\rho)$ vs ρ. At roughly 5 keV we observe maxima in Q_{2sA}, Q_{2pA}, a minimum in Q_{2pB}, and a shoulder in Q_{2sB}, whereas at about 10 keV, Q_{2sA}, Q_{2pA} have pronounced minima and Q_{2sB}, Q_{2pB} are large (see Figs. 8 and 9). This may be explainable in terms of $P_{1sB}(\rho)$ vs ρ plotted in Figs. 5 and 7 for $E=5.16$ and 11.11 keV, respectively. At the lower energy, $P_{1sB}(\rho)$ has a minimum at that ρ where $\rho P_{2p\alpha}(\rho)$ has a maximum, whereas at the upper energy it has a maximum there. Thus, at the lower energy the

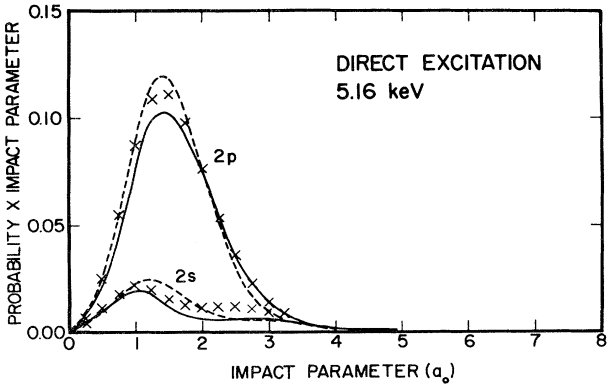

FIG. 4. Probability times impact parameter as in Fig. 2, but for 5.16-keV collisions and with the exception that the larger triple-center basis has 36 states.

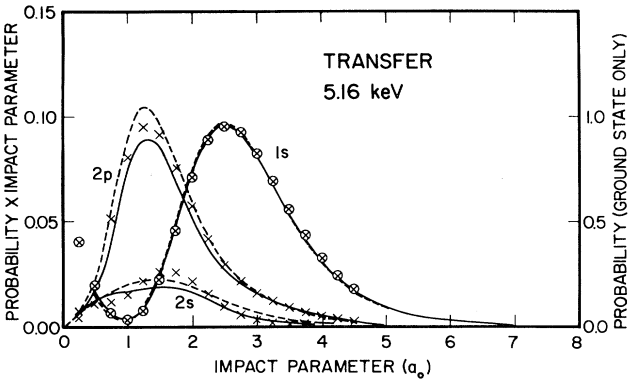

FIG. 5. Probability times impact parameter for electron transfer to the $2s$ and $2p$ states and probability for electron transfer to the ground state as in Fig. 3, but for 5.16-keV collisions and with the exception that the larger triple-center basis has 36 states.

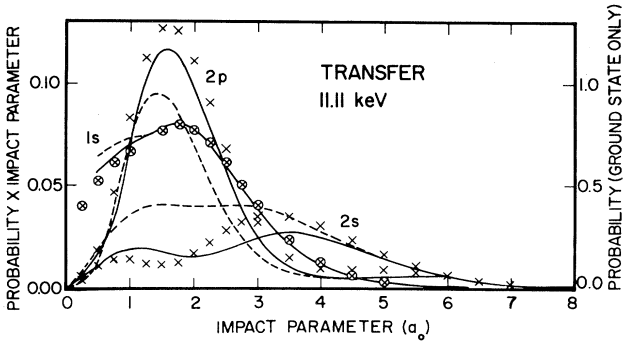

FIG. 7. Probability times impact parameter for electron transfer to the $2s$ and $2p$ states, and probability for electron transfer to the ground state as in Fig. 5 but for 11.11-keV collisions.

charge cloud is mainly centered on the target nucleus at the important peak impact parameter so that direct excitation to the $n=2$ levels is relatively large, whereas at the higher energy the charge cloud is mainly centered on the projectile, and, thus, electron-transfer excitation is relatively large.

We now consider how the triple-center cross sections depend on the size of basis, and also compare these cross sections with AO + results. Consider first the ground-state cross section Q_{1sB}. It is seen in Table II that 15-state and 36- or 28-state triple-center values agree to within 1% at 1.563, 5.16, and 11.11 keV and 3% at 15 keV. This agreement holds for individual impact parameters as well, at least for $\rho \gtrsim 0.5$ (see Figs. 3, 5, and 7), so the ground-state triple-center results may be considered converged even using the limited 15-state basis. At least for $\rho \gtrsim 0.5$ there is close agreement with AO + values of $P_{1sB}(\rho)$ using a 22-state basis analogous to the 15-state triple-center basis.

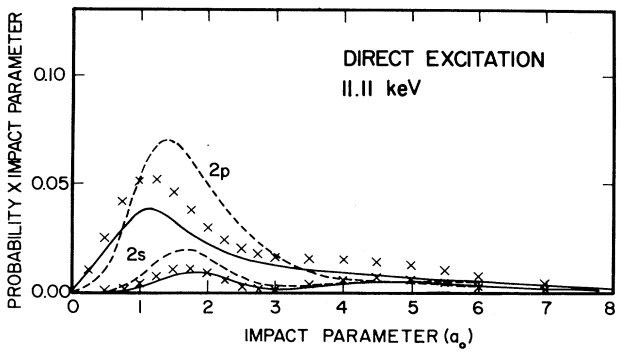

FIG. 6. Probability times impact parameter for electron excitation as in Fig. 4, but for 11.11-keV collisions.

Consider secondly the excited-state cross sections Q_{2pA}, Q_{2pB} at the lowest energy of 1.563 keV. It is seen in Table II that there is close agreement (within 3%) between 15- and 28-state triple-center results; this agreement holds for individual impact parameters as well (see Figs. 2 and 3). Furthermore, the 15- and 28-state results agree closely (within 3% and 1%, respectively) with the 22-state AO + values, and this agreement also holds for individual impact parameters.

The unimportance of individual triple-center states can be further confirmed by referring to Table III. It is seen that all the individual states tested each contribute less than 1% to the cross sections, with the exception of the $3s_C$, $3p_{0,1C}$ states (probably mainly the $3p_{0,1C}$ states, which correlate to $3p\sigma_u$, $3p\pi_u$ in the united-atoms limit), which contribute about 14%; the states $4p_{0,1C}$ and $3d_{0,1,2\alpha}$, $\alpha=A,B$—neglected in the 28-state basis—contribute less than 1% to either $Q_{2p\alpha}$ or $[\rho P_{2p\alpha}(\rho)]_{\max}$, $\alpha=A$, B. (To reduce the computing time in these and subsequent tests for other states and other energies, approximate cross sections have been calculated using few values of ρ (four to six values); in almost all cases, the agreement between these cross sections and the corresponding "exact" values (obtained using about 16 ρ's) was within 5%, so the estimate of convergence based on these approximate cross sections is generally accurate. For comparison, values near $[\rho P(\rho)]_{\max}$ are also given; for many states use of these values rather than the approximate Q somewhat overestimates the effect of these states.)

Consider now the other excited-state cross sections Q_{2sA}, Q_{2sB} at the same low energy (1.563 keV). These cross sections are much smaller than those for the $2p$ states and, hence, are expected to be more sensitive to the inclusion of additional basis states. It is seen in Table II that the 15-state and 28-state cross sections now differ by 22—28 %, although the absolute differences are actually less than those for the $2p$ cross sections. The 15-state results differ by 15% from the corresponding 22-state AO + values while the 28-state results differ by 37—42 % from these values. The closer agreement when analogous

TABLE II. Cross sections (in units of 10^{-17} cm^2) for electron excitation to the $2s$ and $2p$ states and electron transfer to the $1s$, $2s$, $2p$, and all states in collisions between protons and hydrogen atoms. The triple-center results are the present results; the AO + results are those of Fritsch and Lin (Ref. 27).

		Excitation			Transfer		
Basis	E (keV)[a]	$2s$	$2p$	All[b]	$1s$	$2s$	$2p$
22 AO +	1.563	0.135	2.67			0.128	2.66
15 triple-center	1.563	0.116	2.74	151	148	0.110	2.72
28 triple-center	1.563	0.0927	2.65	152	150	0.0833	2.63
22 AO +	3.0	0.482	3.07			0.380	2.92
28 triple-center	3.0	0.341	2.97	129	125	0.260	2.93
22 AO +	5.16	0.777	3.16			0.764	2.73
15 triple-center	5.16	0.708	3.14	103	99.7	0.831	2.89
36 triple-center	5.16	0.603	2.94	105	101	0.697	2.51
22 AO +	8.0[c]	0.662	2.73			1.44	3.78
36 triple-center	8.0	0.384	2.43	90.2	84.9	1.07	3.45
22 AO +	11.11	0.524	2.46			2.17	4.47
15 triple-center	11.11	0.662	2.44	76.8	70.9	2.92	2.98
36 triple-center	11.11	0.436	1.71	77.8	71.1	1.88	3.80
22 AO +	15.0	1.22	3.64			3.70	3.39
15 triple-center	15.0	0.815	3.27	62.0	54.3	4.34	3.38
36 triple-center	15.0	0.880	2.30	63.1	55.8	3.65	2.44

[a]Proton energy.
[b]Cross sections marked "*all*" are for capture into all *available* states.
[c]The AO + values at this energy are interpolated.

bases are used suggests that certain united-atom states ($3p_C$, $4f_C$) included in the triple-center basis but neglected in the AO + basis may be important, as was found to be true for the triple-center basis and as Kimura and Thorson[13] found to be true of the molecular states $3p\sigma_u$ and $4f\sigma_u$. The contribution of individual states in the triple-center basis is given in Table IV. It is seen that each block of states $4p_{0,1C}$ and $3d_{0,1,2\alpha}$, $\alpha=A$, B, neglected in the 28-state basis only contributes an estimated 6—7 % to the total cross sections. On the other hand, some retained states contribute significantly: For example, the states $3s_C$ and $3p_{0,1C}$ (probably mainly $3p_{0,1C}$) contribute about 35%, and the states $2s_C$ and $3s_C$ contribute about 10%. Interestingly, the $1s_C$ state has only a 5% effect on the cross sections since it only affects the probabilities at small impact parameters; this state has previously been noted by us to improve significantly the $1s\sigma_g$ molecular energy at small internuclear separations and by Lin, Winter, and Fritsch[25] to improve significantly $P_{1sB}(\rho)$ at small impact parameters.

Overall, the very good agreement at low energies between the results of the triple-center and AO + methods shows that these methods are consistent. At low energies the different placement of united-atom states for nonzero internuclear separations does not seem to be important. (There are also different translational factors, but this may not be significant until higher energies.)

Consider now the excited-state cross sections Q_{2pA} and Q_{2pB} at those three higher energies 5.16, 11.11, and 15.0 keV where somewhat detailed studies have been made. At all energies of at least 5.16 keV, 36 states were used in the final calculations. It is seen in Table II that 15- and 36-state cross sections differ by 7—14 %, 35—24 %, and 35—32 %, respectively, at the three energies studied—these differences therefore being somewhat increasing functions of energy; for the lower two energies, see also the impact-parameter dependence in Figs. 4—7. At these three energies the 15-state triple-center values differ from 22-state AO + values by 1—6 %, 1—40 %, and 11—0 %, respectively, while using 36 rather than 15 states the corresponding differences are 7—8 %, 36—16 %, and 45—33 %. Usually (as at 1.563 keV) the agreement is better in the former case. However, at 15 keV, $\rho P_{2pA}(\rho)$ (not shown) using 36-state triple-center and 22-state AO + bases agree more closely in shape (but not in magnitude) than when the smaller triple-center basis is used. In all cases, the 36-state, triple-center values of Q_{2pA} and Q_{2pB} are below the AO + values. A more detailed study of the contribution of various states to the triple-center cross sections (in the manner of that shown in Table III for $E=1.563$ keV) has been carried out for $E=5.16$ and 11.11 keV (not shown). It is found that the three blocks of states $4d_{0,1,2\alpha}$ ($\alpha=A$, B), $4d_{0,1,2C}$, and $5p_{0,1C}$—neglected in the 36-state basis—each contribute at most 2%, except at 5.16 keV for $4d_{0,1,2\alpha}$ ($\alpha=A$, B), where, based on a study at only one impact parameter, the effect

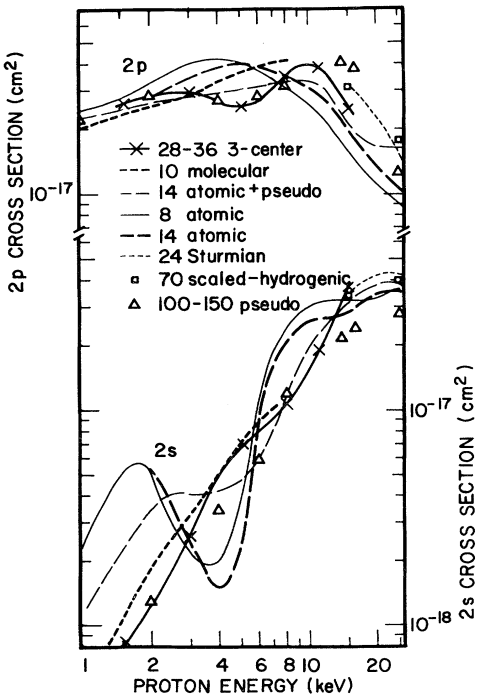

FIG. 8. Cross sections for electron transfer to the $2p$ state (left scale) and $2s$ state (right scale) in collisions between protons and hydrogen atoms. The theoretical results are as follows: triple center, present results; molecular-state, Kimura and Thorson (Ref. 13); atomic-state—plus—pseudostate and eight-atomic-state, Cheshire *et al.* (Ref. 18); 14-atomic-state, Rapp and Dinwiddie (Ref. 19); Sturmian and scaled-hydrogenic, Shakeshaft (Refs. 22 and 23); and 100—150 pseudostate, Lüdde and Dreizler (Ref. 28).

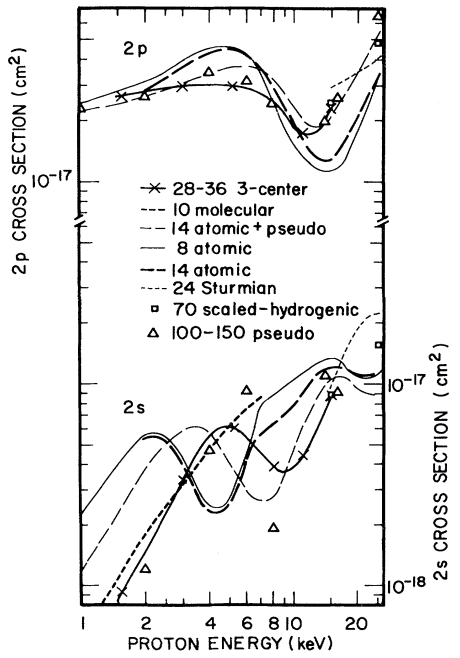

FIG. 9. Cross sections for electron excitation to the $2p$ state (left scale) and $2s$ state (right scale) in collisions between protons and hydrogen atoms. The notation is as in Fig. 8.

is estimated to be 5—6 %. Of the retained blocks of states in the 36-state basis, those tested with contributions sometimes exceeding 10% are $3s_C$, $3p_{0,1C}$; $3d_{0,1,2\alpha}$ ($\alpha=A$, B); and $4f_{0,1,2,3C}$; the estimated contribution of each of the latter two blocks of states was tested and found to depend significantly on whether the other block of states was also present, due presumably to the nonorthogonality of the basis or to interference among the states. The states $3d_{0,1,2\alpha}$, $\alpha=A$, B, which were found to be important in the triple-center basis at these energies, were neglected in the AO + basis.

Consider, finally, the excited-state cross sections Q_{2sA} and Q_{2sB} at the same three higher energies 5.16, 11.11, and 15.0 keV. It is seen in Table II that 15- and 36-state cross sections differ by 16—18 %, 41—43 %, and 8—17 %, respectively, at these three energies. For these $2s$ cross sections (as well as their impact-parameter dependence) it is the middle energy which is most sensitive to the size of the basis. At these three energies the 15-state triple-center values differ from 22-state AO + values by 9—8 %, 23—29 %, and 40—16 %, respectively, while using 36 rather than 15 states, the corresponding differences are 25—9 %, 18—14 %, and 32—1 %; the somewhat closer agreement for most cases than when using 15 states suggests that, as far as the $2s$ cross sections are concerned, the AO + basis quite adequately represents the united-atoms limit at these energies despite the lack of $3p$ and $4f$ united-atoms orbitals. A more detailed study of the contribution of various states to the triple-center cross sections has been carried out for $E=5.16$ and 11.11 keV. It is found that the three blocks of states $4d_{0,1,2\alpha}$ ($\alpha=A$, B), $4d_{0,1,2C}$, and $5p_{0,1C}$—neglected in the 36-state basis—each contribute at most 5%, with the exceptions of the $4d_{0,1,2C}$ states at 5.16 keV (contributing 5—7 %) and the $4d_{0,1,2\alpha}$, $\alpha=A$, B states at 5.16 keV (contributing an estimated 10%, based on a study at only one impact parameter). These effects are somewhat larger than those on the $2p$ cross sections but they are still generally small. Of the retained blocks of states in the 36-state basis, those tested ones with contributions sometimes exceeding 10% are $3d_{0,1,2C}$; $3s_\alpha$, $3p_{0,1\alpha}$ ($\alpha=A$, B); $4p_{0,1C}$; $3s_C$, $3p_{0,1C}$; $3d_{0,1,2\alpha}$ ($\alpha=A$, B); and $4f_{0,1,2,3C}$, the latter three blocks being especially significant. As for the $2p$ cross sections, the effects of the states were found, where tested, to depend on which other states are present.

In summary, the triple-center cross sections Q_{2pA} and Q_{2pB} using a 28-state basis are estimated to be converged to within 5% with respect to the size of the (bound-state) triple-center basis at 1.563 keV; at higher energies, the 36-state cross sections are estimated to be converged to within 10%. For Q_{2sA} and Q_{2sB}, the convergence is estimated to be about 20% over the energy range 1.5—15 keV using 28 states at the lower energies and 36 states at the higher energies. At the four energies 1.563, 5.16, 11.11, and 15 keV, the 15-state triple-center and 22-state AO + values of Q_{2sA}, Q_{2sB}, Q_{2pA}, and Q_{2pB} agree on the average to within 14%; the average agreement between 36-state (or 28-state) triple-center and 22-state AO + values is 21% and differences do not exceed 45% at these

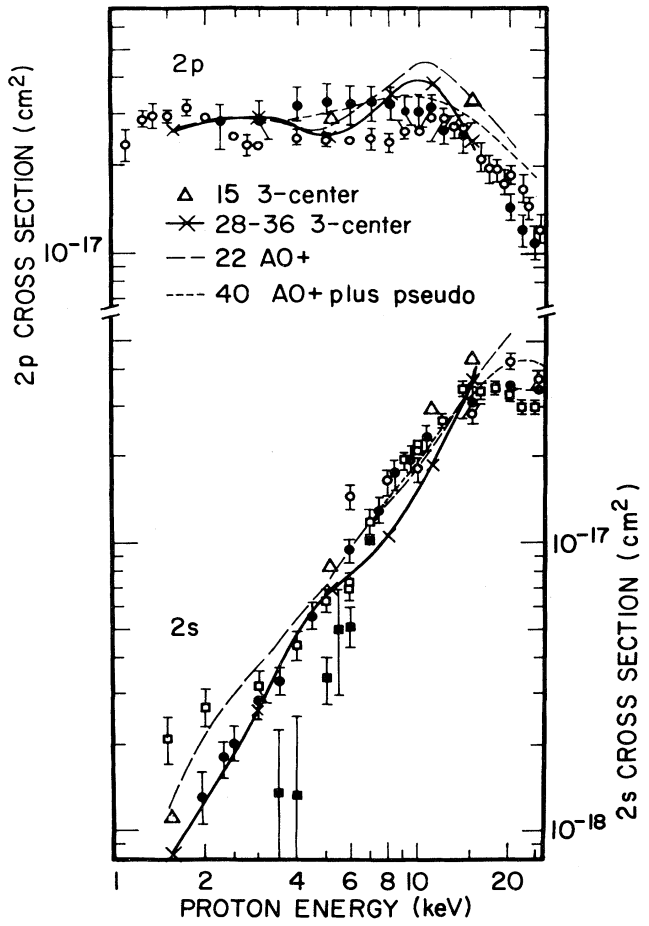

FIG. 10. Cross sections for electron transfer to the $2p$ state (left scale) and $2s$ state (right scale) in collisions between protons and hydrogen atoms. The theoretical results are as follows: triple-center, present results; AO + and augmented AO +, Fritsch and Lin (Refs. 27 and 29). The experimental results are as follows: ●, Morgan, Geddes, and Gilbody (Ref. 32) ($2p$) and Morgan, Stone, and Mayo (Ref. 38) ($2s$); ○, Kondow, Girnius, Chong, and Fite (Ref. 33) ($2p$) and Chong and Fite (Ref. 34) ($2s$); □, Hill, Geddes, and Gilbody (Ref. 37) ($2s$); and ■, Bayfield (Ref. 36) ($2s$).

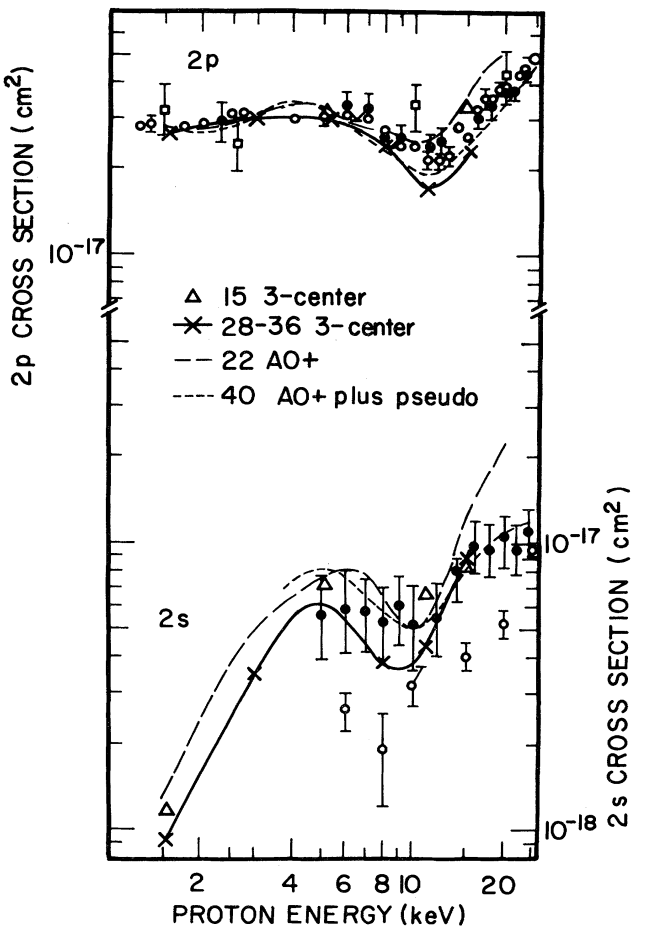

FIG. 11. Cross sections for electron excitation to the $2p$ state (left scale) and $2s$ state (right scale) in collisions between protons and hydrogen atoms. The notation is as in Fig. 10, with these exceptions: □, Young, Stebbings, and McGowan (Ref. 35) ($2p$) and ●, Morgan, Geddes, and Gilbody (Ref. 32) ($2s$).

energies. At almost all energies, the 22-state AO + cross sections lie above the 36-state (or 28-state) triple-center values (see Figs. 10 and 11). At 1.563 keV, 15-state triple-center and 22-state AO + cross sections agree to within 2—15 %.

C. Comparison with other theoretical results

1. Capture into all states

Since they are nearly converged, the ground-state, electron-transfer cross section, and the cross section for electron transfer into all *available* states, are not always presented along with excited-state cross sections. However, there are small but non-negligible differences among some of the theoretical results. We have found that the 36-state (or 28-state) triple-center cross sections and the 14-atomic-state—plus—pseudostate and 8-atomic-state cross sections of Cheshire *et al.*[18] for electron transfer into all *available* states agree to within 2% between 3 and 15 keV; the disagreement is negligible. However, below 3 keV the atomic-state—plus—pseudostate cross section rises more rapidly than the triple-center and atomic-state cross sections, the difference being about 9% at 1.5 keV. (The original two-atomic-state result of McCarroll[16] lies within a few percent of the ground-state, triple-center cross section and the eight-atomic-state cross section over the full energy range from 1.5 to 15 keV, and even at 15 keV its difference from the triple-center cross section for capture into all available bound states is only 10%.) All three values are roughly 5% below Shakeshaft's scaled-hydrogenic[23] value at 15 keV, this difference not being significant since at this energy the neglected excited-state contributions (those from states with $n \geq 4$) are of this order. (At lower energies excited-state contributions even from the $n=3$ states are negligible.) At low energies the 100—150-pseudostate cross section of Lüdde and Dreizler[28] is significantly below the triple-center value, differences increasing from 6% at 8 keV to 13% at 2 keV; it lies even farther below the 14-atomic-state—plus —pseu-

TABLE III. Probability times impact parameter $\rho P_{2p\alpha}(\alpha)$ and total cross sections $Q_{2p\alpha}$ for direct ($\alpha=A$) and electron-transfer ($\alpha=B$) excitation to the $2p$ state in 1.563-keV proton-hydrogen collisions using various triple-center bases.

Basis states[a]	$\rho P_{2pA}(\rho)$ $\rho=1$	Q_{2pA} (10^{-17} cm^2) Approx.[b]	Exact[c]	$\rho P_{2pB}(\rho)$ $\rho=1$	Q_{2pB} (10^{-17} cm^2) Approx.	Exact
12 states[d]	0.126	2.64	2.75	0.126	2.61	2.71
$+3d_{0,1,2C}$	0.126	2.64	2.74	0.126	2.61	2.72
$+3s_C$, $3p_{0,1C}$	0.111	2.28	2.37	0.111	2.27	2.36
22 states[d]	0.1213	2.54		0.1212	2.54	
$+1s_C$	0.1212	2.54[e]		0.1213	2.54[e]	
$+2s_C$, $3s_C$	0.1212	2.54[e]		0.1214	2.53[e]	
$+3d_{0,1,2C}$	0.1213	2.55	2.65	0.1213	2.53	2.63
22 states	0.1213	2.54		0.1212	2.54	
$+4p_{0,1C}$	0.1219	2.55		0.1218	2.55	
22 states	0.1213	2.54		0.1212	2.54	
$+3d_{0,1,2\alpha}$, $\alpha=A,B$	0.1210	2.54		0.1215	2.55	

[a]In a given row, the basis in each group consists of all functions listed down to and including those in that row.
[b]The approximate $Q_{2p\alpha}$'s were obtained using a five-point trapezoidal rule with the points $\rho=0$, 0.5, 1, 1.75, and 2.5. The same points were also used in Table IV.
[c]The "Exact" values were obtained using a 13-point Simpson's rule, accurate to about one unit in the third digit.
[d]The 12 states are $1s_\alpha$, $2s_\alpha$, $2p_{0,1\alpha}$, $\alpha=A, B, C$; the 22 states are $1s_\alpha$, $2s_\alpha$, $2p_{0,1\alpha}$, $3s_\alpha$, $3p_{0,1\alpha}$ ($\alpha=A, B$), $2p_{0,1C}$, $3p_{0,1C}$, $4f_{0,1,2,3C}$.
[e]These values were obtained using the states noted, except at $\rho=2.5$, where the 22-state basis was used.

dostate cross section. However, the experimental cross section of McClure[31] lies between the cross section of Lüdde and Dreizler and the other group of three cross sections and does not favor either.

2. *Capture to the 2p state*

The present triple-center and most other theoretical cross sections for electron-transfer and direct excitation to the $n=2$ levels are shown in Figs. 8 and 9, respectively. The triple-center results, as well as the AO + and the recent extended AO + results of Fritsch and Lin,[27,29] are compared later with experimental results in Figs. 10 and 11.

Consider first the cross section Q_{2pB} for electron transfer to the $2p$ state. A comparison will first be made with the recent results of a large calculation by Kimura and Thorson[13] using ten molecular states and their own state-dependent electron translational factors. It is seen

TABLE IV. Probability times impact parameter $\rho P_{2s\alpha}(\rho)$ and total cross sections $Q_{2s\alpha}$ for direct ($\alpha=A$) and electron-transfer ($\alpha=B$) excitation to the $2s$ state in 1.563-keV proton-hydrogen collisions using various triple-center bases.[a]

Basis states	$\rho P_{2sA}(\rho)$ $\rho=0.5$	Q_{2sA} (10^{-17} cm^2) Approx.	Exact	$\rho P_{2sB}(\rho)$ $\rho=0.5$	Q_{2sB} (10^{-17} cm^2) Approx.	Exact
12 states	0.005 4	0.10_5	0.11_6	$0.005\,4_5$	0.10_7	0.11_3
$+3d_{0,1,2C}$	0.005 5	0.11_0	0.11_6	$0.005\,3_5$	0.10_3	0.11_0
$+3s_C$, $3p_{0,1C}$	0.007 5	0.14	0.15	0.007 2	0.13	0.14
22 states	0.005 14	0.082 0		0.004 88	0.083 2	
$+1s_C$	0.004 63	0.078 0		0.005 41	0.087 5	
$+2s_C$, $3s_C$	0.005 12	0.086 9		0.004 90	0.078 4	
$+3d_{0,1,2C}$	0.005 14	0.088 4	0.092 7	0.004 88	0.077 4	0.083 3
22 states	0.005 14	0.082 0		0.004 88	0.083 2	
$+4p_{0,1C}$	0.005 33	0.087 7		0.005 06	0.088 5	
22 states	0.005 14	0.082 0		0.004 88	0.083 2	
$+3d_{0,1,2\alpha}$, $\alpha=A,B$	0.005 31	0.088 2		0.005 01	0.088 5	

[a]The footnotes are as in Table III.

that, up to 3 keV, there is good agreement (within about 12%) between their values and the present triple-center values of Q_{2pB}. At higher energies their Q_{2pB} rises monotonically while the triple-center Q_{2pB} dips, the difference at the triple-center dip being about 35%. Kimura and Thorson have fairly thoroughly tested their cross section with respect to including additional bound molecular states in the basis; the only other possible problem, besides the neglect of ionization channels in both approaches, is their neglect of terms of order higher than quadratic in the velocity. The other recent large molecular-state calculation was carried out by Crothers and Hughes[12(b)] using 8—10 molecular states and their own optimized electron translational factors. Their results (not shown) agree more closely (to within about 18%) with the present triple-center values than do the results of Kimura and Thorson. The calculations of Crothers and Hughes, like those of Kimura and Thorson, were carried out to second order in the velocity. There are fairly large differences between first- and second-order results using their own method, in contrast to the case for Kimura and Thorson.

As a further test of the consistency among methods, consider the results of the very large pseudostate calculation by Lüdde and Dreizler[28] with about 100 to 150 states. These pseudostates are molecular in character, being expressed in spheroidal coordinates with foci at the nuclei, and do not include translational factors. There is excellent agreement (within 10%) up to 10 keV with the triple-center values. At 15 keV there is a difference of about 50%. Our value agrees well with experimental values there (see Fig. 10). It is possible that a lack of translational factors in their basis might cause difficulties at higher energies.

Consider also the earlier 14-atomic-state—plus—pseudostate results of Cheshire, Gallaher, and Taylor.[18] Their basis includes the eight atomic states up to $2p$ on both nuclei plus $3\bar{s}$, $3\bar{p}_0$, and $3\bar{p}_1$ pseudostates designed to give some overlap with united-atoms states and with the continuum. It is seen that these cross sections are significantly lower than atomic-state cross sections at lower energies and higher at higher energies. (There are differences of 0—18% between the eight-atomic-state results of Cheshire *et al.*, and Rapp and Dinwiddie[19] for Q_{2sA}, Q_{2sB}, Q_{2pA}, and Q_{2pB} at overlapping energies, the average difference being 4%. At 25 keV, where differences range from 1% to 7%, Winter[39] recalculated the cross sections and found agreement to within 1% with the values of Cheshire *et al.* In view of this, the 14-atomic-state values of Rapp and Dinwiddie may be questionable.) Although the atomic-state—plus—pseudostate cross section is less oscillatory than the triple-center cross section, the agreement is to within 18%. Cheshire *et al.* did not test the convergence of their cross section with respect to the size of their pseudostate basis, but considering the estimated 10% accuracy in our own cross section this agreement is reasonable.

Finally, consider Shakeshaft's Sturmian and scaled-hydrogenic (scaled-Sturmian) results[22,23] which agree between themselves to within 2% at the single energy 15 keV which overlaps our energy range. At this energy, Shakeshaft's values are about 25% higher than our own. It has been noted that our value agrees with the experimental results at this energy.

3. *Excitation to the 2p state*

Consider now the cross sections Q_{2pA} for direct excitation to the $2p$ state in Fig. 9. Kimura and Thorson do not present molecular-state values for this process, but note that they agree to within 8% with their values of Q_{2pB}. This would imply good agreement with our triple-center values except at about 8 keV where their value of Q_{2pB} is rising while our value of Q_{2pA} is falling. Differences between triple-center results and the recent molecular-state results of Crothers and Hughes[12(b)] are also small (within 9%) except at about 8 keV where the molecular-state result is 40% higher. According to Crothers and Hughes, a definitive comparison at this and higher energies must await their calculation to all orders in the velocity. There is good agreement at all energies (within about 14%) with the pseudostate results of Lüdde and Dreizler; especially outstanding is the agreement within a few percent at the cross section's dip. At energies below the dip the atomic-state—plus—pseudostate results of Cheshire *et al.* rise noticeably, unlike ours, though at the dip the results agree fairly closely. The atomic-state cross sections oscillate with larger amplitude and differ from ours by up to about 50%. Finally, at 15 keV, our triple-center cross section agrees with Shakeshaft's scaled-hydrogenic value to 7%; at this energy his scaled-hydrogenic and (probably less accurate) Sturmian values differ by 17%.

4. *Capture to the 2s state*

Owing to their smaller size at low energies, the cross sections Q_{2sB} and Q_{2sA} are expected to be considerably more difficult to calculate than Q_{2pB} and Q_{2pA}. Consider first Q_{2sB}, referring to Fig. 8.

At low energies, the molecular-state cross section of Kimura and Thorson lies 30% above our own—somewhat puzzling since they and we have checked convergence (bound state only) at low energies. However, we noted an uncertainty of 20% in our $2s$ value, and the effect of including the neglected states $4p_{0,1C}$ and $3d_{0,1,2\alpha}$ ($\alpha=A, B$) would probably be to raise Q_{2sB} (see Table IV). At higher energies, although their cross section varies more smoothly than ours with energy, agreement is satisfactory.

The molecular-state result of Crothers and Hughes (not shown), which is second order in the velocity, has a pronounced shoulder at about 5 keV. This shoulder is less pronounced in the triple-center result (and is absent in the molecular-state result of Kimura and Thorson, which is also second order in the velocity), the difference being a factor of 2. The situation is unclear since Crothers and Hughes have noted a large difference between their own first- and second-order results.

There are disagreements of up to about 40% with the values of Lüdde and Dreizler. The highly oscillatory nature of their Q_{2sA} (see below) suggests that they may have had difficulty in extracting both $2s$ cross sections; they have noted difficulty at higher energies in projecting out the $2s_A$ cross section.

The atomic-state—plus—pseudostate cross section of Cheshire *et al.* has a more pronounced shoulder at 5 keV than does our own, and the atomic-state cross sections oscillate with large amplitude. At 15 keV the former agrees with our value within 17% and the atomic-state results are not very different. There the triple-center value agrees within 7% with the identical scaled-hydrogenic and Sturmian values of Shakeshaft.

5. *Excitation to the 2s state*

Finally, consider the cross sections Q_{2sA} for direct excitation to the 2*s* state shown in Fig. 9. At low energies, the agreement between the triple-center values and the molecular-state values of Kimura and Thorson is within 25%—closer than it was for Q_{2sB}. There is fair agreement up to 5 keV, beyond which the molecular-state value continues to rise while the triple-center value dips in at least partial agreement with experimental results (see Fig. 11). A comparison with the molecular-state results of Crothers and Hughes (not shown), which are also second order in the velocity, is fairly similar. The pseudostate—plus—atomic-state, atomic-state, and triple-center cross sections all show dips, but at different energies, and the triple-center dip is somewhat smaller. The cross section of Lüdde and Dreizler oscillates with larger amplitude than does any of the others, suggesting that their cross section is not converged. Finally, there is complete agreement with Shakeshaft's scaled-hydrogenic value at 15 keV, where the scaled hydrogenic and Sturmian values agree to within 10%.

D. Comparison with experimental results

The triple-center and experimental cross sections for electron transfer and excitation to the $n=2$ states are graphed in Figs. 10 and 11, respectively. Also shown are the previously discussed 22-state AO + results of Fritsch and Lin[27] and their recent results using a basis of AO + functions augmented by pseudostates, 40 functions in all.[29] Fritsch and Lin report their cross sections to be stable with respect to the inclusion of additional pseudostates to within 10%, but they have not included states of angular momentum greater than 1 in their basis.

Consider first the cross sections for electron transfer to the 2*p* state shown in Fig. 10. The error bars on the experimental results of Kondow, Girnius, Chong, and Fite[33] are given as one standard deviation; in addition, they note a systematic error due to polarization of the radiation which, for energies less than 15 keV, does not extend beyond the graphed error limits. The error bars on the experimental results of Morgan, Geddes, and Gilbody[32] do not include their estimated 30% absolute uncertainty. Considering the estimated absolute errors, the two sets of experimental results agree over the energy range of interest. However, the cross section of Kondow *et al.* shows a broad shallow dip from 3 to 8 keV which is not present in that of Morgan *et al.*; in addition, the former data display maxima at about 1.75 and 12 keV. The triple-center results also evidence a minimum and maxima; however, the minimum is more pronounced and the low-energy maximum is less pronounced and is at about 2.75 keV. It will be recalled that, except at 15 keV, the triple-center results are very close to those of the 100—150-pseudostate calculation of Lüdde and Dreizler.[28] Unlike the (28—36-state) triple-center results, the 40-state AO + (augmented by pseudostate) results of Fritsch and Lin do not dip at 5 keV and, unlike the triple-center and experimental results, do not drop rapidly by 15 keV. Based on the previously noted convergence tests, the neglected states in the triple-center basis may raise the cross section at 5 keV (by up to 10%), bringing it more in line with the results of Morgan *et al*; however, based on previous tests, it does not seem that these states would lower the cross section at 11 keV.

Consider, secondly, the cross sections for direct excitation to the 2*p* state shown in Fig. 11. The error limits on the experimental results of Kondow *et al.* and Morgan *et al.* have been described in the previous paragraph. For the present case the two sets of experimental results agree within the graphed estimated errors, i.e., ignoring absolute errors; however, the results of Kondow *et al.* show a deeper dip at about 11 keV. Also shown are the earlier experimental results of Young, Stebbings, and McGowan,[35] which agree with the later results. There is good agreement (within 10%) at all energies between the triple-center and augmented AO + results. Except for a somewhat deeper dip at 10 keV, the triple-center results agree with the experimental results of Kondow *et al.* within 10%; considering total experimental error limits, they also agree with the results of Morgan *et al.*

Consider, thirdly, electron transfer to the 2*s* state. Not shown in Fig. 10 are the earlier results of Morgan, Geddes, and Gilbody[32] which Morgan, Stone, and Mayo[38] note agree with their own results and those of Hill, Geddes, and Gilbody.[37] At energies of at least 2 keV, the results of Morgan, Stone, and Mayo and Hill *et al.* agree within the graphed error limits. (Hill *et al.* estimate an additional 30% absolute error in their measurements; Morgan *et al.* normalize their cross sections to the average of three previous measurements[32,34,36] at 24.5 keV, which they note agree to within about 20%.) At lower energies, the results of Hill *et al.* are larger. Also shown for energies of at least 6 keV are the generally closely agreeing results of Chong and Fite,[34] who estimate calibration uncertainties of somewhat less than 30%. Also shown are the earlier measurements of Bayfield[36] which agree with the other measurements at higher energies but are below them at energies lower than 5.5 keV. Hill *et al.* have suggested that at low energies there may have been difficulties in the measurements of Bayfield due to the small acceptance angle of his apparatus. It is seen that at lower energies, the experimental results of Morgan *et al.* agree with the 28—36-state triple-center results, while at higher energies, the experimental results favor the augmented AO + results. If the results of Morgan *et al.* were shifted uniformly downward, there would be agreement in magnitude with the triple-center results at all energies. However, there is a noticeable shoulder in the triple-center results at 5—8 keV which is hinted at by the rapid rise in the cross section of Hill *et al.* between 6 and 7 keV, but which is absent in the augmented AO + results and the

results of Morgan *et al.*

Consider finally cross sections for excitation to the $2s$ state shown in Fig. 11. The absolute error limits (not shown) on the experimental results of Morgan, Geddes, and Gilbody[32] and Chong and Fite[34] have previously been noted. There are no experimental results below 5 keV. The triple-center results agree in magnitude but not in shape with the results of Morgan *et al.*, the triple-center results showing a more pronounced dip at 10 keV. Below 10 keV, the augmented AO + results lie above (and parallel to) the triple-center results by about 30%, a not-too-large disagreement, except that the neglected triple-center states are expected to *lower* the cross section. The data of Chong and Fite roughly agree in shape with the triple-center cross section, but (ignoring questions of absolute calibration) are lower by 40% at about 8 keV.

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[1]A. F. Ferguson, Proc. R. Soc. London Ser. A 264, 540 (1961).
[2]D. R. Bates and D. A. Williams, Proc. Phys. Soc. London 83, 425 (1964).
[3]R. D. Piacentini and A. Salin, J. Phys. B 7, 1666 (1974); 9, 563 (1976); 10, 1515 (1977).
[4]F. J. Smith, Proc. Phys. Soc. London 84, 889 (1964).
[5]S. K. Knudson and W. R. Thorson, Can. J. Phys. 48, 313 (1970).
[6]R. McCarroll and R. D. Piacentini, J. Phys. B 3, 1336 (1970).
[7]D. R. Bates, K. Ledsham, and A. L. Stewart, Philos. Trans. R. Soc. London A 246, 215 (1953).
[8]G. J. Hatton, J. C. Y. Chen, T. Ishihara, and K. M. Watson, Phys. Rev. A 12, 1281 (1975).
[9]H. Rosenthal, Phys. Rev. Lett. 27, 635 (1971).
[10]U. C. Chidichimo-Frank and R. D. Piacentini, J. Phys. B 7, 548 (1974).
[11]R. Schinke and H. Krüger, J. Phys. B 9, 2469 (1976).
[12](a) D. S. F. Crothers and J. G. Hughes, Proc. R. Soc. London Ser. A 359, 345 (1978); Philos. Trans. R. Soc. London 292, 56 (1979); (b) unpublished.
[13]M. Kimura and W. R. Thorson, Phys. Rev. A 24, 1780 (1981).
[14]D. R. Bates and R. McCarroll, Proc. R. Soc. London Ser. A 247, 175 (1958).
[15]D. R. Bates, Proc. R. Soc. London Ser. A 247, 294 (1958).
[16]R. McCarroll, Proc. R. Soc. London Ser. A 264, 547 (1961).
[17]T. G. Winter and C. C. Lin, Phys. Rev. A 10, 2141 (1974).
[18]I. M. Cheshire, D. F. Gallaher, and A. J. Taylor, J. Phys. B 3, 813 (1970).
[19]D. Rapp and D. Dinwiddie, J. Chem. Phys. 57, 4919 (1972).
[20]E. J. Shipsey, T. A. Green, and J. C. Browne, Phys. Rev. A 27, 821 (1983); T. A. Green (private communication).
[21]D. F. Gallaher and L. Wilets, Phys. Rev 169, 139 (1968).
[22]R. Shakeshaft, Phys. Rev. A 14, 1626 (1976).
[23]R. Shakeshaft, Phys. Rev. A 18, 1930 (1978).
[24]D. G. M. Anderson, M. J. Antal, and M. B. McElroy, J. Phys. B 7, L118 (1974); 14, 1707(E) (1981); M. J. Antal, D. G. M. Anderson, and M. B. McElroy, *ibid.* 8, 1513 (1975).
[25]C. D. Lin, T. G. Winter, and W. Fritsch, Phys. Rev. A 25, 2395 (1982).
[26]W. Fritsch and C. D. Lin, J. Phys. B 15, 1255 (1982).
[27]W. Fritsch and C. D. Lin, Phys. Rev. A 26, 762 (1982). There are some numerical errors in the integrated cross sections reported in Table I of this paper: The $2p_1$ excitation cross section at 11.11 keV is 15.55×10^{-18} cm^2 rather than 9.89×10^{-18} cm^2. Values of the $2s$ cross sections at 1.563 keV and the $2s$ and $2p$ cross sections at 15 keV are in error by 7—8 % (except for the $2s$ capture cross section at 15 keV, which is in error by 4%). All other $2p$ and $2s$ cross sections are correct to within 2% and 5%, respectively. Corrected values are reported in Table II and Figs. 10 and 11 of the present paper.
[28]H. J. Lüdde and R. M. Dreizler, J. Phys. B 15, 2703 (1982).
[29]W. Fritsch and C. D. Lin, Phys. Rev. A 27, 3361 (1983).
[30]G. Terlecki, N. Grün, and W. Scheid, Phys. Lett. 88A, 33 (1982).
[31]G. W. McClure, Phys. Rev. 148, 47 (1966).
[32]T. J. Morgan, J. Geddes, and H. B. Gilbody, J. Phys. B 6, 2118 (1973).
[33]T. Kondow, R. J. Girnius, Y. P. Chong, and W. L. Fite, Phys. Rev. A 10, 1167 (1974).
[34]Y. P. Chong and W. L. Fite, Phys. Rev. A 16, 933 (1977).
[35]R. A. Young, R. F. Stebbings, and J. W. McGowan, Phys. Rev. 171, 85 (1968).
[36]J. E. Bayfield, Phys. Rev. 185, 105 (1969).
[37]J. Hill, J. Geddes, and H. B. Gilbody, J. Phys. B 12, L341 (1979).
[38]T. J. Morgan, J. Stone, and R. Mayo, Phys. Rev. A 22, 1460 (1980).
[39]T. G. Winter, Phys. Rev. A 25, 697 (1982).
[40]E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1961).
[41]In Eq. (33) of Ref. 39, the first subscript on every $\mathscr{Y}$ should be L, not l.
[42]K. Gottfried, *Quantum Mechanics, Volume I: Fundamentals* (Benjamin, New York, 1966).
[43]The sign in Eqs. (22) and (23) was inadvertently omitted in the corresponding Eqs. (46) and (47) of Ref. 39.