Triple-center treatment of ionization in p-H collisions

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A triple-center atomic-state method is proposed for treating ionization in low-energy ion-atom collisions. This method intrinsically accounts for the Wannier mechanism, in which the electron will not have been removed in a slow collision unless it is asymptotically at the point of unstable equilibrium between the nuclei (the chosen third center). When applied to p-H collisions, the method shows that most of the ionized electrons stay near the third center and that direct Coulomb ionization and charge transfer to the continuum—accounted for by normal double-center methods—are less important: The triple-center method dramatically raises the cross section above that obtained using a double-center pseudostate basis, bringing it closer to the single early experimental curve at energies below 15 keV.

I. INTRODUCTION

In electron-atom collisions at near-threshold energies, Wannier[1] proposed 30 years ago that ionization will not occur unless both electrons move directly away from the target nucleus in *opposite* directions, with the nucleus remaining midway between the electrons, at the point of unstable equilibrium. The energy dependence of the cross section (the Wannier threshold law) was obtained by an analysis of the three-body system when the particles are widely separated and hence move classically. The absolute magnitude of the cross section, however, could not be determined, since it depends on the detailed quantum-mechanical interactions when the particles were still close together. In recent years, efforts have been made with some success to make the arguments more rigorous, and to generalize them to any breakup process among three charged particles.[2,3]

In the case of ionization in very low-energy proton-hydrogen-atom collisions, for example, one would expect that the electron will not become free unless it moves along the equiforce point (the midpoint of the internuclear line) as the nuclei slowly separate. What is a very low-energy collision? According to Klar, the threshold energy dependences which he derived for a large number of breakup processes, including the p-H process, are only valid up to a few eV above threshold.[2] However, it is proposed here that the basic mechanism—in which the free electron remains localized at the equiforce point—may persist to much higher energies, perhaps up to energies not far below 25 keV (corresponding to 1 a.u. of velocity).

The triple-center atomic-state method[4–6] may be well suited to treating this mechanism. *Bound* atomic states centered on the equiforce point C might be expected to describe the electron localized there. In contrast, conventional double-center methods (employing only basis functions centered on the two nuclei A and B) might well fail to represent such a mechanism unless a very large basis of pseudostates, including those with large angular momenta ≥ 2, is used: The (double-center) 46-atomic-state-plus-pseudostate results of Fritsch and Lin[7] are about a factor of 5 below the only available experimental result[8] at the low energy of 7 keV; the (double-center) 70-scaled-hydrogenic-pseudostate results of Shakeshaft[9] (which only extend down to 15 keV) also appear to be decreasing too rapidly with decreasing energy. Single-center methods, while correct in a purely formal sense, would require even larger bases than double-center bases to describe ionization.

In contrast, direct and charge-transfer excitation to the $2s$ and $2p$ states are treatable at low energies by a double-center basis, at least provided intermediate coupling to ionization states is small: The double-center results of Fritsch and Lin generally agree well with the 1.5—15-keV triple-center results[6] of the present authors. (The scaled-hydrogenic-pseudostate results of Shakeshaft also generally agree in the overlapping energy range.) The different placement of united-atoms orbitals in the modified AO + method (the Fritsch-Lin method[7]) and the triple-center method is not very important for treating excitation and electron transfer.

In the present study of ionization, the energy range of interest is again 1.5—15 keV. In this range, the bound and continuum states may be strongly coupled, and the relative importance of individual states—states in the "normal continuum" (centered on A and B) and states in the localized continuum (centered on C) (as well as bound states centered on A and B)—must be tested.

At lower energies (≤ 500 eV), SethuRaman, Thorson, and Lebeda[10] have argued that first-order perturbation theory within a molecular framework is valid. They have found that only couplings from the $2p\sigma_u$ and $2p\pi_u$ states (which correlate to *ungerade* combinations of $1s_A$, $1s_B$ and $2p_{1A}, 2p_{1B}$, respectively, in the separated-atoms limit)

to the first few continuum σ_u and π_u states are important. These couplings will be seen to be of crucial importance in the present triple-center calculation.

Further, in the energy range of their calculations they have assumed the nuclei follow a classical $2p\sigma_u$ trajectory. In the higher-energy range of the present calculations, the trajectory has reasonably been assumed to be straight.[11]

The outline of the paper is as follows: In Sec. II the triple-center method will be summarized and numerical checks presented; in Sec. III the role of individual states in the basis will be assessed, ionization probabilities versus impact parameter and total ionization cross sections will be presented, and cross sections will be compared with other theoretical and with experimental results. Unless otherwise indicated, Hartree's atomic units are used.

II. THEORY
A. Formulation

What follows is a summary of the triple-center method. Generalizations from that described previously[6] will be noted.

The time-dependent electronic wave function $\Psi(\vec{r},t)$ is expanded in a basis of exact or approximate traveling atomic orbitals $f_{k\alpha}(\vec{r},t)$ on three centers $\alpha = A$, B, and C:

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

where

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

$$(2)$$

$$q_\alpha = \begin{cases} -\tfrac{1}{2}, & \alpha = A , \\[4pt] +\tfrac{1}{2}, & \alpha = B , \\[4pt] p - \tfrac{1}{2}, & \alpha = C , \end{cases} \qquad (3)$$

each $\psi_{k\alpha}$ being an exact or approximate atomic wave function—bound or continuum—centered on nucleus α with corresponding eigenvalue $\epsilon_{k\alpha}$, and $\vec{r}_\alpha$ and $\vec{r}$ being the electronic position vectors relative to the center α and the origin (here taken to be the midpoint of the internuclear line), respectively. (The velocity of nucleus B relative to nucleus A is $\vec{v}$.)

The quantity p is here taken to be $Z_A^{1/2}/(Z_A^{1/2}+Z_B^{1/2})$. This fixes C to be the equiforce point. For proton-hydrogen collisions (and other collisions involving equal nuclei), the equiforce point coincides with the center of charge. In our two previous papers,[5,6] which treated electron transfer and excitation in proton-hydrogen collisions, we suggested that the proper generalization to asymmetric systems was to choose C to be the center of charge (nearer the more highly charged nucleus). The Wannier mechanism for ionization, however, strongly suggests that one choose C to be the equiforce point (nearer the less highly charged nucleus). With this present choice of C, the above definition of p follows, rather than $p = Z_B/Z_C$ (with $Z_C = Z_A + Z_B$) as in Refs. 5 and 6; the formulation

described at greater length in Ref. 6 otherwise follows through unchanged except for the generalization of basis functions described in this section.

The orthonormal atomic wave functions $\psi_{k\alpha}$ and eigenvalues $\epsilon_{k\alpha}$ in Eq. (2) are obtained by diagonalizing the atomic Hamiltonian

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

in a finite basis of hydrogenic functions $\phi_{j\alpha}(z_{j\alpha},\vec{r}_\alpha)$ of effective charges $z_{j\alpha}$:

$$\langle \psi_{k\alpha} | H_\alpha | \psi_{k'\alpha} \rangle = \epsilon_{k\alpha}\delta_{kk'} ,$$

$$(5)$$

$$\langle \psi_{k\alpha} | \psi_{k'\alpha} \rangle = \delta_{kk'} ,$$

where

$$\psi_{k\alpha} = \sum_{j=1}^{j_{\max}} C_{kj\alpha}\phi_{j\alpha} . \qquad (6)$$

The orthonormal basis functions $\phi_{j\alpha}(z_{j\alpha},\vec{r}_\alpha)$ are themselves exact bound-state eigenfunctions of the Hamiltonians

$$h_{j\alpha} = -\tfrac{1}{2}\nabla^2 - z_{j\alpha}/r_\alpha$$

with eigenvalues $e_{j\alpha}$; that is,

$$h_{j\alpha}\phi_{j\alpha} = e_{j\alpha}\phi_{j\alpha} .$$

This set of hydrogenic basis functions can possibly be made sufficiently complete by choosing the effective charges $z_{j\alpha}$ appropriately. (Alternatively, a basis of Slater-type orbitals of various effective charges could be used.) If $z_{j\alpha} = Z_\alpha$, then $e_{j\alpha} = \epsilon_{j\alpha}$ and $\phi_{j\alpha} = \psi_{j\alpha}$ (i.e., the basis function $\phi_{j\alpha}$ is also an eigenfunction of H_α), and the traveling orbital $f_{j\alpha}$ is "exact." If not, then some of the eigenvalues $\epsilon_{k\alpha}$ of H_α will usually be positive, partially representing the continuum of H_α; this is the way in which the present calculation for ionization may depart from our previous one[6] for excitation and electron transfer. The role, if any, of the normal continuum on A and B in the triple-center method can now be tested. The specific choices of the effective charges $z_{j\alpha}$ will be deferred to Sec. III.

As in Ref. 6, the expansion for $\Psi(\vec{r},t)$, given by Eq. (1), is substituted into the full time-dependent Schrödinger equation, multiplied by $f_{k\alpha}^*$, and integrated over all space, yielding a set of coupled, first-order differential equations for the expansion coefficients $a_{k\alpha}(t)$. As in Ref. 6, the matrix elements in the coupled equations connect $f_{k\alpha}$ and $f_{k'\beta}$, and hence the eigenfunctions $\psi_{k\alpha}$ and $\psi_{k'\beta}$ of $H_{\alpha,\beta}$. In the present case, however, each matrix element between $\psi_{k\alpha}$ and $\psi_{k'\beta}$ is now expressible [by means of Eq. (6)] as a linear combination of matrix elements between the similar basis functions $\phi_{j\alpha}$ and $\phi_{j'\beta}$.

The coupled equations for the $a_{k\alpha}(t)$'s are solved as before with the initial condition

$$a_{k\alpha}(-\infty) = \delta_{1sA,k\alpha} ,$$

and the probability for ionization at a given impact pa-

rameter ρ is now

$$P(\rho) = \sum_{k,\alpha} |a_{k\alpha}(\rho,\infty)|^2, \quad \alpha = A,B,C$$

with k here ranging only over states of positive $\epsilon_{k\alpha}$ if $\alpha = A$ or B.

As in Ref. 6, the equations have been integrated numerically with respect to the alternate variable vt. Each integration has now been done in the following two stages: (1) from $vt = -500$ to -84 (or -104), only the (exact) states $1s_A, 2s_A, 2p_{0,1A}$ have been coupled and (2) from $vt = -84$ (or -104) to $+84$ (or $+104$) all *gerade* and *ungerade* states have been separately coupled. The first range has only a small (probably negligible) effect on the ionization probabilities. The second range is sufficient to keep the summed total probability at unity to within about 10^{-5} at the final value of vt and the summed ionization probability stable to one or two units in the third digit with respect to increasing this vt range. [Extending the range (2) to be from -104 to $+104$ was needed for some test calculations with more diffuse functions (larger bases) than those used in the final production runs.]

B. Further numerical tests

Although the change to the formulation in making the hydrogenic basis arbitrary is straightforward, it entails many after-the-fact changes in the triple-center computer program. Particular care must be taken to ensure that (1) the effective charge $z_{j\alpha}$, formerly equal to Z_α, is now arbitrary and (2) the number of $z_{j\alpha}$'s for a given nlm, formerly unity, is now also arbitrary. Numerous checks of the revised program have therefore been made: (1) conservation of probability, as previously noted, has been monitored, partially testing the non-Hermitian charge-

exchange matrix elements; (2) the revised program has been checked to give the same probability (for every state) to eight digits as in the unrevised program when the same *bound*-state triple-center basis was used in both programs; (3) the revised program has been checked to give the same probability (for every state) to three digits as in the Sturmian program of Winter[12] when the same double-center Sturmian basis ($nl_\alpha, nl \leq 3p, \alpha = A,B$) was used in both programs (the Sturmian basis being obtained in the present case by appropriately adjusting the $z_{j\alpha}$'s); (4) many double- and triple-center matrix elements involving s and p functions for various bases have been checked by hand in the zero-velocity and zero-internuclear-separation limits; and (5) the eigenvalues have been checked against known values for several hydrogenic[7] and Sturmian[12,13] bases.

III. RESULTS

A. Ionization probabilities and tests of bases

In their calculations at lower projectile energies E using first-order perturbation theory, SethuRaman, Thorson, and Lebeda[10] found that *gerade* states contribute negligibly ($\leq 0.2\%$) to the total ionization cross section. We have largely confirmed this at higher energies using a triple-center basis (with, however, only bound states on each center in this test): the contributions are only 0.04% and 0.4% at $E = 1.563$ and 5.16 keV, respectively, and even at $E = 11.11$ keV, the contribution is only 11%. [These tests were made at the impact parameters $\rho = 1$, 1.25, and 1.5, respectively, each near the peak in $\rho P(\rho)$; see Fig. 1.] As pointed out by them, the dominance of *ungerade* channels reflects the primary importance of $2p\sigma_u \to \epsilon p\pi_u$ and $2p\pi_u \to \epsilon p\sigma_u$ transitions to the continuum; transitions from the $1s\sigma_g$ state are much less impor-

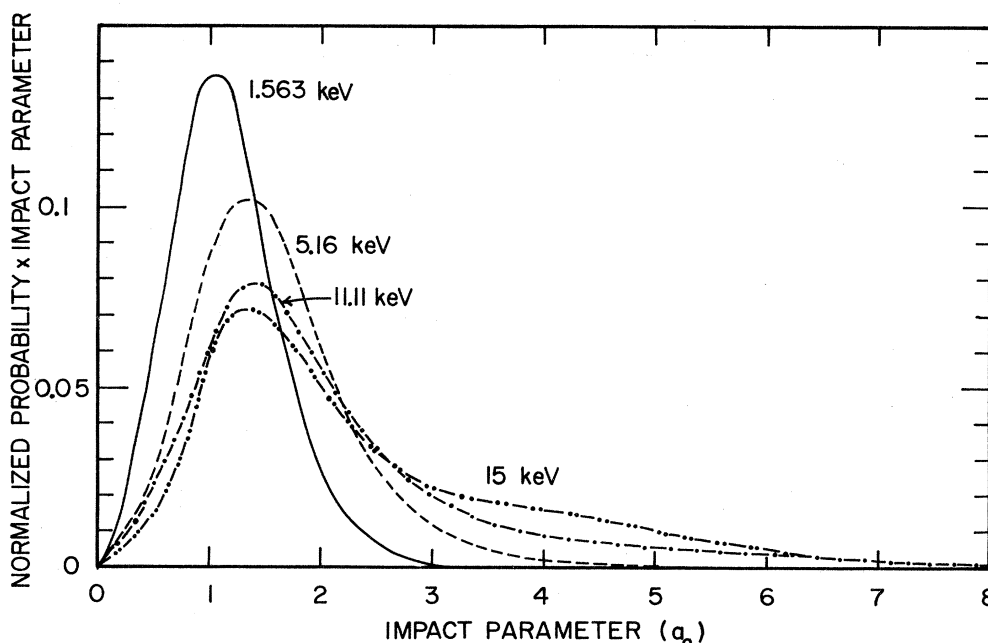FIG. 1. Normalized triple-center probabilities times impact parameter $\rho P(\rho)/Q$ (in a.u.) vs impact parameter ρ for ionization in proton-hydrogen collisions at various proton energies. The area under each curve is $(2\pi)^{-1}$. The basis consists of 20 *ungerade* states and, at the two higher energies, also 16 *gerade* states, defined in footnotes a and f of Table I.

tant, partly due to the larger energy gaps, but also due to the smaller matrix elements (provided carefully chosen translational factors are used). (It should be mentioned here that before doing the first-order calculations, they have, correctly, strongly coupled the $2p\sigma_u$ and $2p\pi_u$ states.) Indeed, the shape of the curve $\rho P(\rho)$ versus ρ is only weakly energy dependent over the entire energy range 1.5–15 keV of the present calculation (see Fig. 1), suggesting an energy-independent mechanism for ionization. That the single peak in the curve at a given energy occurs very near the one for $2p$ excitation[6] (not shown) confirms that the $2p\pi_u$ state plays a critical role in ionization.

Before proceeding further with a discussion of the role of individual states, it is appropriate here to point out what does not appear to be widely understood: that *at low energies* where *ungerade* states predominate in describing ionization, *charge transfer to the continuum and direct ionization must be equally likely* in a double-center-treatment. In his double-center scaled-hydrogenic pseudostate calculations for $E \geq 15$ keV, Shakeshaft[9] found charge-transfer ionization to dominate up to the cross section's peak at 60 keV. (The effect is only meaningful provided the same functions are placed on each nucleus.) (In contrast, direct ionization dominates at higher energies.) However, this dominance does *not* extrapolate to lower energies. Indeed, Fritsch and Lin have found their cross sections for direct- and charge-transfer ionization to nearly merge at about 5 keV. Of course, it is contended here that at low energies, a double-center treatment will not give the correct magnitude of the cross section without an intractably large basis including large angular momenta ≥ 2 to describe the triple-center character of the ionization process; nevertheless, the equality of the two kinds of ionization cross sections must hold at low energies even for a smaller basis if the relevant part of the electronic wave function is to have the correct *ungerade* symmetry.

Since the *ungerade* states are by far the more important ones, the study of the contributions of particular states will largely be restricted to *ungerade* states. The minimal *ungerade* basis has been found to consist of *bound* states on each center: all states up to $3d$ on A and B, and all states up to $4f$ on C, i.e., $1s_{A-B}, 2s_{A-B}, \ldots, 3d_{2A-B}$, $2p_{0,1C}, 3p_{0,1C}, 4p_{0,1C}, 4f_{0,1,2,3C}$. Note that there are ten bound *ungerade* states on A and B (when combined to give the correct symmetry) and ten bound *ungerade* states on C, each of the latter having the effective charge $Z_C = 2$ of the united atom. The states on C, in addition to representing molecular wave functions in the united-atoms limit, represent the continuum localized at the third center C, the point of unstable equilibrium. Note that, by symmetry, the third-center states $1s_C, 2s_C, 3s_C$, $3d_{0,1,2C}, \ldots$ are excluded from the *ungerade* basis; these and other *gerade* states will begin to become important only at higher energies (see below).

That this 20-state *ungerade* triple-center basis is adequate can be seen from the only small effects of additional *ungerade* states shown in Table I. Calculating these tabulated values of the ionization probability $P(\rho)$ has taken considerable computing time: typically 40 min. on an IBM 3081 computer for each E and ρ. (Both the evalua-

tion of matrix elements and the integration of the coupled equations take a long time.) Therefore the tests were restricted to a single impact parameter ρ at each energy E near where $\rho P(\rho)$ is a maximum.

Consider first the effect of the normal continuum centered on A and B. In their double-center atomic-state-plus-pseudostate calculation, Fritsch and Lin[7] augmented their bound-atomic-state basis—the same as ours—with five $1s$ hydrogenic pseudostates having effective charges $z = 0.5$, 0.8, 1.25, 1.5625, and 2.4414 and eight $2p$ hydrogenic pseudostates having effective charges $z = \frac{2}{3}$, 1.8, 2.9, and 4.48. These pseudostates yielded some small positive eigenvalues ϵ_{kA} ($= \epsilon_{kB}$) of the true atomic Hamiltonian H_A (and H_B), and led to ionization cross sections quite stable (to within 10%) with respect to the enlargement of the basis of angular momentum 0 and 1. (They did not include pseudostates of angular momentum greater than 1.) We will consider the effect of essentially these same pseudostates when added to the previously described 20-state *ungerade* triple-center basis. As far as s states are concerned, the only differences (from the Fritsch-Lin basis) are that at 5.16 and 11.11 keV, the eigenfunctions ψ_{kA} and ψ_{kB} of the highest eigenvalue $\epsilon_{kA} = \epsilon_{kB} \cong + 13$ were dropped and that at 1.563 keV the eigenfunctions $\psi_{k'A}$ and $\psi_{k'B}$ of the next highest eigenvalue $\epsilon_{k'A} = \epsilon_{k'B} \cong + 2.3$ were also dropped. A test by us at 1.563 keV with a limited basis (not shown) indicated that even dropping the second eigenfunction pair affects the ionization probability by only 1%. (Owing to the energy phase, the corresponding matrix elements oscillate so rapidly, particularly at the lowest energy, that very little flux goes into these states.) Referring to Table I, it is seen that the effect of adding these s-state wave functions to the 20-state basis is only 7.2–14.7%. In the case of p pseudostates, the pseudostates of the highest effective charge, $z = 4.48$, were dropped rather than the eigenfunctions of highest eigenvalue, $\epsilon_{A,B} \cong + 4.6$; the effects of the two basis reductions would probably be similar since compact pseudostates have components of short wavelength and hence high energy. Referring again to Table I, it is seen that the effect of adding these p-state functions to the 20-state basis is also small: 2.0–9.5%. Thus the s and p parts of the normal continuum are estimated to separately change the *ungerade* part of the triple-center ionization probability by less than 15%; their combined effects (if they are simply additive) are still less than 15%.

At energies $E \geq 10$ keV, their effects on the small but now non-negligible *gerade* ionization probability need also to be considered. Expressed in absolute terms or as a percent of the total ionization probability, their effects on the *gerade* probability are seen in Table I to be small at 11 keV: less than 10%, and the total effect (*gerade* plus *ungerade*) is also less than 15%. In summary, we have the important result that the *bound states localized on the equiforce point C are the primary ionization channels*.

Some additional tests were carried out to ensure that this bound-state basis on center C is itself stable. Referring to Table I, it is seen that at each of the three energies given, the combined effects of the $5p_{0,1C}$ and $6p_{0,1C}$ states do not exceed 9%. Two other tests were carried out at only the lowest energy: The pseudostates $5\bar{p}_{0,1C}$ and

TABLE I. Probabilities of ionization $P(\rho)$ in p-H collisions using various triple-center bases. At each of the given projectile's energies E (keV), the impact parameter ρ is near where $\rho P(\rho)$ is a maximum.

Ungerade basis	$(E,\rho)=$	(1.563,1)	(5.16,1.25)	(11.11,1.5)
20 states[a]		0.004 42	0.0306	0.0517
$+ 4\bar{s}_{A-B}, 5\bar{s}_{A-B}, 6\bar{s}_{A-B}$ [b]		0.005 07		
$+ 7\bar{s}_{A-B}$ [c]			0.0272	0.0554
20 states		0.004 42	0.0306	0.0517
$+ 4\bar{p}_{0,1A+B}, 5\bar{p}_{0,1A+B}, 6\bar{p}_{0,1A+B}$ [d]		0.004 18[h]	0.0300[h]	0.0468[h]
20 states$-4p_{0,1C}$		0.002 19		
$+ 4p_{0,1C}$		0.004 42	0.0306	0.0517
$+ 5p_{0,1C}$		0.004 65	0.0301	0.0517
$+ 6p_{0,1C}$		0.004 30	0.0292[h]	0.0562[h]
20 states		0.004 42		
$+ 5\bar{p}_{0,1C}, 6\bar{p}_{0,1C}$ [e]		0.003 80		
20 states		0.004 42		
$+ 5f_{0,1,2,3C}$		0.004 08		
Gerade basis				
16 states[f]				0.0062
$+ 4\bar{s}_{A+B}, 5\bar{s}_{A+B}, 6\bar{s}_{A+B}, 7\bar{s}_{A+B}$ [g]				0.0038
16 states				0.0062
$+ 4\bar{p}_{0,1A-B}, 5\bar{p}_{0,1A-B}, 6\bar{p}_{0,1A-B}$ [g]				0.0041[h]

[a]The 20 states include all *ungerade* combinations of states on A and B up to $3d$ and all *ungerade* states on C up to $4f$. (In a given row, the basis in each group consists of all functions listed down to and including those in that row.)

[b]The pseudostates have been obtained by means of the additional $1s_{A-B}$ basis functions with effective charges 0.5, 0.8, 1.25, 1.563, and 2.4414 (Ref. 7). The pseudostates with the two highest eigenvalues have been deleted.

[c]The pseudostates are as in footnote b except that only the pseudostate with the highest eigenvalue has been deleted.

[d]The pseudostates are obtained by means of the additional $2p_{0,1A+B}$ basis functions with effective charges 0.666 67, 1.8, and 2.9 (Ref. 7, with the function of effective charge 4.48 deleted).

[e]The pseudostates are obtained by means of the additional $2p_{0,1C}$ basis functions with effective charges 0.666 67 and 1.0.

[f]The 16 states include all *gerade* combinations of states on A and B up to $3d$ and all *gerade* states on C up to $3d$.

[g]These pseudostates are the *gerade* counterparts of those in footnotes c and d.

[h]The *ungerade* state $3s_{A-B}$ or the *gerade* state $3s_{A+B}$ has been deleted.

$6\bar{p}_{0,1C}$ defined in Table I were found to have an effect of 14%, and the bound states $5f_{0,1,2,3C}$ were found to have an effect of 8%. In summary, the combined effects of the neglected states centered on C are probably not more than 20%. The $np_{0,1C}$ states are the most important ionization states, which is not inconsistent with the observation of SethuRaman, Thorson, and Lebeda[10] for lower energies that the $\epsilon p\sigma_u$ and $\epsilon p\pi_u$ states are the most important ones.

B. Comparison of ionization cross sections with experimental and other theoretical values

There are no experimental ionization cross sections at the very lowest energies of the present results. Consider first the low-energy results of SethuRaman, Thorson, and Lebeda[10] using first-order perturbation theory with molecular states, as shown in Fig. 2. (The present results are also given in Table II.) It is seen that on a log-log scale, their four cross sections lie closely on a straight line which obeys the simple power law $Q = cE^{3.0}$. (The two lower points give an exponent of 2.912, while the two higher ones give 3.005.) This line, when extrapolated by 1.5 orders of magnitude, ties in fairly well with our lowest-energy triple-center point (within a factor of 1.8). The deviation of the ionization cross section from a straight line at higher energies may well reflect the closely coupled nature of the states at these energies. The exponent of 3.0 which fits the power law of their results is far smaller than the exponent determined by Klar[2]—of the order of 100—in the power law for ionization near threshold: At 100 to 500 eV the cross section drops by 3,
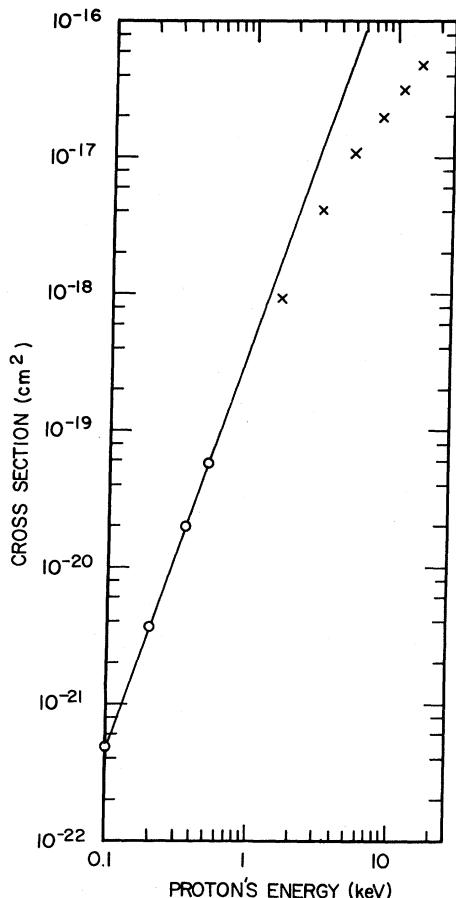
FIG. 2. Cross sections for ionization in proton-hydrogen collisions using the triple-center coupled-atomic-state method (×, present results) and a first-order-perturbation molecular-state method (○, SethuRaman, Thorson, and Lebeda, Ref. 10). The straight line is an extrapolation of the first-order results to higher energies.

FIG. 3. Cross sections for ionization in proton-hydrogen collisions. The theoretical results are as follows: —— and ×, triple center, present results; — — —, double-center atomic-state-plus-pseudostate, Fritsch and Lin (Ref. 7); — · — · —, double-center scaled-hydrogenic pseudostate, Shakeshaft (Ref. 9) (at 15-30 keV displaced from dashed curve for clarity); △, numerical solution, Terlecki, Grün, and Scheid (Ref. 17). The experimental results are as follows: ○, Fite, Stebbings, Hummer, and Brackmann (Ref. 8); ●, Shah and Gilbody (Ref. 14); □, Park, Aldag, George, Peacher, and McGuire (Ref. 15, renormalized to the data of Ref. 14 at 200 keV).

rather than roughly 100, orders of magnitude for every order-of-magnitude decrease in energy. Nevertheless, it appears that the fundamental mechanism—ionization to states localized near the equiforce point—holds over the entire range of energies from threshold to at least 15 keV.

The present triple-center results are compared with experimental and other theoretical results at higher energies

TABLE II. Cross sections Q for ionization in p-H collisions at various projectile energies E using a triple-center basis.[a]

E (keV)	Q $(10^{-16}$ cm$^2)$
1.563	0.00921
3.0	0.0407
5.16	0.106
8.0	0.193
11.11	0.313
15.0	0.480

[a]The basis consists of 20 ungerade states and, at the four higher energies, also 16 gerade states, defined in footnotes a and f of Table I.
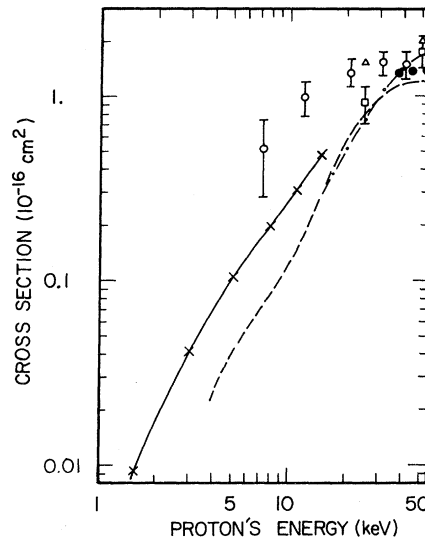
in Fig. 3. Only the data of Fite, Stebbings, Hummer, and Brackmann[8] extend at least partly down into the energy range of the present results. Although they are at somewhat higher energies, the experimental data of Shah and Gilbody[14] and Park, Aldag, George, Peacher, and McGuire[15] are also shown up to 50 keV. The omitted total error limits on the data of Shah and Gilbody are less then 10%; the data of Park et al. have been renormalized to that of Shah and Gilbody at 200 keV and thus have a small uncertainty in normalization (also omitted). The uncertainty in the normalization of the data of Fite et al. is not clear.[16] All three sets of data agree closely near the cross section's peak at roughly 50 keV. However, the very limited data of Park et al. appears to decline more steeply with decreasing energy than the data of Fite et al. The data of Park et al. may slightly favor the triple-center results over the double-center results. Despite the disagreement of the data of Fite et al. with both the double- and triple-center results, these data clearly favor the latter: At the lowest experimental energy of 7.2 keV, the lower experimental error limit is "only" 48% above the triple-center result whereas it is a factor of 4 above the double-center atomic-state-plus-pseudostate result of Fritsch and Lin.[7] Although not calculated to as low an energy, the trend of the double-center scaled-hydrogenic-pseudostate results of Shakeshaft[9] appears to be very similar to that of Fritsch and Lin. At their lowest energy, the double-center results of Fritsch and Lin differ by a large factor of 3 from the triple-center result.

At energies of at least 25 keV there also exist theoreti-

cal cross sections which Terlecki, Grün, and Scheid[17] obtained by numerically solving the time-dependent Schrödinger equation. At 25 keV the cross section is significantly—about a factor of 2—above that of the double-center methods,[7,9] but agrees with the experimental result of Fite *et al.* The extrapolation to lower energies cannot be predicted.

Not shown in Fig. 3 are the three other theoretical cross sections which extend down to the range of energies of the present results: the results of a single-center calculation by Janev and Presnyakov,[18] a Glauber calculation by Golden and McGuire,[19] and a fully classical calculation by Banks, Barnes, and Wilson.[20] The single center and Glauber results enjoy good agreement with the experimental results of Fite *et al.* However, both of these calculations are based on lower-order theories of questionable validity at these low energies: The double-center results of Fritsch and Lin and of Shakeshaft clearly show that charge transfer to the continuum—not explicitly included in the single-center calculation—is important. Further, at most three states (the initial state, a particular continuum state, and the $2p$ target state) were simultaneously coupled in each single-center calculation. The Glauber calculation is based on a higher-energy first-order method which has no *a priori* validity in the strong-coupling region at lower energies. The classical results of Banks *et al.*[20] (which are

consistent with the earlier results of Abrines and Percival[21] and Banks[22] and the later results of Olson and Salop[23]) enjoy no such agreement with experiment: They decrease too rapidly with decreasing energy, being an order of magnitude too low at 12.5 keV. This is not surprising: While even at low energies the electron probably behaves classically at large distances from the nuclei (e.g., when it is asymptotically at the equiforce point), it behaves quantum mechanically in the inner "reaction zone" at these energies.

In summary, the triple-center method yields stable ionization cross sections at low-kilo-electron-volt energies which are much larger than those of double-center methods. The triple-center method intrinsically accounts for the Wannier mechanism, in which the free electron remains localized near the equiforce point—the chosen third center. The limited experimental results favor the triple-center cross sections over those of the double-center methods.

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