Electron capture by protons in helium and hydrogen atoms at intermediate energies

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Cross sections for electron capture into each excited state of hydrogen up to $4f$ by proton impact on hydrogen and on helium in the energy range of 15–1000 keV have been calculated by means of the Born approximation (Bates's version). In addition we have used the method of close coupling to calculate the $2s$, $3s$, $2p$, $3p$, and $3d$ cross sections for the proton-helium process in the energy range of 30–300 keV. Evaluation of the two-center integrals occurring in the Born amplitude was facilitated by expanding the atomic wave functions in terms of Gaussian-type orbitals. At high energies the relative cross sections of the nl states (obtained from the Born approximation) for a given l may be related to the importance of close encounters. For the close-coupling calculations we have included as many as eleven states in the multistate expansion of the total wave function. The effects of the intermediate states on the cross sections of the various excited states have been examined. The convergence of multistate cross sections to the two-state cross sections and to the Born cross sections is found to be slow, particularly for p and d states. Comparison of the 11-state close-coupling cross sections of the proton-helium process with experiment shows substantial agreement for the $2s$ and $2p$ states, and, at lower energies, for the $3s$, $3p$, and $3d$ states. At higher energies, however, differences between theory and experiment for the $3s$, $3p$, and $3d$ states somewhat exceed estimated experimental errors.

I. INTRODUCTION

Theoretical treatment of the problem of charge-exchange collisions[1] between two atomic systems dates back to 1928.[2] For a typical process

$$(A+e)+B \rightarrow A+(B+e), \tag{1}$$

the interaction potential between the two colliding systems may be expressed in terms of the coordinates $\vec{r}$ of the active electron (measured from A or B) and the internuclear distance vector $\vec{R}$ in the *prior* or *post* form as

$$\begin{aligned} V(\vec{r},\vec{R}) &= -Z_B e^2/r_B + Z_A Z_B e^2/R \quad \text{(prior)}, \\ V(\vec{r},\vec{R}) &= -Z_A e^2/r_A + Z_A Z_B e^2/R \quad \text{(post)}, \end{aligned} \tag{2}$$

if A and B are bare nuclei. In the early Born-approximation calculations of Oppenheimer[2] and of Brinkman and Kramers,[3] the potential was taken to include only the first term, with the term $Z_A Z_B e^2/R$ omitted on the ground that the nuclear-nuclear interaction physically should have no effect on charge exchange. Bates and Dalgarno[4] and Jackson and Schiff[5] have pointed out the importance of including the nuclear repulsion term, as it partially offsets the errors incurred from the nonorthogonality of the initial and final states. Extensive application of this scheme for calculating charge-exchange cross sections has been made by Mapleton and co-workers.[6–10] The problem of nonorthogonality of the initial and final states has been treated by Bates,[11] who has shown that the nonorthogonality can be properly taken into account if one replaces (2) by an effective interaction potential

$$V_{\text{eff}} = (1-S^2)^{-1}(V - \langle V \rangle), \tag{3}$$

where V is the prior (or post) potential in (2) and $\langle V \rangle$ is the result of averaging over the prior (or post) electron distribution, and $S = |S_{ij}|$ is the overlap integral between the prior and post electron orbitals (traveling orbitals) distinguished by subscripts i and j, respectively. Nevertheless, even with the effective potential (3), the use of the Born approximation is justifiable only for high impact energy. To extend the calculation to the lower-energy range, more refined methods such as the method of close coupling should be used.[11]

In the last few years, experimental measurements of charge-exchange cross sections for electron capture into the various excited states of H by H^+ impact on gases (especially helium) have been reported.[12] To make a comprehensive comparison between theory and experiment we have calculated charge-exchange cross sections of the processes

$$H^+ + He(1s^2) \rightarrow H(nl) + He^+(1s)$$

by means of the Born approximation (Bates's version) and by a multistate close-coupling scheme. Analyses of these results give us a quantitative measure of the validity of the Born approximation as well as an assessment of the over-all accuracy of the multistate close-coupling calculations. For the purpose of checking our computational programs and of providing additional data for comparison, we have also performed similar calculations for the proton-hydrogen charge-exchange

processes:

$$H^+ + H(1s) \rightarrow H(nl) + H^+.$$

II. BORN APPROXIMATION

The calculation of cross sections by means of the Born approximation with Eq. (3) for the interaction potential entails the evaluation of a number of two-center integrals. Mapleton[9] expressed some of these integrals in terms of double Feynman integrals which he evaluated numerically. To simplify the computational work, we have made use of Gaussian-type orbitals[13] (GTO) which have been employed extensively in the calculations of the electronic structure of molecules[14] and solids[15] and of electron-molecule excitation cross sections.[16,17] Here we express the atomic wave functions in terms of Gaussian orbitals[18] so that the two-center oscillatory integrals readily reduce to a number of one-center ones, some of which can be expressed in a simple analytic form, and the others, in terms of Dawson's integral,

$$Y(x) = e^{-x^2} \int_0^x dt\, e^{t^2}, \tag{4}$$

an analytic function of a single variable whose properties are well known.[19-21]

To further simplify the scope of computations, we introduce the approximation of neglecting the S^2 term in Eq. (3). Justification of this approximation for the resonant proton-hydrogen process of electron capture at energies of the order of 100 keV or larger has been noted by McCarroll.[22] For the proton-helium case, by considering the magnitude of the overlap integral $|S_{ij}|$ at $R=0$, we estimate that the error entailed in neglecting $|S_{ij}|^2$ in the $(1-|S_{ij}|^2)$ denominator should be no more than a few percent for $j=nl \geq 2s$ at energies above 50 keV. The effective interaction potential in Eq. (3) with the $1-S^2$ denominator missing has been derived by Bassel and Gerjuoy in a different way.[23]

The amplitude for electron capture by the proton into the jth state of the resulting hydrogen atom is given by

$$f_j = -(M\sqrt{N}/2\pi)B_j, \tag{5}$$

where N is the number of electrons in the target atom (either one or two), M is the reduced nuclear mass, and the Born integral B_j is

$$B_j = \int d\vec{R}\, d\vec{r}_1 \cdots d\vec{r}_N\, e^{i(\vec{K}_i\cdot\vec{R}_i - \vec{K}_j\cdot\vec{R}_f)} \Phi_j^* V_{\text{eff}} \Phi_i. \tag{6}$$

Unless otherwise specified, Hartree's atomic units are used throughout. Here $\vec{R}$ is the position vector of the projectile B relative to the target nucleus A; $\vec{r}_k$ is the position vector of the kth electron; $\vec{R}_i$ is the position vector of the projectile relative to the center of mass of the target atom; $\vec{R}_f$ is the position vector of the center of mass of the final hydrogen atom relative to the center of mass of the residual target ion; and $\vec{K}_i$ and $\vec{K}_j$ are the corresponding propagation vectors. The initial and final atomic wave functions are designated by Φ_i and Φ_j, respectively. Using the approximation which neglects S^2 terms, the interaction potential is written in the form

$$V_{\text{eff}} = V_i - \langle V_i \rangle, \tag{7}$$

where V_i is the prior potential energy, i.e.,

$$V_i = -Z_B \sum_{\lambda=1}^{N} r_{\lambda B}^{-1} + \frac{Z_A Z_B}{R} \tag{8}$$

and

$$\langle V_i \rangle = \int d\vec{r}_1 \cdots d\vec{r}_N\, \Phi_i^* V_i \Phi_i. \tag{9}$$

The nuclear-nuclear term $Z_A Z_B/R$ is not affected by the integration over the electron coordinates, and therefore cancels out in V_{eff}.[11] Following the procedure outlined in Refs. 3 and 4, we express the phase of the plane-wave factor in Eq. (6) in terms of the coordinates of the electrons relative to the nuclei A and B as

$$\vec{K}_i\cdot\vec{R}_i - \vec{K}_j\cdot\vec{R}_f = \vec{\alpha}\cdot\vec{r}_A + \vec{\beta}\cdot\vec{r}_B \quad \text{(for one electron)}, \tag{10}$$

$$\vec{K}_i\cdot\vec{R}_i - \vec{K}_j\cdot\vec{R}_f = \vec{\alpha}\cdot\vec{r}_{1A} + \vec{\beta}\cdot\vec{r}_{1B} + \vec{\gamma}\cdot\vec{r}_{2A} \quad \text{(for two electrons)}, \tag{11}$$

where $\vec{\alpha}$, $\vec{\beta}$, and $\vec{\gamma}$ are related to $\vec{K}_i, \vec{K}_j$, and the masses of the two nuclei, M_A and M_B. As an example, we cite

$$\vec{\alpha} = (M_A + N)^{-1}(M_A + N - 1)\vec{K}_i - \vec{K}_j. \tag{12}$$

It can be shown that $\vec{\gamma} = -\vec{\alpha}/(M_A+1)$. This implies that the momentum transfer of the passive electron is completely negligible. Accordingly, the $\vec{\gamma}$ term in Eq. (11) will be dropped. Defining Δ to be the total increase in atomic energy measured in rydbergs, one finds, to first order in $1/M_A$ and $1/M_B$,

$$\beta^2 = \alpha^2 + \Delta, \tag{13}$$

$$\vec{\alpha}\cdot\vec{\beta} = -\alpha^2 - \tfrac{1}{2}\Delta + \tfrac{1}{2}v^2, \tag{14}$$

where v is the projectile speed. The total cross section is then obtained by integrating $|f_j|^2$ over the scattering angle θ. We have found it convenient to change the variable of integration from $\cos\theta$ to α^2 through Eq. (12) and the conservation of energy.

Consider the evaluation of B_j in Eq. (6) for the two-electron case. The integral corresponding to the first term $(-Z_B/r_{1B})$ of four terms in V_{eff} as given by Eqs. (7) and (8) is the familiar Brinkman-Kramers term which has been evaluated by several

authors.[24] The integration of the three remaining terms is accomplished by the Gaussian method. The initial atomic wave function is that of a helium atom in the ground state, i.e.,

$$\Phi_i = \phi_{1s}^{\mathrm{He}}(r_{1A})\phi_{1s}^{\mathrm{He}}(r_{2A}), \tag{15}$$

whereas the final state which consists of two hydrogenic atoms (He^+ centered on A and H centered on B) may be described by

$$\Phi_j = R_{nl}(r_{1B})Y_{lm}(\hat{r}_{1B})R_{1s}^{(2)}(r_{2A})/\sqrt{4\pi}\,, \tag{16}$$

where R and $R^{(2)}$ are the radial hydrogenic wave functions with nuclear charges of 1 and 2, respectively. The two-center integrals may be factored into one-center ones by expanding the radial wave functions in terms of 1s GTO's. In calculating the capture cross sections to all the $n=1, 2, 3, 4$ states, the number of distinct integrals was kept small in the following way. For each n, the n similar functions R_{nl}/r^l were simultaneously fit with the same set of 1s GTO's and the two very similar functions $|\phi_{1s}^{\mathrm{He}}(r)|^2$ and $R_{1s}^{(2)}(r)\phi_{1s}^{\mathrm{He}}(r)$ were also fit with the same set of 1s GTO's. The integrals to be evaluated are of the form

$$\int d\vec{R}\, d\vec{r}_1\, d\vec{r}_2 \exp[i(\vec{\alpha}\cdot\vec{r}_{1A}+\vec{\beta}\cdot\vec{r}_{1B})] \times \exp[-(ar_{1A}^2+br_{1B}^2+cr_{2A}^2)]\, r_{1B}^l Y_{lm}(\hat{r}_{1B})\frac{1}{r_{2B}}\,, \tag{17}$$

which can be obtained by appropriate partial differentiation of the following basic integral with respect to the components of $\vec{\beta}$:

$$I(a,b,c,\vec{\alpha},\vec{\beta}) = \int d\vec{R}\, d\vec{r}_1\, d\vec{r}_2 \exp[i(\vec{\alpha}\cdot\vec{r}_{1A}+\vec{\beta}\cdot\vec{r}_{1B})] \times \exp[-(ar_{1A}^2+br_{1B}^2+cr_{2A}^2)]\frac{1}{r_{2B}}\,. \tag{18}$$

It will be shown in the Appendix that

$$I(a,b,c,\vec{\alpha},\vec{\beta}) = G_1(a+b,p^2)G_2[ab/(a+b),c,q^2], \tag{19}$$

where

$$\vec{p} = \vec{\alpha}+\vec{\beta}, \tag{20}$$

$$\vec{q} = (b\vec{\alpha}-a\vec{\beta})/(a+b), \tag{21}$$

$$G_1(a,p^2) = (\pi/a)^{3/2}e^{-p^2/4a}, \tag{22}$$

$$G_2(a,b,q^2) = 4\pi^{5/2}[Y(x)/bq\sqrt{ab}\,]\,e^{-ax^2/b}, \tag{23}$$

$$x^2 = bq^2/[4a(a+b)]\,. \tag{24}$$

Dawson's integral [Eq. (4)] satisfies the differential equation

$$\frac{dY(x)}{dx} = 1-2xY, \tag{25}$$

so that generation of the $r^l Y_{lm}$ factor in the integrand by partial differentiation introduces no new integrals.

In the Born-approximation calculations we chose for the ground state of helium the analytic Hartree-Fock wave function given by Clementi.[25] For the purpose of comparison, we also have computed capture cross sections based on the simple hydrogenic-type function with an effective charge 1.6875. Conversion of wave functions of H, He^+, and He to the Gaussian form was facilitated by the use of results of Huzinaga.[26] For the simultaneous fitting of several functions with 1s GTO's, we devised a program for a nonlinear integral least-squares fit based on an algorithm due to Marquardt.[27] Because of the steep decline of the Gaussians, one has to use several long-range GTO's in order to give a good representation of the tail end of each wave function. This is especially important since the electron cloud of the atoms over a wide range of distance may contribute significantly to the cross sections; however, particularly at high energies, it is most important that the head of each wave function be well represented. We have found that nine-term fits, and sometimes five-term fits, are adequate for the purpose of computing cross sections to better than 10% accuracy. At large distances, the nine-term fits are generally accurate to about 1% when the functions are reduced to 0.1% of their values at $r=0$, while the five-term fits are roughly accurate to 5–10% when the functions are reduced to 0.5% of their values at $r=0$.

III. RESULTS OF BORN-APPROXIMATION CALCULATIONS

A. Test calculations

To test the Gaussian method we have calculated the electron-capture cross sections for the proton-hydrogen process of capture into the 1s, 2s, and 2p states using five-term Gaussian fits at energies of 25, 50, 100, 200, and 400 keV and compared them with results reported previously by other authors using true hydrogenic wave functions.[23,28] Agreement is generally within a few percent. We have also performed the calculations of the 2s and 2p cross sections with nine-term GTO fits, and the results differ by no more than 2% from those reported in Ref. 28. For the proton-helium process, cross sections for electron capture to the 1s-state of H have been calculated by Mapleton[9] using the interaction potential of Eq. (7) and an approximate helium wave function of the hydro-

genic type with an effective charge. We have repeated this calculation by means of nine-term GTO fits to the same helium wave function for incident energies of 100 and 400 keV. Our cross sections agree with Mapleton's values to within 3%. Recently Mapleton, Doherty, and Meehan[10] have reported cross sections for the proton-helium process of capture into the $3p$ and $3d$ states using the interaction potential of Eq. (7) and the effective-charge helium wave function. Our corresponding $3p$ and $3d$ cross sections, given in Table I, differ from their results by an average of 7% and by at most 13%. These results confirm the validity of the GTO scheme as well as serve as a check of our computer program.

Various researchers have calculated cross sections for the *ground-state* proton-helium process in the Born approximation[8] (with the schemes of Jackson and Schiff[5] and of Brinkman and Kramers[3]) and in the close-coupling approximation[29,30] using different approximate helium wave functions. Their cross sections typically differ by (5–15)% (and by at most 23%) in the energy range from 30 keV to 1 MeV.

We have extended the study of variations of cross sections with respect to the choice of an approximate helium wave function to the excited-state capture processes using the Born approximation with the effective potential given by Eq. (7). For this purpose we applied the nine-term Gaussian fits to the analytic Hartree-Fock wave function as well as the simple effective-charge function of helium (ground state) and used them to calculate the (H^+, He) electron-capture cross sections to the $2s$, $2p$, $3s$, $3p$, and $3d$ states. These values are given in Table I. Averaged over energy, the difference is between 10% and 13%. The effective-charge function gives smaller cross sections than does the Hartree-Fock function over the energy range from 25 to 125 keV. For a fixed nl, the difference typically decreases with increasing energy in the intervals 15–25 and 125–1000 keV. In the interval 25–125 keV, the difference typically peaks at 30%. This peaking is attributable to considerable cancellation between the V_i and $-\langle V_i\rangle$ terms in Eq. (7).

B. High-energy behaviors of cross sections

It has been pointed out that the capture cross sections into the ns states for the proton-hydrogen process are proportional to n^{-3} at high energies.[2] Cross sections calculated by using the schemes of Brinkman and Kramers[3] and of Jackson and Schiff[5] are both found to follow the n^{-3} rule quite well at energies of about 100 keV and above for the proton-hydrogen, as well as the proton-helium, processes.[6,7] To explore the high-energy behaviors more fully, we present the results of our Born-approximation calculations of the cross sections for the formation of $H(nl)$ for both the proton-hydrogen and proton-helium processes in Figs. 1–4 for nl from $1s$ to $4f$. We see from Figs. 1 and 3 that the n^{-3} rule also holds with the improved interaction potential [Eq. (7)] for both the proton-hydrogen and proton-helium cases. For the $2s$, $3s$, and $4s$ states it is satisfied to at least 7% for energies above 125 keV and to at least 5% at 1 MeV. From the analysis of Oppenheimer,[2] one may attribute this dependence to the importance of close encounters at high energy, since for $r=0$,

$$R_{ns}(r=0)=2n^{-3/2}. \tag{26}$$

The n^{-3} rule should also hold for the ratio of the $2s$ to $1s$ cross sections, since Eq. (26) is valid for $n\geq 1$. The ratio $\frac{1}{8}$ is indeed approached at high energy, albeit more slowly than ratios involving higher values of n.

The results in Figs. 1–4 also indicate that Q_{nl} for $l\geq 1$ fall off faster with increasing energy than Q_{ns}, consistent with the observation of Oppenheimer.[2] Upon inspecting Figs. 2 and 4 we notice that for each fixed l ($l\geq 1$), the Q_{nl}'s also approach constant ratios (though different from the n^{-3} relation) at high energies. Like the n^{-3} rule, the constancy of these ratios can be explained by the pre-

TABLE I. Comparison of Born-approximation cross sections (in units of πa_0^2) for the proton-helium process of capture into the $2s$, $2p$, $3s$, $3p$, and $3d$ states calculated by using the Hartree-Fock wave function of helium (columns I) and using the effective-charge wave function (columns II). Each integer inside a parenthesis denotes the power of 10 by which the preceding number is multiplied.

E	$Q(2s)$		$Q(2p)$		$Q(3s)$		$Q(3p)$		$Q(3d)$	
(keV)	I	II	I	II	I	II	I	II	I	II
15	1.23(−1)	1.41(−1)	5.99(−2)	5.56(−2)	2.66(−2)	3.22(−2)	1.70(−2)	1.59(−2)	4.63(−3)	3.78(−3)
25	1.67(−1)	1.53(−1)	3.68(−2)	3.40(−2)	4.14(−2)	3.94(−2)	9.77(−3)	9.37(−3)	2.29(−3)	1.96(−3)
75	6.38(−2)	5.32(−2)	2.09(−2)	1.58(−2)	1.83(−2)	1.52(−2)	6.07(−3)	4.53(−3)	4.47(−4)	3.66(−4)
125	2.21(−2)	2.04(−2)	6.74(−3)	5.88(−3)	6.50(−3)	5.96(−3)	2.06(−3)	1.76(−3)	1.13(−4)	1.00(−4)
400	5.69(−4)	6.18(−4)	8.61(−5)	9.48(−5)	1.71(−4)	1.86(−4)	3.27(−5)	3.60(−5)	7.05(−7)	7.85(−7)
1000	1.17(−5)	1.13(−5)	8.51(−7)	8.39(−7)	3.48(−6)	3.37(−6)	2.93(−7)	2.89(−7)	3.31(−9)	3.31(−9)

dominant importance of close encounters, as the hydrogenic wave functions for fixed l, to the lowest order in r, have a similar radial dependence. Thus at high energies Q_{nl} (for a given l) should be proportional to the square of the leading term of the radial wave function expanded as a power series in r, e.g.,

$$Q_{3p}/Q_{2p} = (16/27)^2,$$
$$Q_{4p}/Q_{2p} = (\sqrt{5}/4\sqrt{2})^2, \qquad (27)$$
$$Q_{4d}/Q_{3d} = (81\sqrt{6}/256)^2.$$

The ratios of our calculated cross sections do approach these limiting values; at 125 keV and 1 MeV the average deviations from Eqs. (27) are 14% and 8%, respectively. In addition we observe that the cross sections calculated by means of the scheme of Brinkman and Kramers[3] and of Jackson and Schiff[5] also conform to these asymptotic ratios to within a few percent above 100 keV.[6,7]

It is thus seen that at high energies, the cross sections for $Q_{1s}, Q_{2p}, Q_{3d}, \ldots$ determine all the other cross sections as well. It should perhaps be emphasized, however, that the rule for partial cross sections with $l \geq 1$ is not an n^{-3} rule, as is sometimes suggested, or as is tacitly assumed in the relation[5,31]

$$Q_{\text{total}} = Q_{1s} + 1.62(Q_{2s} + Q_{2p}).$$

C. Impact-parameter formulation

The problem of charge-exchange collisions can be alternatively formulated by means of the impact-parameter method, from which one can derive the corresponding Born approximation.[11] The wave version of the Born approximation as outlined in Sec. II and the impact-parameter version should be equivalent in the energy range of interest.[11] We have applied the impact-parameter version of the Born approximation to calculate the capture cross sections into the $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ states for the (H^+, He) case. Here we adopt the simple effective-charge wave function for He, and evaluate all the integrals by using the Slater-type orbitals directly, without converting them into Gaussian form. At 30 and 100 keV there are at least 1%, 1%, and 3% agreements for $1s$, $2s$, and $2p$,

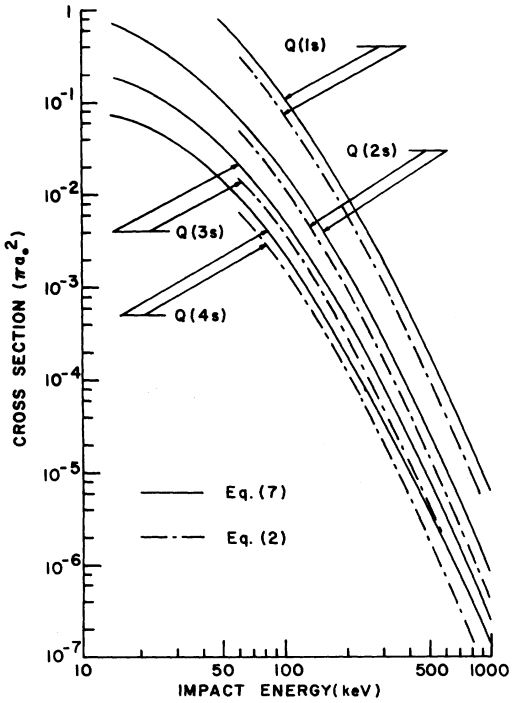

FIG. 1. Theoretical cross sections (Born approximation) for the proton-hydrogen processes of electron capture to the $1s$, $2s$, $3s$, and $4s$ states. The solid curves were calculated by using the effective potential of Eq. (7). For comparison the cross sections derived from the potential of Eq. (2) as given in Refs. 5 and 7 are included as the long-short dashed curve.

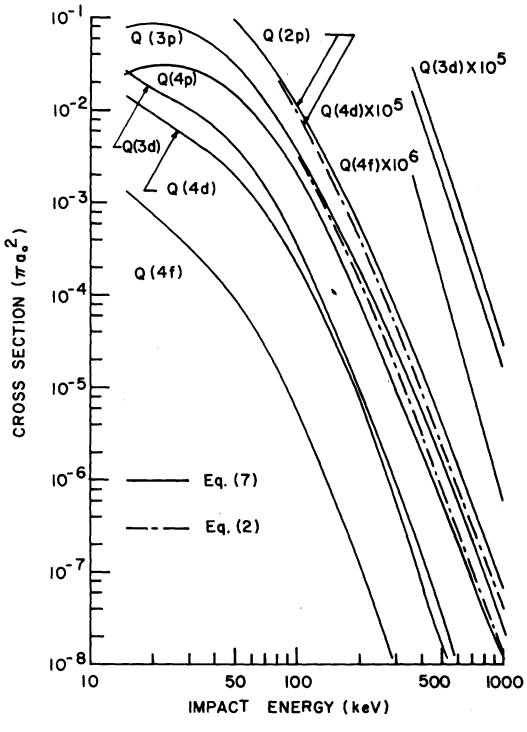

FIG. 2. Theoretical cross sections (Born approximation) for the proton-hydrogen processes of electron capture to the $2p$, $3p$, $4p$, $3d$, $4d$, and $4f$ states. The solid curves were calculated by using the effective potential of Eq. (7). For comparison the cross sections derived from the potential of Eq. (2) for the $2p$ and $3p$ cross sections as given in Ref. 7 are included as the long-short dashed curves.

respectively, and at 100 keV there are 1%, 9%, and 4% agreements for 3*s*, 3*p*, and 3*d*, respectively. These results serve as an additional check for our computation.

D. Comparison with other Born-type calculations

Mapleton[7] has calculated electron-capture cross sections for the *proton-hydrogen* process using the potential of Eq. (2), i.e., the scheme of Jackson and Schiff. His results for the 2*s*, 3*s*, 4*s*, 2*p*, and 3*p* states as well as the results of Refs. 4 and 5 for the 1*s* state are included in Figs. 1 and 2. The use of Eq. (2) instead of Eq. (7) for the potential may be seen to lower the cross sections by (35–55)% at energies above 300 keV. For the proton-helium process, Mapleton[6] has also reported similar calculations using the potential of Eq. (8). Since Mapleton used the simple effective-charge wave function of helium, we shall compare his results with the corresponding numbers in columns II of Table I for the 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* states which were derived from the same wave function. For the 1*s*, 3*p*, and 3*d* states, Mapleton and co-workers[9,10] have obtained cross sections using both Eqs. (7) and (8) as the interaction potentials. For the 1*s*, 2*s*, and 3*s* states, cross sections resulting from the potential of Eq. (8) are lower than those resulting from Eq. (7) by (35–50)% above 300 keV, whereas for the 2*p*, 3*p*, and 3*d* states, cross sections based on the two potentials cross at energies of a few hundred keV.

IV. METHOD OF CLOSE COUPLING

To improve over the Born approximation, we now turn to the method of close coupling. Inclusion of several states in the close-coupling manifold would enable us to make allowance for distortion and back coupling, as well as for the influence of intermediate states on the cross sections. The formulation of the close-coupling treatment of charge-exchange collisions has been discussed in the literature.[11] In this paper we shall outline only the key steps. Here we use the time-dependent impact-parameter formulation, which is valid at energies above a few hundred eV[32] and has the advantage that the coupled differential equations are first order rather than second order.

Let $H(\vec{r}_1, \ldots, \vec{r}_N, t)$ be the time-dependent Hamiltonian of the N-electron system. The Schrödinger equation is solved by expanding the electronic

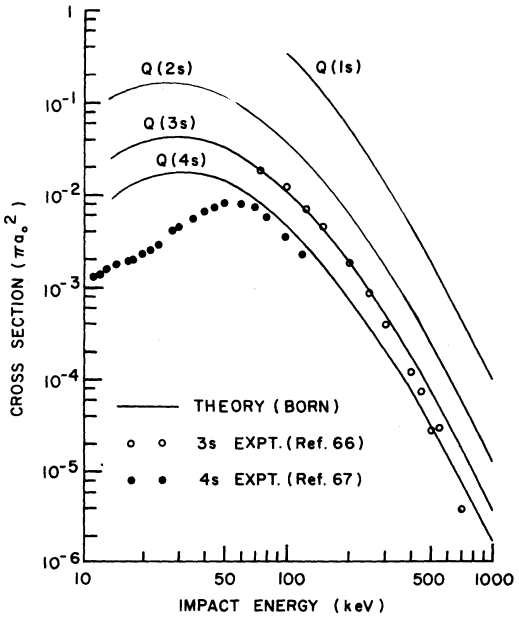

FIG. 3. Theoretical cross sections for the proton-helium processes of electron capture to the 1*s*, 2*s*, 3*s*, and 4*s* state of hydrogen calculated by using the Born approximation with the effective potential of Eq. (7) together with the Hartree-Fock helium wave function of Ref. 25. Included are also the experimental 3*s* cross sections at high energies (open circles) of Ref. 66 and the experimental 4*s* cross sections (closed circles) of Ref. 67.

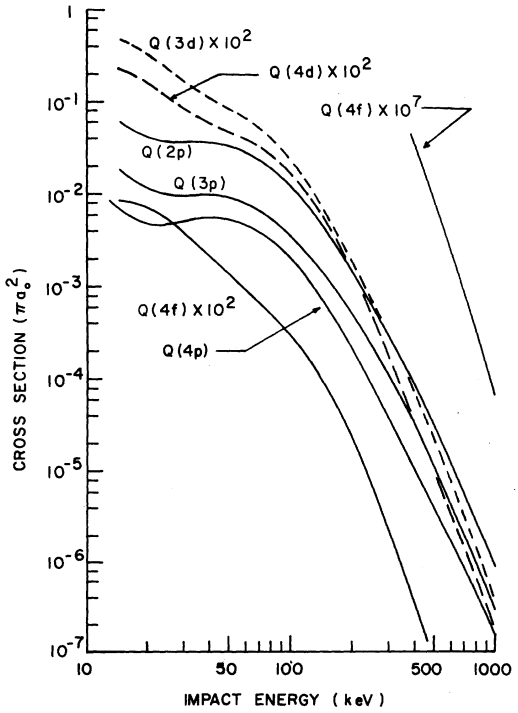

FIG. 4. Theoretical cross sections for the proton-helium processes of electron capture to the 2*p*, 3*p*, 4*p*, 3*d*, 4*d*, and 4*f* states of hydrogen calculated by using the Born approximation with the effective potential of Eq. (7) together with the Hartree-Fock helium wave function of Ref. 25.

wave function $\Psi(\vec{r}_1, \ldots, \vec{r}_N, t)$ in terms of a set of functions $\psi_k(\vec{r}_1, \ldots, \vec{r}_N, t)$ as

$$\Psi = \sum_k a_k(t)\psi_k. \tag{28}$$

The differential equations for the a_k's may be written in matrix form as

$$iS(t)\frac{d\vec{a}(t)}{dt} = G(t)\vec{a}(t), \tag{29}$$

where

$$\begin{aligned}
&[\vec{a}(t)]_k = a_k(t),\\
&[S(t)]_{kl} = \langle \psi_k(\vec{r}_1, \ldots, \vec{r}_N, t)\\
&\qquad \times | \psi_l(\vec{r}_1, \ldots, \vec{r}_N, t)\rangle,\\
&[G(t)]_{kl} = \langle \psi_k(\vec{r}_1, \ldots, \vec{r}_N, t)|H - i\,\partial/\partial t\\
&\qquad \times | \psi_l(\vec{r}_1, \ldots, \vec{r}_N, t)\rangle,\\
&[S(t \to \pm\infty)]_{kl} = \delta_{kl}.
\end{aligned} \tag{30}$$

The system is assumed to be initially in the state characterized by ψ_1, i.e.,

$$a_k(t \to -\infty) = \delta_{1k}, \tag{31}$$

so that the probability of making a transition to the j state is

$$P_j = |a_j(t \to \infty)|^2. \tag{32}$$

Upon computing P_j for various impact parameters ρ, the cross section may be obtained as

$$Q_j = 2\pi \int_0^\infty d\rho\, \rho P_j. \tag{33}$$

For the one-electron problem of (H^+, H) electron capture, Bates[11] has adopted the following basis functions:

$$\begin{aligned}
\psi_i(\vec{r}, t) &= \phi_i^A(\vec{r}_A)\exp[-i(\tfrac{1}{2}\vec{v}\cdot\vec{r} + E_i t + \tfrac{1}{8}v^2 t)],\\
\psi_j(\vec{r}, t) &= \phi_j^B(\vec{r}_B)\exp[-i(-\tfrac{1}{2}\vec{v}\cdot\vec{r} + E_j t + \tfrac{1}{8}v^2 t)],
\end{aligned} \tag{34}$$

where ϕ_i^A and E_i, ϕ_j^B and E_j are, respectively, the atomic wave functions and energies for nucleus A + electron, i.e., the target atom, and for nucleus B (the projectile) + electron; and $\vec{r}$, $\vec{r}_A$, and $\vec{r}_B$ are the position vectors of the electron relative to the midpoint of the internuclear line and relative to each of the nuclei, respectively. The internuclear vector $\vec{R}$ from A to B and the impact parameter $\vec{\rho}$ are related by

$$\vec{R} = \vec{\rho} + \vec{z} = \vec{\rho} + \vec{v}t. \tag{35}$$

In this paper $\vec{v}$ is assumed to be constant. The prior and post functions ψ_i and ψ_j satisfy the time-dependent Schrödinger equation in the respective limits $t \to -\infty, \infty$. Equations (34) have been generalized to the case in which a nucleus B is incident on nucleus A to which are bound two indistinguishable[29] or distinguishable[33] electrons. The validity of assuming distinguishable electrons is born out by the close agreement of close-coupling results with[29] and without[30] indistinguishability for the ground-state proton-helium process above a few keV. Assuming distinguishability we write the prior and post functions for the proton-helium case as

$$\begin{aligned}
\psi_i(\vec{r}_1, \vec{r}_2, t) &= \phi_i^A(\vec{r}_{1A})\phi_{i'}^A(\vec{r}_{2A})\\
&\quad \times \exp\{-i[\tfrac{1}{2}\vec{v}\cdot(\vec{r}_1 + \vec{r}_2) + (E_i + \tfrac{1}{4}v^2)t]\},\\
\psi_j(\vec{r}_1, \vec{r}_2, t) &= \phi_j^B(\vec{r}_{1B})\,\phi_{j'}^A(\vec{r}_{2A})\\
&\quad \times \exp\{-i[\tfrac{1}{2}\vec{v}\cdot(-\vec{r}_1 + \vec{r}_2) + (E_j + \tfrac{1}{4}v^2)t]\}.
\end{aligned} \tag{36}$$

The basis functions which we select consist of the initial state (of the form ψ_i, $i = 1$ and $i' = 1$) and a series of $\psi_j (j \neq 1)$ in which $\phi_{j'}^A(\vec{r}_{2A})$ is fixed as the ground state of He^+ and $\phi_j^B(\vec{r}_{1B})$ covers the states $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ of hydrogen. As noted by Wilets and Gallaher,[34] the invariance of the Hamiltonian under reflection with respect to the collision plane ensures that such states as p_y, d_{xy}, and d_{zy} play no role in the collision process if the x direction is defined to be along $\vec{\rho}$. This makes a total of 11 states for the active electron in the expansion [Eq. (28)], the passive electron remaining in the ground state. No excited target states (ψ_i with $i = 1$ and $i' \neq 1$) are included in the basis set. The use of excited target states amounts to a two-center expansion, but in view of the discussion of Green, Stanley, and Chiang,[29] we expect to gain little variational freedom by employing a two-center expansion rather than a one-center expansion at high energies, where capture takes place predominantly at small internuclear separations. Results will be presented in Sec. V A, suggesting that this is true at energies down to as least 25 keV.

To simplify the numerical work we adopt the simple helium wave function with effective charge 1.6875. In the Born-approximation calculation we have seen that the use of this approximate function usually introduces errors of about 10% in the cross sections. The matrix elements necessary for the close-coupling calculations may be divided into two kinds, the charge-exchange matrix elements S_{1j}, G_{1j}, G_{j1}, and the Coulombic matrix elements $G_{jj'}(j, j' \neq 1)$. The charge-exchange matrix elements may be obtained from the basic integral

$$\begin{aligned}
&I_0(\xi, \eta, \vec{v}, \vec{R} = \vec{B} - \vec{A})\\
&\quad = \int d\vec{r}(r_A r_B)^{-1}\exp[-(\xi r_A + \eta r_B) + i\vec{v}\cdot\vec{r}]
\end{aligned} \tag{37}$$

by partial differentiation with respect to ξ, η, and the components of $\vec{A}$ and $\vec{B}$. Following the approach of Sin Fai Lam,[33] one can derive the relation

$$I_0 = 2\pi e^{i(\vec{v}\cdot\vec{B})} \int_0^1 du\, e^{-i(1-u)\vec{v}\cdot\vec{R}} e^{-\Omega R}/\Omega, \tag{38}$$

where

$$\Omega^2 = \xi^2 u + \eta^2(1-u) + v^2 u(1-u). \tag{39}$$

The required partial derivatives of I_0 were integrated over the interval $(0,1)$ by means of Gauss-Legendre quadrature with at most 64 mesh points for each ρ, v, and z (or t). The maximum error in the higher partial derivatives was 1%; usually it was 0.001%. The Coulombic integrals $G_{jj'}$ are expressible as partial derivatives of the basic integral (37) with $v = 0$,[35] i.e.,

$$I_0(\xi, \eta, 0, R) = 4\pi[(\xi^2 - \eta^2)R]^{-1}(e^{-\eta R} - e^{-\xi R}). \tag{40}$$

Since Eq. (40) and its derivatives are poorly conditioned for small R, a power-series version of each expression was also derived. For both the small-R and larger-R forms, recurrence relations were derived for the coefficients of the various powers of ξ, η, and R.

To solve the n-channel coupled differential equations as given in Eqs. (29) which contain complex coefficients, it is expedient to convert them into $2n$ real equations.[36] The solution $\vec{a}(z)$ is integrated over the interval $(-z_0, z_0)$ with z_0 sufficiently large so that charge-exchange matrix elements are negligible for $|z| \geq z_0$. For the numerical solution of the differential equations we use a method due to Hamming as described by Ralston.[37] This method employs a fifth-order predictor-corrector-modifier procedure in which the step size is automatically varied to keep the truncation error within prescribed bounds. It requires evaluation of matrices S and G only once per z step. Truncation errors were kept in the range of 10^{-5} and 10^{-6} to ensure probability conservation to at least six places. For the full 22 coupled equations, step sizes for $v = 2$ ranged from 0.8 at $|z| = 40$ to 0.05 at $z = 0$; values at $v = 1$ were typically twice as small. A Runge-Kutta method described by Ralston[38] was used to start the integration.

The charge-exchange matrix elements did not affect any component a_k of the solution by more than 0.05% in extending the range of z integration beyond $z_0 = 40$. For the region $z_m > z > z_0$ (z_m to be defined later) we still solve the coupled differential equations numerically, but set all charge-exchange matrix elements to zero. Outside z_m an extrapolation procedure was employed. The extrapolation procedure is important, because Coulombic matrix elements $G_{jj'}$ can considerably redistribute probability among the states j even for $z > z_m$. Wilets and Gallaher developed the method of trajectory extrapolation in the region $z > z_m$, in which exponentially decaying Coulombic terms were neglected, the common $1/R$ terms were removed and certain approximations were introduced so that the coupled equations could be integrated analytically from z_m to ∞. We proceed differently, replacing their approximations by a second-order iterative scheme. The extrapolatory corrections could themselves be quite large for the $3p$ and $3d$ states; thus we prefer to calculate the correction terms rather accurately. For $z > z_m$, the incident channel ψ_1 decouples from the final channels ψ_j, and Eqs. (29) take on the simplified form

$$\frac{da_j}{dz} = -\frac{i}{v} \Sigma_{j'} G_{jj'}(z) a_{j'}(z), \quad z > z_m \tag{41}$$

where the Coulombic matrix elements are given by

$$G_{jj'}(z) = (\Sigma_k b_{jj'k} \rho^\lambda z^\mu / R^\nu) \times \exp[i(E_j - E_{j'})z/v], \quad \nu - \mu > 1, \quad z > z_m \tag{42}$$

after transforming out the $1/R$ terms in the diagonal matrix elements and neglecting exponentially decaying terms. The coefficients $b_{jj'k}$ are constants, and the exponents λ, μ, and ν are nonnegative integers depending on j, j', and k. To second order in $G_{jj'}$, the extrapolated jth amplitude for $z \to \infty$ is

$$a_j^{ex} = a_j(z_m) + \delta a_j^{(1)}(z_m) + \delta a_j^{(2)}(z_m), \tag{43}$$

where

$$\delta a_j^{(1)}(z_m) = -\frac{i}{v} \Sigma_{j'} \int_{z_m}^{\infty} du\, G_{jj'}(u) a_{j'}(z_m), \tag{44}$$

$$\delta a_j^{(2)}(z_m) = -\frac{1}{v^2} \Sigma_{j'j''} \int_{z_m}^{\infty} du\, G_{jj'}(u) \times \int_{z_m}^{u} dw\, G_{j'j''}(w) a_{j''}(z_m). \tag{45}$$

The only further approximation made is to neglect terms in Eq. (45) for which $E_j \neq E_{j'} \neq E_{j''}$ (doubly-nondegenerate second-order coupling). By using values of z_m from 50 to 150, it was found that $z_m = 50$ ensured convergence in each extrapolated probability to at least 1%. On the other hand, the $3d$ unextrapolated probability at $z = 50$ was converged to only 15%.

V. RESULTS OF CLOSE-COUPLING CALCULATIONS

Application of the method of close coupling to the proton-hydrogen process with electron capture

into the $1s$ state has been made by McCarroll.[22] Close-coupling calculations of cross sections for capture into a number of excited states as well as the ground state have been performed for the proton-hydrogen process by Cheshire, Gallaher, and Taylor[39] ($1s, 2s, 2p$), by Rapp, Dinwiddie, Storm, and Sharp[40] ($1s$, $2s$, $2p$), and by Rapp and Dinwiddie[41] ($1s, 2s, 2p, 3s, 3p$). For the proton-helium process, a two-state close-coupling calculation of the capture cross section (into the $1s$ state) has been reported by Bransden and Sin Fai Lam,[30] and a five-state calculation for the $1s, 2s, 2p$ cross sections, by Sin Fai Lam.[33]

In our close-coupling calculations for the proton-helium process we have employed several sets of basis functions of the final states; the largest set includes the $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ states. Discussion of the results will be presented in the following subsections.

A. Test calculations

To test our computational procedure, we first performed a two-state close-coupling calculation of the cross sections for the resonant proton-hydrogen capture process at four energies from 1 keV to 1 MeV and compared them with the tabulated cross sections of McCarroll obtained under the identical approximation.[22] Disagreement in the cross sections is, in all cases, less than 0.5%. We then extended our proton-hydrogen work to include electron capture into the $2s$ and $2p$ states of H using a five-state ($1s_A, 1s_B, 2s_B, 2px_B, 2pz_B$) expansion. Calculations of the $2s$ and $2p$ capture cross sections of the proton-hydrogen system have also been reported by Cheshire *et al.*[39] and by Rapp and Dinwiddie.[41] Both of their calculations employ the same basis set—the eight states $1s_A$, $2s_A$, $2px_A$, $2pz_A$, $1s_B$, $2s_B$, $2px_B$, and $2pz_B$. In other words they have included the $2s$ and $2p$ excited states of the *target* which we neglect in this work. Nevertheless, comparison of the three sets of cross sections in Table II shows that the differences are all in the range (1–10)%. The close agreement between the five-state and eight-state cross sections lends support to our approximation of neglecting the excited target states.

TABLE II. Comparison of our cross sections (in units of πa_0^2) for the proton-hydrogen process of capture into the $2s$ and $2p$ states with the cross sections of Cheshire *et al.* (Ref. 39) and of Rapp and Dinwiddie (Ref. 41).

E	$Q(2s)$			$Q(2p)$		
(keV)	Ref. 39	Ref. 41	Ours	Ref. 39	Ref. 41	Ours
25	0.4158	0.406	0.411	0.1051	0.113	0.101
100	0.029 95	0.028	0.0319	0.005 978	0.006	0.006 64

For the proton-helium problem, Bransden and Sin Fai Lam have reported a two-state close-coupling calculation of cross sections for electron capture into the ground state.[30] We have performed a similar two-state calculation, and our cross sections at 30.16 and 100 keV agree with the results of Bransden and Sin Fai Lam to better than 1%. Finally in Table III we compare our five-state close-coupling cross sections for the proton-helium process of capture into the $2s$ and $2p$ states with the corresponding results of Sin Fai Lam.[33] At 1 MeV the $2s$ cross sections agree to within the estimated 10% reading error of Sin Fai Lam's graphs. All other cross sections differ by considerably more than this reading error. Since our results for the proton-hydrogen process with $nl = 1s$, $2s$, and $2p$ and for the proton-helium case with $nl = 1s$ check very well with those reported by previous workers, it is natural for us to conclude that our calculations for the proton-helium process with $nl = 2s$ and $2p$ are also correct. This conclusion is supported further by the observation that our $2s$ and $2p$ close-coupling cross sections converge to (within 7% and 26%, respectively) the corresponding Born-approximation (impact-parameter version) cross sections at 1 MeV, while Sin Fai Lam's $2p$ cross sections differ from all our $2p$ cross sections by at least a factor of 4 at this energy. At this time we are unable to offer any concrete explanation for the discrepancy between the results of Sin Fai Lam and ours.

B. Convergence of the close-coupling expansion

For a multistate close-coupling calculation it is important to assess the convergence of the expansion of the time-dependent electronic wave functions in terms of traveling atomic orbitals such as those given by Eqs. (34) and (36). One would expect that at moderately high energies the cross sections for capture into a state of principal quantum number n would be less influenced by states with principal quantum number $n' > n$ than

TABLE III. Comparison of our five-state close-coupling cross sections (in units of πa_0^2) for the proton-helium process of capture into the $2s$ and $2p$ states with the cross sections of Sin Fai Lam (Ref. 33). Each integer inside a parenthesis denotes the power of 10 by which the preceding number is multiplied.

E	$Q(2s)$		$Q(2p)$	
(keV)	Ref. 33	Ours	Ref. 33	Ours
30.16	6.9(−2)	7.30(−2)	9.0(−2)	2.44(−2)
75	5.8(−2)	8.36(−2)	2.0(−2)	1.15(−2)
100	3.5(−2)	5.07(−2)	1.0(−2)	7.06(−3)
300	1.8(−3)	2.04(−3)	1.6(−4)	2.87(−4)
1000	1.1(−5)	1.19(−5)	2.3(−7)	1.05(−6)

those with $n' < n$, since as seen in Sec. III B the Born cross sections decrease rapidly with increasing n.

Before studying in detail the convergence of cross sections for the proton-helium process, let us briefly examine the previously determined cross sections for the proton-hydrogen process. Close-coupling calculations with two states $(1s_A - 1s_B)$[22] and eight states $(nl_A - nl_B, nl \leq 2p)$[39,41] have been reported, and we have carried out a five-state $(1s_A - nl_B, nl \leq 2p)$[42] calculation in order to compare with the results of Refs. 22, 39, and 41. For the ground-state capture cross sections, the two-state results are found to converge generally to within a few percent at all energies; i.e., the $n=2$ states negligibly affect the $n=1$ cross section. Results of Rapp and Dinwiddie[41] with $3s$ and $3p$ states included in the expansion suggest that at energies not less than 25 keV, the $n=3$ states do not affect the $n=2$ cross sections by more than 10%.

Turning now to the *ground-state*, proton-helium process, comparison of the two-state $(1s_A - 1s_B)$ results of Ref. 30 with our five-state $(1s_A - nl_B, nl \leq 2p)$[42] and 11-state $(1s_A - nl_B, nl \leq 3d)$[42] cross sections reveal convergence at energies of above 30 keV to be at least the few percent observed for the proton-hydrogen case. An alternative criterion for checking convergence was carried out by considering probability times impact parameter ρP_j at some fixed ρ near the maximum value of ρP_j. At 30 keV, the change in ρP_j (for electron capture into the ground state) on increasing from a two-state to a five-state expansion and from a five-state to an 11-state expansion are 3% and 0.6%, respectively, while at 100 keV, these changes are reduced to 0.8% and 0.3%. The convergence of the $n=2$ cross sections with respect to the inclusion of more highly excited states is slower than for the case of the ground state, as may be seen by comparing our five-state and 11-state cross sections given in Tables III and IV, respectively. At 100 keV the $n=3$ states affect the $2s$ cross section by no more than 3%, while for the $2p$ cross section, the effect is 11% at 100 keV and 9% at 300 keV. On this basis the $n=4$ states are expected to have a smaller influence on the $3s$ cross sections than on the $3p$ and $3d$ cross sections. We would estimate the $3p$ and $3d$ cross sections to be affected by somewhat more than 10% by the inclusion of the $n=4$ states at energies of 100–300 keV. The estimated over-all effect of roughly 10% is of about the same size as the error, discussed in Sec. III A, incurred by the use of the simple one-parameter helium wave function.

We also attempted to determine which states $n'l'$ in the close-coupling expansion with $n' \leq n$ are more important to the nl-state cross sections. As an example, the $2s$ and $2p$ cross sections were studied at 100 keV. The $2s$ cross sections in the two-state $(1s_A - 2s_B)$, three-state $(1s_A - 1s_B - 2s_B)$, four-state $(1s_A - 2s_B - 2px_B - 2pz_B)$, and five-state $(1s_A - nl_B, nl \leq 2p)$ approximations are, respectively, $0.0455\pi a_0^2$, $0.0368\pi a_0^2$, $0.0535\pi a_0^2$, and $0.0507\pi a_0^2$. The $2p$ cross sections in the three-state $(1s_A - 2px_B - 2pz_B)$, four-state $(1s_A - 2s_B - 2px_B - 2pz_B)$, and five-state $(1s_A - nl_B, nl \leq 2p)$ approximations are, respectively, $0.0134\pi a_0^2$, $0.005\,22\pi a_0^2$, and $0.007\,06\pi a_0^2$. It is seen that the $2s$ state has a very large effect on the $2p$ cross section, whereas the effect of $2p$ states on the $2s$ cross section is smaller, though still quite appreciable. This is understandable inasmuch as the $2s$ amplitude is a factor of 3 larger than the $2p$ amplitudes. Also, the $1s_B$ state is important to both $2s$ and $2p$ cross sections. Moreover, the $1s_B$ state is seen to affect the $2s$ cross section more in the absence than in the presence of the $2p$ states, indicating that there is considerable interference among the various amplitudes.

The basis set for the close-coupling expansion can also be augmented by including in Eq. (28) functions corresponding to final products of H^+ and $He(n^1L)$. This is equivalent to using the functions ψ_i [defined in Eqs. (36)] with $i=1$ and $i' \neq 1$ which are neglected in this work. Justification for excluding such excited target states has been given in the discussion following Eqs. (36) in Sec. IV. This is further supported by the close agreement between our $2s$ and $2p$ capture cross sections of the proton-hydrogen process based on a five-state $(1s_A, 1s_B, 2s_B, 2px_B, 2pz_B)$ expansion and those of Refs. 39 and 41 in which the basis set includes $1s_A$, $2s_A$, $2px_A$, $2pz_A$, $1s_B$, $2s_B$, $2px_B$, and $2pz_B$, as discussed in the first paragraph of Sec. V A.

TABLE IV. Eleven-state close-coupling cross sections (in units of πa_0^2) for the proton-helium process of capture into five excited states. Each integer inside a parenthesis denotes the power of 10 by which the preceding number is multiplied.

E (keV)	$Q(2s)$	$Q(2p)$	$Q(3s)$	$Q(3p)$	$Q(3d)$
30.16	7.92(−2)	2.39(−2)	1.23(−2)	1.00(−2)	2.06(−3)
100	4.98(−2)	6.33(−3)	1.62(−2)	3.17(−3)	3.51(−4)
200	8.03(−3)	1.08(−3)	2.72(−3)	5.06(−4)	3.04(−5)
300	1.99(−3)	2.63(−4)	6.65(−4)	1.18(−4)	5.20(−6)

C. Comparison with Born-approximation results

We shall begin with the proton-hydrogen system for the comparison of the close-coupling cross sections with the results of the Born approximation. For the ground state, these two kinds of cross sections agree with each other to within 5%

at 100 keV.[22,23] On the other hand for $2s$ and $2p$, eight-state[39,41] and Born[28] cross sections differ by a factor of about 2 at this energy.

Analogous to the case of proton-hydrogen capture, convergence of close-coupling cross sections[30] to the Born values[9] for proton-helium capture is most rapid for the ground state, the convergence being to within 20% at 100 keV. The close-coupling cross sections which we have computed for the (H^+, He) process with nl from $2s$ to $3d$ are shown in Figs. 5 and 6 along with the corresponding Born-approximation values. These two sets of cross sections, on the whole, converge at about the same rate as do the $2s$ and $2p$ cross sections for the proton-hydrogen case. Convergence is especially slow for the $3p$ and $3d$ states. While the $3p$ cross sections are remarkably close to the Born cross sections even at energies below 100 keV, the rate of convergence with respect to increasing energy for this state does not appear to be any more rapid than for the other states. Convergence for the $3d$ case is slow, the close-coupling and Born results differing by almost a factor of 2 at 100 keV.

It is instructive to analyze in some detail the distinction between the cross sections of the ns states and those of nl ($l \geq 1$). For instance the $2s$ amplitude is much larger than the $2p$ amplitude (and, of course, also much larger than the amplitudes for the states of higher n). As far as the $2s$ cross sections are concerned, the results of several multistate (11-state, five-state, four-state, and three-state) close-coupling calculations do not differ greatly from the result of the two-state one (about 20%) at 100 keV (although successive improvements are generally of opposite sign), and the five-state cross sections converge to the Born values to within 25% and 7% at 300 keV and 1 MeV, respectively. The disparity between the $2s$ and $2p$ amplitudes also causes the $2p$ cross sections to be very susceptible to the influence of the $2s$ state; as a result, even at 1 MeV the Born cross section is 26% higher than the cross section of the five-state close-coupling method. Based on this con-

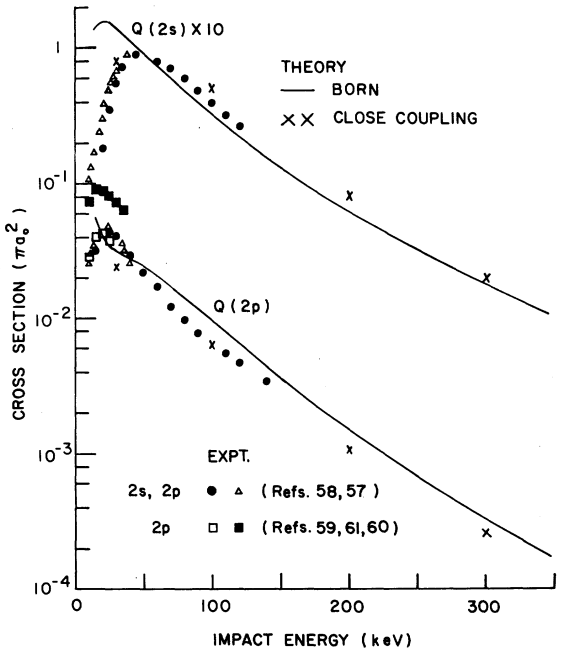

FIG. 5. Theoretical and experimental cross sections for the proton-helium processes of electron capture to the $2s$ and $2p$ states of hydrogen. The solid curves and the × points represent, respectively, the theoretical cross sections calculated by using the Born approximation and using 11-state close coupling (with the one-parameter helium wave function in both cases). The experimental cross sections include those for $2s$ and $2p$ of Ref. 58 (●), for $2s$ and $2p$ of Ref. 57 (△), for $2p$ of Refs. 59 and 61 (□), and for $2p$ of Ref. 60 (■).

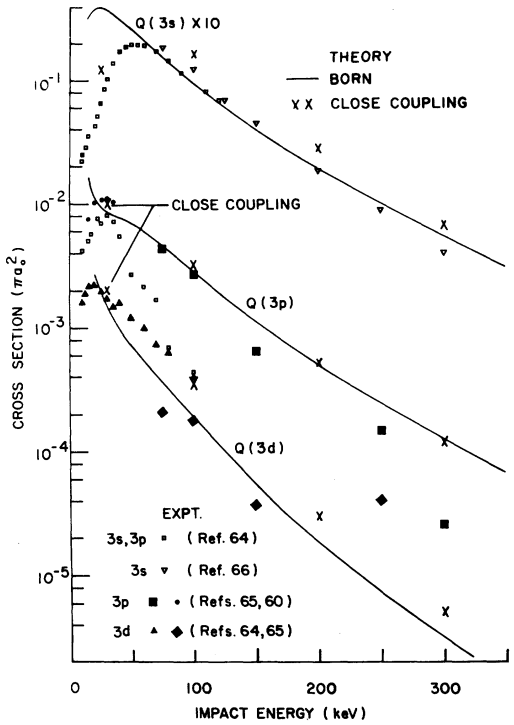

FIG. 6. Theoretical and experimental cross sections for the proton-helium processes of electron capture to the $3s$, $3p$, and $3d$ states of hydrogen. The solid curves and × points represent, respectively, the theoretical cross sections calculated by using the Born approximation and using 11-state close coupling (with the one-parameter helium wave function in both cases). The experimental cross sections include those for $3s$ and $3p$ of Ref. 64 (□), for $3s$ of Ref. 66 (▽), for $3p$ of Ref. 65 (■), for $3p$ of Ref. 60 (●), for $3d$ of Ref. 64 (▲), and for $3d$ of Ref. 65 (◆).

sideration we can understand the slow convergence of the 11-state close-coupling cross sections to Born cross sections, as well as the large discrepancy even at 300 keV for the case of $3d$, since coupling with such "intermediate states" as $2s$ and $3s$ undoubtedly plays an important role in the $3d$ cross sections. On the other hand, the rather close agreement for the $3p$ state between the Born and close-coupling cross sections (much better than for the corresponding case of the $2p$ state) is most probably due to the cancellation of coupling effects of the various "intermediate states." It may be mentioned that the importance of indirect coupling through intermediate states in the calculation of electron-impact excitation cross sections of atoms has been discussed in the literature.[43]

VI. COMPARISON WITH EXPERIMENT

Experimental measurements of electron capture cross sections have been performed in several different laboratories.[44] For the proton-hydrogen process, absolute measurements have been made of the total electron-capture cross sections (to all states)[45,46] and of the capture cross sections into the $2s$ and $2p$ states [46-48] at energies in the keV region. For the case of helium, total capture cross sections have been measured up to several MeV,[49-55] and measurements have been reported for energies up to a few hundred keV covering all excited states of $n=2$ and 3, as well as $4s$.[56-68]

A. Proton-hydrogen collisions

We shall review briefly the status of the proton-hydrogen case. Since the experimental measurements were made in the energy range where the Born approximation is not expected to be valid, comparison with theory should be made with the close-coupling calculations. Recently, measurements have been made from 2 to 26 keV for the $2s$ and $2p$ states; these[48] and other measurements[46,47] have been compared with close-coupling cross sections. It is noted[48] that close-coupling cross sections which include $3s$ and $3p$ pseudostates, as well as $1s$, $2s$, and $2p$ bound states agree, on the whole, better with experiment than do close-coupling cross sections which include $1s$, $2s$, $2p$, $3s$, and $3p$ bound states.[41] However, this statement should be qualified as follows: Firstly, if one shifts both the $2s$ and $2p$ experimental curves upward within the ±30% absolute error limits, the bound-state results agree with experiment as well as do the pseudostate results; secondly, the $2p$ pseudostate results have a shoulder at 25 keV which is absent in the measurements and in the bound-state results, and which lies outside the experimental error bounds. It may be added that in the lower energy range, close-coupling calculations provide substantial improvement over the Born approximation.

B. Proton-helium collisions

For the ground-state (H^+, He) capture process, Green *et al.* in 1965 have compared their two-state close-coupling cross sections[29] with experimental data.[49-51] Results of measurements published subsequently[52-55] are in substantial agreement with the earlier ones.[49-51] Experimental and theoretical cross sections agree to within 25% at about 100 keV, but the two-state values exceed the experimental ones by about a factor of 2 at energies above several hundred keV. There is no significant improvement by using the eleven-state cross sections of the present authors, since, as noted in Sec. V B, two-state and eleven-state cross sections agree to within a few percent above 30 keV. It has been suggested that approximations which include continuum states should be used at high energies.[69]

The $2s$ close-coupling cross sections lie nearly uniformly above the experimental data of Hughes, Stokes, Choe, and King[58] by about 25% over the experimental energy range 30–130 keV (see Fig. 5). Compared to the Born approximation, the 11-state cross sections agree more closely with experiment at lower energies but not at higher energies, particularly if one adjusts the 11-state values upward to correct for the approximate wave function used (since under the Born approximation the Hartree-Fock helium wave function[25] gives about 10% larger cross sections than does the simple effective-charge function). No estimate of experimental error is given; however, the agreement is probably satisfactory. For the $2p$ case, the close-coupling cross section is about 50% below the experimental value of Hughes *et al.*[58] at 30 keV; part of this discrepancy may be attributed to the approximate helium wave function used. At energies higher than about 75 keV there is nearly complete agreement, even after shifting the theoretical cross sections to allow for the approximate helium wave function used, whereas the Born approximation yields cross sections considerably larger than the experimental data of Ref. 58. Measurements of the $2s$ and $2p$ cross sections have been reported also by Andreev, Ankudinov, and Bobashev.[57] Their results, which are included in Fig. 5, agree fairly well with the curve of Hughes *et al.*[58] for the $2s$ state in the energy region where the two sets of

data overlap. Not shown in Fig. 5 are the 2s measurements of Jaecks, Van Zyl, and Geballe[58] in the low-energy range (6–23 keV) which agree generally with the measurements of Ref. 58 in the region of overlap. For the 2p state, part of the data of Ref. 57 lies appreciably below that of Ref. 58, but the difference is not large enough to alter the general features described above concerning the comparison between theory and experiment. Also included in Fig. 5 are the data of Pretzer, Van Zyl, and Geballe[59] and of Gailey, Jaecks, and Geballe.[61] These data agree fairly well with the data of Refs. 57 and 58 above 20 keV. On the other hand, the data of de Heer, van Eck, and Kistemaker[60] (also shown in Fig. 5) lie above the other data by a factor of 1.5 to 2.

For the 3s state, 11-state cross sections lie above the experimental data of Hughes, Stigers, Doughty, and Stokes[64] and of Conrads, Nichols, Ford, and Thomas[66] at lower energies (Fig. 6). Differences between the close-coupling cross sections and the experimental curve of Ref. 66 increase from 22% at 100 keV to 50% at 300 keV. Agreement is satisfactory at the lower-energy side, but at 300 keV disagreement exceeds the experimental error estimated by Ford and Thomas.[65] Above 300 keV we have not performed close-coupling calculations for the $n=3$ states; thus to compare with the experimental data of Ref. 66 in this energy region, we shall use the theoretical cross sections based on the Born approximation with the potential of Eq. (7) and the analytic Hartree-Fock wave function of Ref. 25. The differences increase from 38% at 400 keV to a factor of 1.6 at 550 keV and to a factor of four at 700 keV (see Fig. 3). Not shown in Fig. 6 are the 3s cross sections of Andreev, Ankudinov, and Bobashev[62] in the energy range of 14–30 keV; these data are in good agreement with those of Ref. 64 in the region of overlap. In the case of the 3p state, the 11-state close-coupling cross sections are not much different from the Born-approximation counterpart as noted in Sec. V C. Agreement at lower energies with the experimental data of Ref. 65 is good, but the factor-of-two difference between theory and experiment at higher energies is beyond even the limits of the sum of the various kinds of estimated experimental errors, −84% and +79%. Also clear from Fig. 6 is that 3p theoretical cross sections are much larger than the experimental results of Ref. 64. Ford and Thomas[65] have commented about the difference between their 3p experimental data and those of Ref. 64. Also included in Fig. 6 are the 3p data of Ref. 60. Not shown are the low-energy 3p measurements of Andreev, Ankudinov, Bobashev, and Matveev[63] which lie between the data of Refs. 64 and 60 above 20 keV. The data of Ref. 60 exceed those of Ref. 64 by 35% to 55%. The 3p data of Ref. 60 agree well with our close-coupling cross sections at 30 keV. For the 3d state, the 11-state close-coupling method, as compared to the Born approximation, greatly improves agreement with the curve of experimental results of Ref. 64 in the region of 30–120 keV, but not with the data points of Ref. 65 over the somewhat higher energy range 75–150 keV. (We have not given serious consideration to the data point at 250 keV of Ref. 65, as it is very much out of line with the lower-energy points.) However, the difference between the data of Refs. 64 and 65 amounts to about a factor of 2 or more and is not quite accounted for even if one takes the sum of the various experimental errors (−104% to +79%) given in Ref. 65. Cross sections of the 3d states at low energies reported by Andreev *et al.*[62] (not shown in Fig. 6) show an even larger disagreement, about a factor of 3–5, with the data of Ref. 64, and will not be considered here.

Cross sections of electron capture into the 4s state have been measured by Hughes, Dawson, and Doughty[67] and by Dawson and Loyd.[68] The experimental data as displayed in Fig. 3 show satisfactory agreement with our theoretical cross sections based on the Born approximation at energies above 80 keV. Because of the large number of channels involved, we have not performed any close-coupling calculations involving the $n=4$ states.

It is seen in Figs. 5 and 6 that in passing from the Born approximation to the 11-state close-coupling method, agreement with experiment is substantially improved for the 2s and 3s states at lower energies and for the 2p states at higher energies, but for the 3s and 3d states at high energy and the 3p state over all energies, the agreement is either not improved or is even decreased. We are not able to assess the situation of the 3d state at low energies because of the two sets of conflicting experimental data (Refs. 64 and 65). Two explanations seem plausible. First, one notes that the differences between the 1s close-coupling cross sections of Ref. 29, the present 2s and 3s close-coupling cross sections, and the corresponding experimental cross sections are, at higher energies, all of the same sign and about the same magnitude at each particular energy, despite the fact that the experimental techniques were very different. This tends to reinforce the suggestion that inclusion of coupling with the continuum may be important at high energies.[69] The other possibility is that the experimental errors of the 3s and especially of the 3p and 3d cross sections are larger than what one would expect from the estimated values. This speculation is supported by the dis-

agreement between the experimental $3p$ and $3d$ data of Refs. 64 and 65.

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APPENDIX

To evaluate the Gaussian integral $I(a, b, c, \vec{\alpha}, \vec{\beta})$ defined by Eq. (18), one uses the following two convenient properties of Gaussians[13]:

$$\exp[-(ar_A^2 + br_B^2)] = \exp\{-[(a+b)r_D^2 + ab(a+b)^{-1}R^2]\},$$

$$\int d\vec{r}\, e^{-cr_A^2}/r_B = 2\pi c^{-1}\int_0^1 du\, e^{-cR^2u^2},$$

where

$$\vec{R} = \vec{B} - \vec{A}$$

and

$$\vec{D} = (a+b)^{-1}(a\vec{A} + b\vec{B}).$$

Further, with D defined above, one can show that

$$\vec{\alpha}\cdot\vec{r}_A + \vec{\beta}\cdot\vec{r}_B = \vec{p}\cdot\vec{r}_D + \vec{q}\cdot\vec{R},$$

where $\vec{p}$ and $\vec{q}$ are given by Eqs. (20) and (21). Thus the integral I can be factored into two single-center integrals $G_1(a+b, p^2)$ and $G_2(ab(a+b)^{-1}, c, q^2)$, where

$$G_1(a, p^2) = \int d\vec{r}\, e^{-ar_D^2 + i\vec{p}\cdot\vec{r}_D},$$

which reduces to Eq. (22) and

$$G_2(a, b, q^2) = 2\pi b^{-1}\int d\vec{R}\, e^{-aR^2 + i\vec{q}\cdot\vec{R}}\int_0^1 du\, e^{-bR^2u^2},$$

which reduces to Eq. (23).

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