actions. Notice that they include the mutual *electrostatic polarization within a pair in addition to the usual dispersion forces*. The last three terms are the 3-body "cross-polarization" terms mentioned in the text [see Eq. (50)]. If the atoms A, B, and C are neutral and spherical and if V_{AB} is expanded in a multipole series keeping only the dipole-dipole term, the pair polarization and the cross terms vanish. Then E_2 reduces simply to the sum of the usual London dispersion energies.[13,14]

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Proton-Hydrogen Scattering System*

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The impact parameter treatment of the scattering of protons by hydrogen is derived and is shown to be valid for energies greater than a few electron volts. A novel treatment of the resultant equations is given which significantly modifies previously obtained results for inelastic scattering and charge-exchange scattering.

I. INTRODUCTION

IT has long been realized that the system of two protons and an electron is one of the simpler three-body problems in quantum mechanics because of the large disparity in the electron and proton masses. Born and Oppenheimer[1] used this fact to treat the bound states of H_2^+. They made the approximation that the protons moved very slowly compared with the electrons. The resultant problem, the motion of the electron in the field of two fixed protons, could then be solved exactly.[2] Similar approximations were made for the scattering problem,[3] resulting in good agreement with experiment for low energies. The high-energy problem has been treated by Born approximation,[4] but the discussion of capture collisions has been somewhat clouded by the lack of orthogonality of the initial and final states and the consequent ambiguity in the contribution of the proton-proton potential to these rearrangement processes.[5] The high-energy scattering has also been treated by an "impact parameter method," where it has been shown that a "Born approximation" in this method is equivalent to the usual Born approximation in the limit of the electron-to-proton mass ratio vanishing.[6]

It is the object of this paper to present a systematic derivation of the "impact parameter method" (Sec. II). It will develop that it is suitable for the description of collisions for proton energies of the order of a few hundred electron volts and greater. In Sec. III an expansion is made which is suitable for direct (not rearrangement) collisions. This is used to develop an "improved Born approximation" which is used to calculate the cross section for the transition

$$p+\mathrm{H}(1s)\rightarrow p+\mathrm{H}(2s)$$

as an example. In Sec. IV an expansion is made which is suitable for the description of rearrangement collisions. A similar "improved Born approximation" is developed here with the result that the initial and final states are automatically orthogonalized, thus eliminating the difficulties mentioned above in connection with this calculation. The method is applied to the calculation of the cross section for the process

$$p+\mathrm{H}(1s)\rightarrow \mathrm{H}(1s)+p$$

as an example.

In Sec. V the problem of handling the low-energy and intermediate-energy ranges is briefly discussed.

II. THE IMPACT PARAMETER METHOD

A Born approximation calculation for the total scattering of a proton by atomic hydrogen yields the fact that the mean angle of scattering is of the order $(m|W_0|/ME)^{\frac{1}{2}}$, where $|W_0|=13.6$ ev is the binding energy of hydrogen and E is the incident proton energy.[5] For incident proton energies above an electron volt or so this is an extremely small angle, indicating that the proton travels in essentially a straight line. This means that the protons are distinguishable and that the Pauli

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* This work was performed under the auspices of the U. S. Atomic Energy Commission.

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[2] E. Teller, Z. Physik **61**, 458 (1930).

[3] N. F. Mott, Proc. Cambridge Phil. Soc. **27**, 553 (1931); D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. (London) **A216**, 437 (1953); D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) **A245**, 175 (1958); A. Dalgarno and H. N. Yadav, Proc. Phys. Soc. (London) **A66**, 173 (1953).

[4] H. C. Brinkmann and H. A. Kramers, Proc. Acad. Sci. Amsterdam **33**, 973 (1930); referred to hereafter as B-K.

[5] J. D. Jackson and H. Schiff, Phys. Rev. **89**, 359 (1953); D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) **A66**, 961 (1953).

[6] J. W. Frame, Proc. Cambridge Phil. Soc. **27**, 511 (1931).

principle may therefore be neglected. The mean energy loss of the proton may also be estimated, with the not unexpected result that the fractional energy loss is $\Delta E/E \sim O(m/M)+O(|W_0|/E)$, so that for proton energies of a few hundred electron volts or more the velocity of the proton is almost unchanged. Finally, we may compare the de Broglie wavelength λ with the relevant distance in the atomic system, the Bohr radius a. The result is $(m|W_0|/ME)^{\frac{1}{2}}$. Thus the proton may be localized relative to the atom. We therefore expect that the proton motion may be treated classically and that the electron will move in the field of the two protons. The Schrödinger equation for the electron motion will then be

$$(i\hbar\partial/\partial t - H_{\mathbf{x}})\psi(\mathbf{x},t)=0, \tag{1}$$

where

$$H_{\mathbf{x}} = -\frac{\hbar^2}{2m}\nabla_{\mathbf{x}}{}^2 - \frac{e^2}{|\mathbf{x}-\frac{1}{2}\mathbf{R}|} - \frac{e^2}{|\mathbf{x}+\frac{1}{2}\mathbf{R}|}. \tag{1a}$$

Here $\mathbf{R}(t)$ is the classical interproton coordinate, which must be determined.

Our starting point is the Schrödinger equation for the full three-body problem in the center-of-mass system:

$$(i\hbar\partial/\partial t - H)\Psi(\mathbf{x},\mathbf{R},t)=0, \tag{2}$$

where

$$H = -\frac{\hbar^2}{M}\nabla_{\mathbf{R}}{}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{x}}{}^2 + \frac{e^2}{R} - \frac{e^2}{|\mathbf{x}-\frac{1}{2}\mathbf{R}|} - \frac{e^2}{|\mathbf{x}+\frac{1}{2}\mathbf{R}|}. \tag{2a}$$

Here M is the proton mass, m the electron mass, $\mathbf{R}$ the interproton coordinate, and $\mathbf{x}$ the electron coordinate relative to the center of mass of the protons. In (2a) we have neglected the difference between the electron mass and the electron reduced mass. This difference is of order m/M. It presents some nontrivial difficulties, which have been discussed elsewhere.[7] We shall consistently neglect effects of this order, so they will not be discussed here.

The full wave function, Ψ, may be obtained from the variational expression

$$I = \frac{1}{2}\int d^3x d^3R dt \left\{ \Psi^* i\frac{\partial}{\partial t}\Psi - \Psi^* H\Psi + \text{c.c.} \right\}, \tag{3}$$

where c.c. represents the complex conjugate of the preceding expression in the bracket. This may easily be shown to be stationary with respect to small variations of Ψ and Ψ^* about the exact solution to (2). The considerations above lead us to choose a trial function for Ψ,

$$\Psi_0 = \psi_{\mathbf{R}'}(\mathbf{x},t)\chi_{\mathbf{R}'}(\mathbf{R},t), \tag{4}$$

where ψ satisfies (1) and χ is to be determined. The dependence on the as-yet-arbitrary function $\mathbf{R}(t)$ has been made explicit.

Substitution of Ψ_0 for Ψ in (3) and variation with respect to χ^* leads to the equation for χ:

$$(i\hbar\partial/\partial t - H_{\mathbf{R}})\chi_{\mathbf{R}'}=0, \tag{5}$$

where

$$H_R = -\frac{\hbar^2}{M}\nabla_{\mathbf{R}}{}^2 + \frac{e^2}{R} - e^2\bar{\Delta}_{\mathbf{R}'}(\mathbf{R},t), \tag{5a}$$

with

$$\bar{\Delta}_{\mathbf{R}'}(\mathbf{R},t) = \int d^3x |\psi_{\mathbf{R}'}(\mathbf{x},t)|^2 \times\left\{ \frac{1}{|\mathbf{x}-\frac{1}{2}\mathbf{R}|} - \frac{1}{|\mathbf{x}-\frac{1}{2}\mathbf{R}'|} + \frac{1}{|\mathbf{x}+\frac{1}{2}\mathbf{R}|} - \frac{1}{|\mathbf{x}+\frac{1}{2}\mathbf{R}'|} \right\}. \tag{6}$$

We may look for a solution to (5) in the form of a wave packet. The distance over which Δ changes is of the order of a Bohr radius, so that the collision time will be of the order of $\tau \sim a/V$, where V is the interproton velocity. If we take the original size of the wave packet to be $\Delta x_0 \ll a$, then after a time τ the wave packet will have an extent[8]

$$(\Delta\mathbf{x})^2 = (\Delta x_0)^2 + \frac{\hbar^2}{4M^2}\frac{\tau^2}{(\Delta x_0)^2}. \tag{7}$$

This is minimized by $(\Delta x_0)^2 = \hbar a/2Mv$, with $(\Delta\mathbf{x})^2 = 2(\Delta x_0)^2$. Now the uncertainty of momentum in the wave packet is given by $\Delta p = \hbar/2\Delta x_0$. We require that this uncertainty in momentum be small compared with the momentum, i.e., $\Delta p \ll Mv$. These may be combined to yield

$$(Mva/\hbar)^{\frac{1}{2}} \gg 1. \tag{8}$$

Replacing the inequality by equality, we get

$$E = \tfrac{1}{2}Mv^2 = (m/M)|W_0| \approx 0.007 \text{ ev}. \tag{8a}$$

Thus the inequality is easily satisfied and the Schrödinger equation, (5), may be replaced by a classical equation of motion for $\mathbf{R}$:

$$\tfrac{1}{2}M\frac{d^2\mathbf{R}}{dt^2} - \nabla_{\mathbf{R}}\left(\frac{e^2}{R} - e^2\bar{\Delta}_{\mathbf{R}'}(\mathbf{R},t)\right). \tag{9}$$

The function $\mathbf{R}'(t)$ is still arbitrary at this point. In order to determine it we must consider the correction to Ψ_0 in Ψ.

If we set $\Psi = \Psi_0 + \delta\Psi$, then

$$[i\hbar\partial/\partial t - H]\delta\Psi = -e^2[\Delta_{\mathbf{R}'}(\mathbf{x},\mathbf{R},t) - \bar{\Delta}_{\mathbf{R}'}(\mathbf{R},t)]\Psi_0, \tag{10}$$

where $\bar{\Delta}$ has been defined in (6), and

$$\Delta_{\mathbf{R}'}(\mathbf{x},\mathbf{R},t) = \frac{1}{|\mathbf{x}-\frac{1}{2}\mathbf{R}|} - \frac{1}{|\mathbf{x}-\frac{1}{2}\mathbf{R}'|} + \frac{1}{|\mathbf{x}+\frac{1}{2}\mathbf{R}|} - \frac{1}{|\mathbf{x}+\frac{1}{2}\mathbf{R}'|}. \tag{11}$$

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[7] S. Cohen, D. Judd, and R. Riddell, University of California Radiation Laboratory Report UCRL-8390 (1958); Phys. Rev. **119**, 397 (1960).

[8] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 58.

It is now evident that $\mathbf{R}'$ should be chosen to be the classical interproton coordinate as determined from (9) in order to minimize the right-hand side of (10) and therefore to minimize $\delta\Psi$. We therefore drop the distinction between $\mathbf{R}$ and $\mathbf{R}'$.

In order to completely specify the solution to the set of Eqs. (1) and (9) we need initial conditions. These are

$$\lim_{t\to-\infty}\psi(\mathbf{x},t)=\phi_0(\mathbf{x}+\tfrac{1}{2}\mathbf{R}(t))\exp[-imVx/4\hbar-\epsilon_0(t)] \qquad \mathbf{R}=\mathbf{b}+\mathbf{V}t, \tag{12}$$

where $\mathbf{b}$ is the impact parameter in the collision and $\epsilon_0(t)$ is some phase which still remains to be chosen. Here ϕ_0 is the hydrogen ground-state wave function.

Let us now case these equations into atomic units. We shall measure all distances in units of the Bohr radius a; t in units of the Bohr period $\hbar/|W_0|$; energies in units of the Rydberg, $e^2/2a$; the proton velocity in units of $c\alpha=e^2/2\hbar$. Then $v=2$ represents a proton laboratory energy of about 25 kev. Then we have

$$\left\{i\frac{\partial}{\partial t}+\nabla^2+\frac{2}{|\mathbf{x}-\frac{1}{2}\mathbf{R}|}+\frac{2}{|\mathbf{x}+\frac{1}{2}\mathbf{R}|}\right\}\psi(\mathbf{x},t)=0, \tag{13}$$

$$\frac{d^2\mathbf{R}}{dt^2}=-\frac{8m}{M}\nabla_{\mathbf{R}}\left(\frac{1}{R}-\bar{\Delta}_{\mathbf{R}'}(\mathbf{R},t)\right), \tag{14}$$

with the initial conditions

$$\psi=\phi_0(\mathbf{x}+\tfrac{1}{2}\mathbf{R})\exp[-i\mathbf{V}\cdot\mathbf{x}/4-i\epsilon_0(t)]$$

and

$$\mathbf{R}'=\mathbf{b}+\mathbf{V}t. \tag{15}$$

We remark here that the combination of the equation of motion for the electron [(1) and (1a)] with the equation of motion of the proton [(5) and (5a)] and the definition of $\mathbf{R}'$ conserves energy. Then a literal interpretation of these equations could be applied down to the energy region where the proton energy is comparable with excitation energies (13 electron volts). Such a program is difficult to carry out, so that in practice we shall not use the equation of motion of the proton [(5) or (14)] but instead we shall take the proton coordinate, $\mathbf{R}(t)$, to be an unaccelerated motion. As is evident from (14), the deviation from such motion occurs for impact parameters $b\sim(m/M)^{\frac{1}{2}}$. This region will contribute negligibly to the cross section, of order m/M. In addition, our neglect of the proton accelerations requires that the incident energy be large compared with the excitation energies, say of the order of a hundred electron volts or greater.

III. DIRECT COLLISIONS

By direct collisions we mean collisions in which the electron is bound to the same proton in the final state as it was in the initial state. For such a collision we make the expansion[9]

$$\psi(\mathbf{x},t)=\textstyle\sum_n a_n(t)\phi_n(\mathbf{x}+\frac{1}{2}\mathbf{R}(t))\exp[-\frac{1}{4}i\mathbf{R}\cdot\mathbf{x}-i\epsilon_n(t)], \tag{16}$$

where ϕ_n is the hydrogenic state with energy W_n. The phase in the exponent has been chosen to make each term a solution of the noninteracting problem. Substitution of (16) into (13), with some obvious manipulation, yields

$$\begin{aligned}i\dot{a}_n+a_n\Bigg[\dot{\epsilon}_n-W_n-\frac{\dot{R}^2}{16}-\frac{\mathbf{R}\cdot d^2\mathbf{R}/dt^2}{8}\\+\int d^3y|\phi_n(\mathbf{y})|^2\left(\frac{2}{|\mathbf{y}-\mathbf{R}|}+\frac{\mathbf{y}\cdot d^2\mathbf{R}/dt^2}{4}\right)\Bigg]\\+\sum_{m\neq n}a_m\int d^3y\,\phi_n^*(\mathbf{y})\\\times\left[\frac{2}{|\mathbf{y}-\mathbf{R}|}+\frac{\mathbf{y}\cdot d^2\mathbf{R}/dt^2}{4}\right]\phi_m(\mathbf{y})e^{i(\epsilon_n-\epsilon_m)}=0,\end{aligned} \tag{17}$$

with the initial condition at $t=-\infty$:

$$a_n=\delta_{n0}. \tag{18}$$

We shall now choose ϵ_n to eliminate the diagonal transitions in (18):

$$\begin{aligned}\epsilon_n=W_nt+\left(\frac{\dot{R}^2}{16}+\frac{\mathbf{R}\cdot d^2\mathbf{R}/dt^2}{8}\right)t\\-\int^t dt'\int d^3y|\phi_n(\mathbf{y})|^2\frac{2}{|\mathbf{y}-\mathbf{R}|}.\end{aligned} \tag{19}$$

Here we have used the fact that ϕ_n is a parity eigenfunction, to eliminate the $d^2\mathbf{R}/dt^2$ term. The choice of ϵ_n appears to be arbitrary. However, if we wish to consider the interaction as a perturbation, this choice would be dictated by the normalization condition,

$$\textstyle\sum_n|a_n(t)|^2=1. \tag{20}$$

This choice of ϵ_n has the effect of summing repeated elastic transitions, and so has a similarity to an optical potential.[10] With this choice we obtain

$$\begin{aligned}\dot{a}_n=i\sum_{n\neq m}a_m\int d^3y\,\phi_n^*(\mathbf{y})\\\times\left[\frac{2}{|\mathbf{y}-\mathbf{R}|}+\frac{\mathbf{y}\cdot d^2\mathbf{R}/dt^2}{4}\right]\phi_m(\mathbf{y})e^{i(\epsilon_n-\epsilon_m)}.\end{aligned} \tag{21}$$

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[9] D. R. Bates [Proc. Phys. Soc. (London) **73**, 227 (1959)] has obtained a result identical with our Eq. (25) from his "distortion approximation." Our numerical results, of course, agree with his.

[10] M. H. Mittleman and K. M. Watson, Phys. Rev. **113**, 198 (1959).

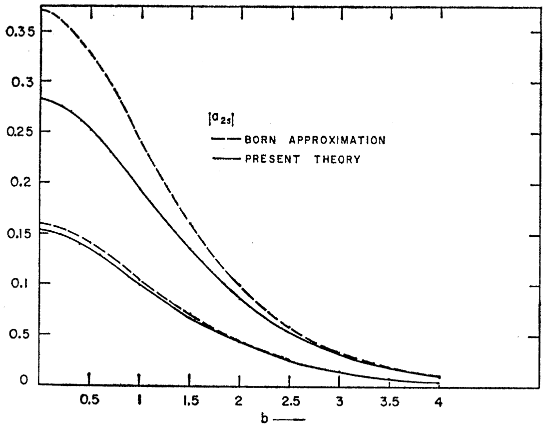

FIG. 1. The amplitude for direct transition to the $2s$ state for $E=2$ (upper curves) and $E=12$ (lower curves).

The a's are transition amplitudes to the various states, so that the cross section for transition to any particular state is given by

$$\sigma_n=a^2\int d^2b\,|a_n(\infty)|^2=2\pi a^2\int_0^\infty bdb\,|a_n(\infty)|^2. \quad (22)$$

Here a word about the transition to the free state is in order. We have, so far, not mentioned the possibility of a rearrangement collision in which the final state is given by

$$\phi_n(\mathbf{x}-\tfrac{1}{2}\mathbf{R})\exp[+\tfrac{1}{4}i(d\mathbf{R}/dt)\cdot\mathbf{x}-i\epsilon_n(t)]. \quad (23)$$

This state is not orthogonal to the states used in (16) for the direct scattering, which has the effect that the superposition of free states in (16) can be used to form a bound state of (23). Thus (22) cannot be used directly to obtain the cross section for the transition to a free state $\bar{q}$ (ionization). Instead of a_q we should use only that portion of a_q which does not go into the superposition mentioned above. Thus we use

$$\theta_q=a_q-\sum_k a_k e^{-i\epsilon_k}\sum_n\int d^3y\,\phi_q{}^*$$
$$\times(\mathbf{y}+\mathbf{R})\phi_n(\mathbf{y})\phi_n{}^*(\mathbf{z})\phi_k(\mathbf{z}+\mathbf{R})d^3z, \quad (24)$$

where the sum over n is restricted to all the bound states, and that over k to all the free states. All these considerations could be trivial if it were not for the fact that there is an infinite number of bound states in a Coulomb field and that the highly excited ones extend out very far. If this were not the case, the cone of "direct" free states that would be needed to construct the "exchange" bound states would shrink down to zero aperture as the protons become infinitely separated.

We may take one of two approaches now. First, we may consider the Coulomb field as being screened, thus obtaining a finite number of bound states and then finally going to the limit of zero screening. In that case the second term in (24) vanishes. Or second, we could directly evaluate the correction to a_q in the limit $t\to\infty$. This yields the same result. Thus (22) may be used for ionization also.

The simplest approximation for evaluating a_n is to replace $a_m(t)$ on the right-hand side of (21) by $a_m(-\infty)=\delta_{m0}$. We obtain

$$\dot{a}_n=i\int d^3y\,\phi_n{}^*(\mathbf{y})\left[\frac{2}{|\mathbf{y}-\mathbf{R}|}+\frac{\mathbf{y}\cdot d^2\mathbf{R}/dt^2}{4}\right]\phi_0(\mathbf{y})e^{i(\epsilon_n-\epsilon_0)}. \quad (25)$$

As an example, we shall consider the transition to the $2s$ state. The term in $d^2\mathbf{R}/dt^2$ vanishes. If we neglect the integral terms in the phases, (19), then the integrations may be performed, yielding

$$a_{2s}(\infty)=\frac{i4\surd 2}{9}\frac{1}{\surd E}\frac{b^2}{1+(1/16E)}K_2\left[\frac{3}{2}b\left(1+\frac{1}{16E}\right)^{\frac{1}{2}}\right] \quad (26)$$

and

$$\sigma_{2s}=a^2\frac{128}{5}\left(\frac{2}{3}\right)^{10}\frac{\pi}{E}\frac{1}{[1+(1/16E)]^5}. \quad (27)$$

This is precisely what one would get from the quantum-mechanical Born approximation[6] in the limit $m/M=0$ if the proton-proton interaction is dropped. When the integrals in ϵ are included, it is no longer possible to perform the integration analytically. However, the modification is expected to reduce the Born approximation. This is borne out by numerical integration. In Fig. 1 the resultant amplitude $|a_{2s}(\infty)|$ is shown graphically in comparison with (26). It is seen that the modification is more important at lower energies and small impact parameters. Thus the higher energies and higher partial waves are left unmodified.

In Fig. 2 the total cross section is plotted in units of the Born-approximation cross section, (27).

IV. CAPTURE COLLISIONS

In this section we turn our attention to collisions in which the electron is captured by the incident proton. We are interested in final states of the form (23), so we

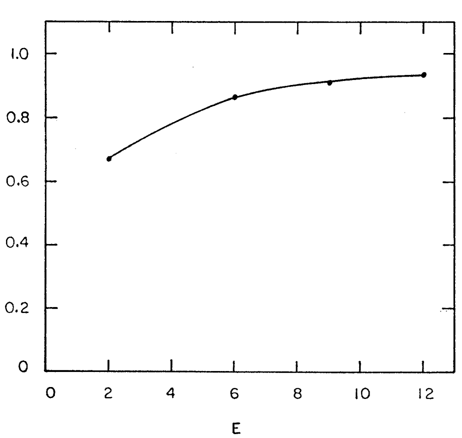

FIG. 2. The ratio of σ_{2s} from present theory to the Born approximation.

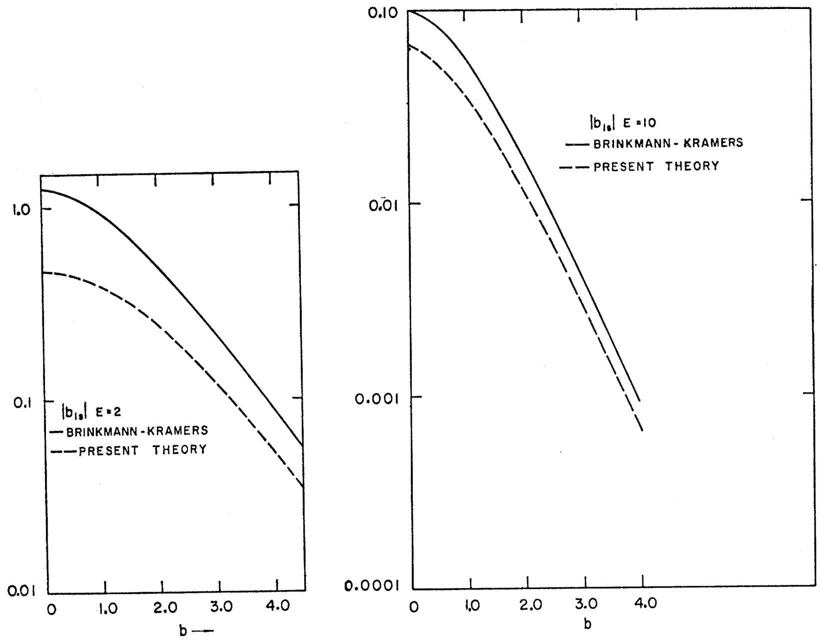

FIG. 3. The amplitude for exchange scattering, (a) for $E=2$; (b) for $E=10$.

make the expansion

$$\psi=\sum_n b_n(t)\phi_n(\mathbf{x}-\tfrac{1}{2}\mathbf{R})\exp[-i\epsilon_n(t)+\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt], \tag{28}$$

with the initial condition

$$b_n(-\infty)=e^{i(\epsilon_n-\epsilon_0)}\int d^3x\,\phi_n^*(x-\tfrac{1}{2}\mathbf{R})\phi_0(x-\tfrac{1}{2}\mathbf{R}) \times\exp(-\tfrac{1}{2}i\mathbf{x}\cdot d\mathbf{R}/dt). \tag{29}$$

The capture cross section to the nth state is then given by

$$\sigma_n=2\pi a^2\int_0^\infty bdb\,|b_n(+\infty)|^2. \tag{30}$$

Substitution of (28) into (13), with manipulation similar to that for the case of direct scattering, (21), leads to

$$\dot{b}_n=i\sum_{m\neq n} b_m\int d^3y\,\phi_n^*(\mathbf{y}) \times\left[\frac{2}{|\mathbf{y}+\mathbf{R}|}-\frac{\mathbf{y}\cdot d^2\mathbf{R}/dt^2}{4}\right]\phi_m(\mathbf{y})e^{i(\epsilon_n-\epsilon_m)}, \tag{31}$$

where ϵ_n is given by (19). Thus, diagonal transitions are eliminated in the representation of the *final* states.

We again make the approximation of replacing $b_m(t)$ in the right-hand side of (31) by $b_m(-\infty)$. This results in

$$\dot{b}_n=ie^{i(\epsilon_n-\epsilon_0)}\int d^3y\,\phi_n^*(\mathbf{y}) \times\exp(-\tfrac{1}{4}i\mathbf{R}\cdot d\mathbf{R}/dt)\left[\frac{2}{|\mathbf{y}+\mathbf{R}|}-\frac{1}{4}\mathbf{y}\cdot\frac{d^2\mathbf{R}}{dt^2}\right] \times\left\{\phi_0(\mathbf{y}+\mathbf{R})\exp(-\tfrac{1}{2}i\mathbf{y}\cdot d\mathbf{R}/dt)-\phi_n(\mathbf{y}) \times\int d^3x\,\phi_n^*(\mathbf{x})\exp(-\tfrac{1}{2}i\mathbf{x}\cdot d\mathbf{R}/dt)\phi_0(\mathbf{x}+\mathbf{R})\right\}. \tag{32}$$

We see that the result of our choice of ϵ_n to eliminate diagonal transitions modifies the initial state, $\phi_0(\mathbf{y}+\mathbf{R})\times\exp(-\frac{1}{2}i\mathbf{y}\cdot d\mathbf{R}/dt)$, in such a way as to make it orthogonal to the final state, $\phi_n(\mathbf{y})$. Thus the difficulty associated with the lack of orthogonality between initial and final states is eliminated.[11] As an example, we shall evaluate the cross section for capture to the ground state, dropping the $d^2\mathbf{R}/dt^2$ term. If we neglect the second term in the bracket of (32), the orthogonality correction, the result for the transition amplitude, $b_0(\infty)$, is

$$\frac{4i}{v}\frac{b^2}{[1+v^2/16]}K_2[b(1+v^2/16)^{\frac{1}{2}}], \tag{33}$$

and the cross section is

$$\pi a^2\frac{256}{5}\frac{1}{E}\frac{1}{[1+E/4]^5}, \tag{34}$$

where E is the proton laboratory energy in units of $Mc^2\alpha^2\approx 24.6$ kev. This is precisely the Brinkmann-Kramers[4] result, which was obtained from a quantum Born approximation by neglecting the proton-proton interaction and taking the limit $m/M=0$.

The contribution of the second term in (32) to the amplitude $b_0(\infty)$ has been evaluated numerically with the aid of the IBM 650. The results are shown in Figs. 3(a) and 3(b), where the Brinkmann-Kramers

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[11] A result equivalent to our Eq. (32) has been obtained previously by K. Takayanagi, Sci. Repts. Saitama Univ. 2, 33 (1955), and D. R. Bates, Proc. Roy. Soc. 247, 294 (1959). The method of derivation of these two authors is similar. It essentially assumes that the wave function is a superposition of the initial and final states. These derivations have conceptual difficulties and lack the unity with the direct excitation collisions which is emphasized here. Neither of these authors presents numerical results for this process.

TABLE I. Ratio of the Brinkmann-Kramers cross section to that obtained in this report.

E (units of 24.6 kev)	$\sigma_{\text{B-K}}/\sigma$
2	4.8
5	3.2
7.5	2.7
10	2.3
12	2.1

amplitude and the results of this calculation are compared. It is seen that the orthogonality correction becomes more important for lower energies and smaller impact parameters. It can also be shown that the orthogonality correction is of order $1/E^{\frac{1}{2}}$ relative to the B-K result. Thus, this theory goes over to the B-K result at high energies, albeit slowly.

It has been pointed out[12,13] that the high-energy behavior of this cross section should be $E^{-11/2}$ and not E^{-6}. This dependence has been shown[12] to come from the second Born approximation, and will presumably arise in the second-order perturbation contribution of this theory.

For $E=2$ it is seen that the B-K amplitude becomes greater than unity for small impact parameters. This is clearly in conflict with the probability interpretation of $|b_n|^2$ implied by (28). Our correction removes this difficulty at this energy and so extends the validity of the perturbation procedure to lower energies.

In Fig. 4 the cross section in units of πa^2 is plotted vs E in units of 24.6 kev. The cross section obtained here is lower than the B-K results at all energies. In Table I the ratio of the B-K result to our result is given for several energies.

Comparison of our results with those of Bassel and Gerjuoy[13] shows close agreement between the two. It is difficult to understand this agreement. Bassel and Gerjuoy make a distorted wave calculation, absorbing the proton-proton interaction into the distortion of the proton wave functions, so that in lowest approximation this interaction does not enter. We have neglected this interaction on quite different grounds (Sec. II). The difference between our result and the B-K result is a consequence of what could be called a distorted wave calculation for the electron. This results in the orthogonalization of our initial and final states. The Bassel-Gerjuoy change seems to arise from a screening of the proton-proton interaction by the electron.

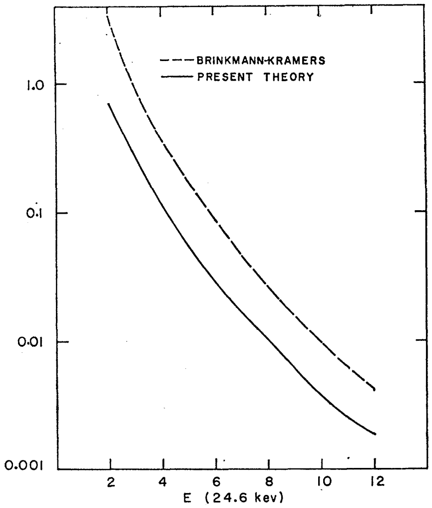

FIG. 4. The charge-exchange cross section in units of πa^2.

We have omitted any comparison with experiment because our calculations are trustworthy only at higher energies, i.e., greater than about 70 kev, say, and at these energies the experiments have only been done in molecular hydrogen. It has been pointed out[14] that the assumption that H_2 is equivalent to two hydrogen atoms at high energies is not valid.

V. LOW AND INTERMEDIATE ENERGIES

Our previous approximations were based upon the fact that the forms of the initial and final states were known. We could then calculate perturbations of these states leading to transitions. The fact that we were allowing only small changes in these states restricted the applicability of our approximation to the high-energy region. We shall now use the fact that the zero-velocity states can be obtained to make expansions that are valid in the low-velocity limit. The states in question are obtained from[2]

$$\left[\nabla_{\mathbf{x}}^2+\frac{2}{|\mathbf{x}-\frac{1}{2}\mathbf{R}'|}+\frac{2}{|\mathbf{x}+\frac{1}{2}\mathbf{R}'|}+\epsilon_n{}^{\pm}(\mathbf{R})\right]U_n{}^{\pm}(\mathbf{x},\mathbf{R})=0, \tag{35}$$

where $\mathbf{R}'$ enters only as a parameter. The eigenstates have been denoted by n and $(\pm)$. The $(\pm)$ indicates the parity of the functions $U_n{}^{\pm}$ under the transformations $\mathbf{R}\rightarrow-\mathbf{R}$. That is,

$$U_n{}^{\pm}(\mathbf{x},\mathbf{R})=\pm U_n{}^{\pm}(\mathbf{x},-\mathbf{R}). \tag{36}$$

These states can be used to expand the electron wave function, ψ, in the low-energy limit. However, again we must make different expansions for direct and exchange scatterings.

For direct scattering we write[15]

$$\psi=\sum_n \{C_n{}^{+}(t)U_n{}^{+}\exp[-i\eta_n{}^{+}(t)]+C_n{}^{-}(t)U_n{}^{-} \times\exp[-i\eta_n{}^{-}(t)]\}\exp(\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt). \tag{37}$$

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[15] D. R. Bates, H. S. W. Massey, and A. L. Stewart[3] have suggested this form without the factor $e^{-i\dot{R}\cdot x/4}$. They then neglect the difficulties associated with the lack of translational invariance. D. R. Bates and R. McCarroll[3] have later corrected this and suggest the form (47).

Substitution of (37) into (13), with some straightforward manipulation and the use of (36), results in

$$\dot{C}_n^{+} = -\sum_{\substack{m\neq n\\ j=(\pm)}} \int d^3x\, U_n^{+*} \times\left[\frac{d\mathbf{R}}{dt}\cdot(\nabla_{\mathbf{R}}-\tfrac{1}{2}\nabla_{\mathbf{x}})-\tfrac{1}{4}i\frac{d^2\mathbf{R}}{dt^2}\cdot\mathbf{x}\right]U_m^{\,j} \times\exp[i(\eta_n^{+}-\eta_n^{\,j})], \tag{38}$$

with a similar equation for C_n^{-}. The diagonal transitions have been eliminated with the choice

$$\eta_n^{\pm} = \int^t \left(\epsilon_n^{\pm}(\mathbf{R})+\frac{\dot{R}^2}{16}\right)dt - i \times\int^t dt\int d^3x\, U_n^{\pm}\frac{d\mathbf{R}}{dt}\cdot\nabla_{\mathbf{R}}U_n^{\pm}. \tag{39}$$

The last term vanishes when the functions $U_n^{\pm}$ are real. The initial condition associated with hydrogen in its ground state is

$$C_n^{\pm}(-\infty)=\delta_{n0}/\sqrt{2}. \tag{40}$$

We may obtain the first term in an expansion in velocity by replacing $C_m(t)$ on the right-hand side of (38) by $C_m(-\infty)$. This yields (dropping $d^2\mathbf{R}/dt^2$)

$$\begin{aligned}\dot{C}_n^{+} &= -\frac{1}{\sqrt{2}}\int d^3x\, U_n^{+*}\frac{d\mathbf{R}}{dt}\cdot(\nabla_{\mathbf{R}}-\tfrac{1}{2}\nabla_{\mathbf{x}})U_0 \times\exp[i(\eta_n^{+}-\eta_0^{-})(t)],\\ C_n^{-} &= -\frac{1}{\sqrt{2}}\int d^3x\, U_n^{-*}\frac{d\mathbf{R}}{dt}\cdot(\nabla_{\mathbf{R}}-\tfrac{1}{2}\nabla_{\mathbf{x}})U_0^{+} \times\exp[i(\eta_n^{-}-\eta_0^{+})(t)],\end{aligned} \tag{41}$$

where we have used the fact that for the ground states, $U_0^{\pm}$, the parity with respect to R is the same as the parity with respect to x. From these we may calculate direct excitations. The elastic cross section can be obtained in the next order.

For exchange scattering, we make the expansion

$$\psi=\sum\nolimits_n \{d_n^{+}(t)U_n^{+}\exp[-i\eta_n^{+}(t)]+d_n^{-}(t)U_n^{-} \times\exp[-i\eta_n^{-}(t)]\}\exp(\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt). \tag{42}$$

The determining equations for the d_n are

$$\dot{d}_n^{+} = -\sum_{\substack{m\neq n\\ j=\pm}}\int d^3x\, U_n^{+*}\frac{d\mathbf{R}}{dt}\cdot(\nabla_{\mathbf{R}}+\tfrac{1}{2}\nabla_{\mathbf{x}}) +\tfrac{1}{4}i\frac{d^2\mathbf{R}}{dt^2}\cdot\mathbf{x}U_m^{\,j}\exp[i(\eta_n^{+}-\eta_m^{\,j})]d_m^{\,j}, \tag{43}$$

where $\eta_n^{\pm}$ is given by (39). The initial condition on the d_n is

$$d_n^{\pm}(-\infty)=\int d^3x\, U_n^{\pm*}\exp\left(-\tfrac{1}{2}i\frac{d\mathbf{R}}{dt}\cdot\mathbf{x}\right) \times\phi_0(\mathbf{x}+\tfrac{1}{2}\mathbf{R})\exp[i(\eta_n^{\pm}-\epsilon_0)(t)]. \tag{44}$$

Again the lowest order term in an expansion in powers of the velocity may be obtained by replacing $d_m^{\pm}(t)$ by $d_m^{\pm}(-\infty)$ on the right-hand side of (43). The result is (dropping $d^2\mathbf{R}/dt^2$)

$$\dot{d}_n^{\pm} = -\int d^3x\, U_n^{\pm*}(\mathbf{x},\mathbf{R})\frac{d\mathbf{R}}{dt}\cdot(\nabla_{\mathbf{R}}+\tfrac{1}{2}\nabla_{\mathbf{x}}) \times[\delta(\mathbf{x}-\mathbf{y})-U_n^{\pm}(\mathbf{x},\mathbf{R})U_n^{\pm*}(\mathbf{y},\mathbf{R})] \times\exp(-\tfrac{1}{2}i\mathbf{y}\cdot d\mathbf{R}/dt)\phi_0(\mathbf{y}+\tfrac{1}{2}\mathbf{R})d^3y. \tag{45}$$

The second term in the bracket has the effect of orthogonalizing the initial and final states.

Bates and McCarroll[3,15] have suggested a more ambitious expansion than either (37) or (42). They suggest forming the states

$$\phi_n^{\pm}=\tfrac{1}{2}\{(U_n^{+}+U_n^{-})\exp(-\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt) \pm(U_n^{+}-U_n^{-})\exp(\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt)\} \tag{47}$$

and making the expansion

$$\psi=\sum\nolimits_n\{\gamma_n^{+}(t)\phi_n^{+}\exp[-i\eta_n^{+}(t)] +\gamma_n^{-}(t)\phi_n^{-}\exp[-i\eta_n^{-}(t)]\}. \tag{48}$$

They point out that the initial conditions take a simple form, $\gamma_n^{\pm}=(1/\sqrt{2})\delta_{n0}$, and that the direct- *or* exchange-scattering final states also take on simple forms. However, the drawback to (47) is that the set $\phi_n^{\pm}$ does not form an orthogonal or a normalized basis, so that it is difficult to obtain equations for the γ_n. Bates and McCarroll avoid this by neglecting all $\gamma_n^{\pm}$ except for $n=0$. This is equivalent to a variational calculation with the assumed wave function

$$\psi=\gamma_0^{+}(t)\phi_0^{+}\exp[-i\eta_0^{+}(t)]+\gamma_0^{-}(t)\phi_0^{-}\exp[-i\eta_0^{-}(t)]. \tag{49}$$

Such a technique is probably useful for the calculation of scattering in the intermediate region $E\approx 1$.

Suppose we define a set of functions

$$\begin{aligned}\chi_n^{\pm}=\tfrac{1}{2}\{&[U_n^{+}\exp(-i\eta_n^{+}(t))+U_n^{-}\exp(-i\eta_n^{-}(t))]\\ &\times\exp(-\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt)\\ &\pm[U_n^{+}\exp(-i\eta_n^{+}(t))-U_n^{-}\exp(-i\eta_n^{-}(t))]\\ &\times\exp(\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt)\}.\end{aligned} \tag{50}$$

This is similar to Bates and McCarroll's $\phi_n^{\pm}$ in that it is not an orthogonal set. It satisfies the equation of motion, (13), for all $\mathbf{R}$ for $v=0$, and for all $\mathbf{v}$ for $R=\infty$, just as theirs does. However, the χ_n has each of the $U_n^{\pm}$ carrying its proper time dependence.

It is easily seen that

$$I=\frac{1}{2}\int d^3x\,dt\left[\psi^*i\frac{\partial}{\partial t}\psi-\psi i\frac{\partial}{\partial t}\psi^*-\psi^*H\psi-\psi H\psi^*\right], \quad (51)$$

is a variational expression for ψ and ψ^*. We propose to use it to determine the cross sections in the intermediate region.[16] A reasonable form for ψ in this region would be a sum of the high- and low-energy forms:

$$\psi=\alpha_+(t)\chi_0^+ +\alpha_-(t)\chi_0^- +\beta_+(t)\phi_0(\mathbf{x}+\tfrac{1}{2}\mathbf{R}) \times\exp[-\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt-i\eta_0(t)]+\beta_-(t)\phi_0(\mathbf{x}-\tfrac{1}{2}\mathbf{R}) \times\exp[\tfrac{1}{4}i\mathbf{x}\cdot d\mathbf{R}/dt-i\eta_0(t)]. \quad (52)$$

Such a form could be used in (51) with the 4 variational functions $\alpha_\pm$, $\beta_\pm$ to determine the exchange to the ground state. Such a calculation is now in progress and will be reported on subsequently.

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Ionization Produced by Atomic Collisions at kev Energies. III*

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The electron evaporation model of the collision-ionization process that occurs when atoms collide at high energies is extended to include atoms with from two to eight electrons in the outer shell. Application of the model to data from collisions of N^+ on Ar and Ne^+ on Ar gives evidence for a resonant electron capture effect taking place in high-energy violent collisions which was heretofore masked by the multiple ionization consequent on such collisions.

1. INTRODUCTION

To account for ionization produced by violent atomic collisions, a phenomenological theory was developed in two previous papers,[1,2] hereafter referred to as I and II. These papers were restricted in scope to the collisions of atoms with outer shells of eight electrons (i.e., the noble gases). Since that time some experimental data have been published for collisions involving nitrogen ions (with five electrons). It was therefore decided to extend the theory to include atoms with from two to eight electrons in the outer shell. In addition, the evaporation theory will be used to show evidence of resonant electron capture, in violent ion-atom collisions.

The theory, as originally developed in I, utilizes an evaporation model of the collision-ionization process. As the two charge distributions sweep through each other, a small amount of kinetic energy of translation of the atoms is transferred to their internal degrees of freedom by a friction-like mechanism. This energy (ordinarily called the "inelastic energy") is assumed to be statistically distributed among the outer-shell electrons of the atoms. Then, upon separation, the "heated" atoms get rid of this excess energy, partly by photon emission and partly by electron evaporation.

In the previous work, ionization probabilities were calculated only for atoms having eight outer electrons and the resulting ionization probability curves compared very closely with the experimental curves for Ar^+ on Ar scattering. In Sec. 2 of the present work, ionization probability curves are calculated for atoms having from two to seven electrons in the outer shell. When the five-electron curves are compared with N^+ on Ar scattering data, the agreement is good, indicating that the evaporation model need not be restricted to the noble-gas atoms, but has validity in other cases as well.

Recent experiments[3,4] have shown evidence for a resonant capture process occurring in ion-neutral atom collisions. Clear-cut evidence for the resonant capture effect was found in collisions involving the very light atoms and for the heavier atoms only in the very gentle collisions. Resonant capture effects, if they occur in the more violent collisions of the heavier atoms, are masked

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