Classical Heavy-Particle Trajectories for Electron Capture in H\textsuperscript{+}-He Collisions and for Other Asymmetric Collisions

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The method of perturbed stationary states, in a two-state approximation, is used to obtain semiclassical differential cross sections for electron capture or excitation in asymmetric ion-atom collisions at energies of the order of 1 keV. Two cases are discussed. In case A it is assumed that transitions between the two states occur only near a fixed internuclear separation; in case B it is assumed that they occur only near the distance of closest approach. Case B is studied in the limit of weak coupling; case A is studied both with and without this assumption. It is found that in each case the differential cross sections can be interpreted in terms of classical trajectories calculated from the potentials for the initial and final molecular states of the ion-atom system. It is also found that the impact-parameter calculation of the differential cross section may be considerably in error except at small impact parameters. The results for case A are shown to apply at least approximately to H\textsuperscript{+}-He collisions and are compared with the experimental data of Helbig and Everhart.

I. INTRODUCTION

The impact-parameter method\textsuperscript{1,2} has proven to be a useful approximate method for the analysis of atomic collisions. As is well known, the method is characterized by the \textit{a priori} specification of a classical heavy-particle trajectory for each impact parameter. Consequently, only the electron motion needs to be determined, a circumstance which often greatly simplifies the calculations.

It is generally agreed that the method is valid for the calculation of total cross sections down to energies of the order of a hundred eV. However, recent work on symmetric-resonant H\textsuperscript{+}-H and He\textsuperscript{+}-He ion-atom collisions has shown that the impact-parameter method leads to incorrect results for differential cross sections at small scattering angles, even at energies of the order of 1 keV.\textsuperscript{3-5} In Refs. 3-5, the wave-theoretic method of perturbed stationary states\textsuperscript{6} (p.s.s.) was used to allow for the influence of the state of electronic excitation on the heavy-particle trajectory. This led to substantial modifications of the impact-parameter results whenever

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the classical cross section for scattering on the molecular potential associated with the gerade state was very different from that for scattering on the potential associated with the ungerade state. The agreement between the wave theories and experiment is not yet completely satisfactory. Nevertheless, it is clear that the wave approach is essential for a correct calculation of differential cross sections at energies below a few keV.

It is to be expected that scattering effects similar to those obtained for symmetric-resonant collisions will also occur for sufficiently analogous asymmetric collisions. For this reason we decided to undertake the study reported below. Our analysis is carried out under assumptions very similar to those employed in Refs. 3-5 in that the p.s.s. method is used in a two state approximation, the effects of momentum transfer being neglected. The scattering amplitudes are evaluated in the stationary-phase approximation. The results apply to both electron capture and excitation. For simplicity, only $\Sigma$-$\Sigma$ transitions are considered but the generalization to other transitions is straightforward.

A basic complication arises in the case of asymmetric collisions. The matrix element which couples the initial and final states must be known, because together with the potential energy curves, it determines the internuclear separations at which transitions occur. This information in turn governs the relative extent to which the scattering of the heavy particles takes place on the initial and final-state potential curves. At present our knowledge of the molecular potential curves for most systems of interest is rather limited and evidently much less is known about the coupling matrix elements. Consequently, at this time the scattering effects in question must be discussed in primarily qualitative terms.

Within the framework of the two-state approximation we consider two cases, A and B, for which a discussion of the scattering can be given and which should be approximately applicable to some actual collisions. In case A it is assumed that transitions between the initial and final molecular-ion states are likely to occur only near a fixed internuclear separation $R=R_e$. In case B it is assumed that transitions are likely to occur only near the distance of closest approach. The assumptions used to treat these two cases will now be discussed. The reader interested in first obtaining a summary of results can skip the next two paragraphs.

Case A includes the situation of pseudocrossing at $R=R_e$ of the molecular electronic energy curves.\textsuperscript{9,11} It also includes the situation in which the coupling matrix element based on the Heitler-London approxi-


\textsuperscript{10} In the symmetric-resonant case the gerade and ungerade states are not coupled at all, their relative amplitudes being determined by the initial conditions.


\textsuperscript{13} In this situation $R_e$ is the value of $R$ at which the above quantities are equal. In our work, case A is treated by using an expression for the amplitude $A_{\ell}(l)$ of the $l$th partial wave in the partial-wave expansion of the final-state scattering amplitude which has the same form as that obtained by Stueckelberg.\textsuperscript{12} It is convenient to discuss this assumption in terms of the customary impact-parameter interpretation of the partial-wave expansion. We therefore introduce the impact parameter $\rho=(l+\frac{1}{2})ba^{-1}$, where $ba$ is equal to the initial relative momentum of the system. Then, as is shown in Eqs. (5), (7), $|A_{\ell}(l)|^2$ can be used to define a probability $\psi(\rho)=|A_{\ell}(l)|^2$ for capture or excitation during collisions with impact parameter $\rho$. At sufficiently high energies $\psi(\rho)$ tends toward the value obtained directly by the impact-parameter method. In these terms Eqs. (14a) and (14b) for $A_{\ell}(l)$ lead to the expression

$$\psi(\rho)=4P_l(1-P_l)\sin^2(\pi-\phi).$$

Here $P_l(\rho)$ is the probability that a transition from one molecular state to the other takes place in a single passage of $R=R_e$ and $2\pi$ is the phase difference which develops between the molecular electronic wave functions during the lapse of time between the two passages of $R=R_e$.\textsuperscript{13} The angle $\phi$, which turns out to be zero in Stueckelberg's and most other approximate treatments of case A, is introduced to represent a possible additional change in phase developed in the region of transitions near $R=R_e$.\textsuperscript{14} When the average over $\sin^2(\pi-\phi)$ is taken in the expression for $\psi(\rho)$, the familiar form of the Landau-Zener formula is obtained. The quantities $P_l$ and $\phi$ are not specified explicitly in our treatment because we feel that existing theory, with its neglect of momentum transfer in particular, is not sufficiently accurate to determine them. However, it is assumed that they vary slowly enough with impact parameter that $P_l$ and $\exp(\pm ik\rho)$ can be treated as constants during the stationary-phase evaluation of the partial-wave sum in the final-state scattering amplitude. This assumption is not made in the case of $\exp(\pm ik\rho)$, for at low velocities this quantity oscillates rapidly as a function of $l$. Since the above expression for $\psi(\rho)$ is closely connected with the standard theories for case A,\textsuperscript{13-17} its basis is open to valid criticism.\textsuperscript{18} However, in
some cases at least, more accurate calculations lead to qualitatively very similar results. The formula above is used only for \( \rho < R_e \); for \( \rho > R_a \), where the theory predicts that \( \phi(\rho) \) is nonoscillatory and decreasing, it is assumed that the partial-wave amplitude is slowly varying in the sense described above.

Our treatment of case B, i.e., the case of transitions only near the distance of closest approach, is suggested (in a somewhat nonrigorous way) by the formulas used for case A. When the transitions occur only near the distance of closest approach, the quantity \( \tau \) above should be set equal to zero. On this basis, we treat case B simply by supposing that \( \phi(\rho) \) and the partial-wave amplitude are slowly varying functions of \( \rho \) and \( l \).

Case B should apply to a pair of states for which the molecular electronic energy difference decreases monotonically with decreasing internuclear separation.

The general results of our study can be summarized as follows:

1. When case B applies, the inelastically scattered particles scatter on the initial-state potential \( V_0 \) during the first half of the collision and on the final-state potential \( V_\rho \) during the second half. The elastically scattered particles scatter entirely on \( V_0 \).

2. When case A applies, for impact parameters less than \( R_a \), the scattering effects are similar to those obtained for symmetric resonant collisions. Both elastic- and inelastic-scattering amplitudes are superpositions of two terms, each of which corresponds to a different classical trajectory. The first inelastic trajectory corresponds to scattering on \( V_0 \) until \( R_a \) is reached for the first time and thereafter on \( V_\rho \); the second inelastic trajectory corresponds to scattering on \( V_0 \) until \( R_a \) is reached for the second time and thereafter on \( V_\rho \). The first trajectory for the elastically scattered particles corresponds to scattering entirely on \( V_0 \); the second trajectory corresponds to scattering on \( V_0 \) for internuclear separations \( K > R_a \) and on \( V_\rho \) for \( K < R_a \). For impact parameters greater than \( R_a \), the scattering is as described in (1).

3. When \( V_0 \) and \( V_\rho \) are very different, as is the case for example when \( V_0 \) supports bound vibrational states and \( V_\rho \) is repulsive, the different trajectories described above may be very different for moderate to large impact parameters. In this case the impact-parameter expressions for the differential cross sections will be considerably in error. For very small impact parameters, the scattering is dominated by the Coulomb repulsion of the nuclei, regardless of the state of electronic excitation. The impact-parameter method then becomes a good approximation.

The spirit of our semiclassical approach has much in common with that of Bates and Holt. These authors use the three-dimensional J.W.K.B. approximation to give a semiclassical analysis of the many-state wave equations. The primary concern in Ref. 17 is the case in which the differences in the potential curves of the various states in the calculation can be neglected in the determination of the heavy-particle motion. For this case, Ref. 17 provides a justification for and improvement of the impact-parameter method. Our work is aimed at a complementary case, namely that in which the potential curves for the two most important states are sufficiently different that the impact-parameter method, with its single trajectory, can be considerably in error.

The rest of the paper is organized as follows: In Sec. II cases A and B are treated on the basis of weak-coupling theory, following Ref. 6. In Sec. III Stueckelberg's strong coupling theory is applied to case A and the points of similarity and difference in the weak and strong coupling treatments are discussed. In addition, the effect of coupling near the distance of closest approach between the original excited state and an additional excited state is discussed, using the method of Smith. In Sec. IV it is shown that case A applies approximately to \(^{3}H\)-He collisions. Numerical results are obtained for the \(^{3}H\)-He differential electron-capture probability and these are compared with the data of Hettig and Everhart.

Atomic units are used except in Sec. IV where the units of Ref. 18 are introduced in comparing theory and experiment.

II. WEAK-COUPLING THEORY

Our object in this section is to obtain semiclassical approximations for the differential cross sections for elastic and inelastic scattering. The coupling is assumed to be weak. For the sake of concreteness we consider an electron-capture reaction for which the initial and final molecular states are \( \Sigma \) states. Formulas for the elastic and charge-exchange scattering amplitudes can be obtained from Eqs. (63) and (65) of Ref. 6, the notation of which we follow where possible. Because of the assumption of weak coupling, the elastic-scattering amplitude \( f_0(\Theta) \) is given by

\[
f_0(\Theta) = (2ik_0)^{-1} \sum_{l=0}^{\infty} (2l+1) \exp(2i\eta_l) - 1 \right) P_l(\cos\Theta) \tag{1}
\]

In Eq. (1) \( \Theta \) is the c.m. scattering angle, \( k_0 = M \nu \), where \( M \) is the system's reduced mass and \( \nu \) is the initial relative speed of the heavy particles; \( \eta_l \) is the phase shift for elastic scattering on the potential \( V_0 \).

19 The same formulas are applied to the final molecular state corresponding to excitation of the target rather than to capture. The results can be generalized to the case of \( \Sigma \)-\( \Pi \) transitions, etc.
The capture amplitude $f_p(\Theta)$ can be written in the form

$$f_p(\Theta) = (2ik_p^{1/2}k_p^{1/2})^{-1} \sum_{l=0}^{\infty} (2l+1) \exp[i(\eta_p l + \eta_p')] A_p(l) P_l(\cos \Theta). \quad (2)$$

In Eq. (2), $k_p = M \nu_p$, $\nu_p$ being the relative speed of the heavy ions after capture; $\eta_p$ is the phase shift for elastic scattering on $V_p$. A semiclassical formula for $A_p(l)$ is given by

$$A_p(l) = i \int_{R^2}^{\infty} dR \left( \mu_p/\mu_0 \right)^{1/2} M \rho_p$$

$$\times \sin \left[ \int_{R_0}^{R} \mu_p dR' - \int_{R_0}^{R} \mu_p dR'' \right], \quad (3)$$

where $\mu_p$ and $\mu_0$ are equal to $2\pi$ times the local J.W.K.B. wave numbers for scattering with angular-momentum quantum number $l$ on the potentials $V_p$ and $V_0$. The quantities $R_p$ and $R_0$ are the distances of closest approach and $R_0$ is the greater of $R_p$ and $R_0$. The coupling matrix element $M_{\rho_0}$ in Eq. (3) is given by

$$M_{\rho_0} = -2 \int \chi_p(\nabla/\partial R) \partial \chi_0 dR, \quad (4)$$

where $\chi_0$ and $\chi_p$ are the molecular eigenfunctions and the partial derivative is taken with the electron coordinates relative to the target nucleus held fixed. At present $M_{\rho_0}$ is known for most scattering systems.

The quantity $A_p(l)$ is what was called the partial-wave amplitude in Sec. I. As was stated there, it is closely related to the impact-parameter capture probability. Indeed, the total capture cross section $Q_\rho$ is given by

$$Q_\rho = 2\pi k_0^{-2} \sum_{l=0}^{\infty} (l+\frac{1}{2}) |A_p(l)|^2 \to 2\pi \int \rho d\rho \Theta(\rho), \quad (5)$$

where the impact-parameter $\rho$ is defined by

$$\rho = (l + \frac{1}{2})k_0^{-1}, \quad (6)$$

and $\Theta(\rho)$ is defined by

$$\Theta(\rho) = |A_p(l)|^2. \quad (7)$$

The analysis given in Sec. 2.3 of Ref. 6 shows that if the impact energy is not too low the value of $\Theta(\rho)$ which follows from Eqs. (7) and (3) is just that obtained from the impact-parameter method.

We next evaluate $f_0(\Theta)$ and $f_p(\Theta)$ by means of the stationary-phase approximation. In the case of $f_0(\Theta)$ this leads to the classical cross section $\sigma_c(\Theta)$. Thus

$$\sigma_c(\Theta) = |f_0(\Theta)|^2 = \left( \sin \Theta \right)^{-1} p_0 d\rho_0 / d\Theta = \sigma_c(\Theta). \quad (8)$$

In Eq. (8), $\rho(\Theta)$ is determined via Eq. (6) from the value of $l$ for which

$$\Theta = 2(d\rho_0 / dl). \quad (9)$$

In order to evaluate $f_p(\Theta)$, given that $M_{\rho_0}$ in Eq. (3) is not known, we make the assumptions concerning $A_p(l)$ which were discussed in Sec. I. Let us consider case B first. For this case $A_p(l)$ is taken outside the sum in Eq. (2). The stationary-phase approximation then leads directly to the result that

$$\sigma_p(\Theta) = (k_0/k_p) |f_p(\Theta)|^2 = \Theta(\rho(\Theta)) \delta_c(\Theta). \quad (10)$$

In Eq. (10), the impact parameter $\rho(\Theta)$ is determined via Eq. (6) from the value of $l$ for which

$$\Theta = (d\rho_0 / dl) + (d\eta_p / dl), \quad (11)$$

and the classical cross section $\delta_c$ is related to $\rho_0$ in the usual way; $\Theta$ is related to $A_p(l)$ via Eq. (7). Equations (10) and (11) associate a definite classical trajectory and cross section with the capture process and relate $\sigma_p(\Theta)$ of the wave theory to $\Theta(\rho)$ of the impact-parameter method. The appearance through Eq. (11) of the average deflection angle shows that the scattering takes place on $V_0$ during the first half of the collision and on $V_p$ during the second half.

The capture probability $P(\Theta)$ is calculated according to

$$P(\Theta) = \frac{\sigma_p(\Theta)}{\sigma_T(\Theta)} = \frac{\Theta'(\rho(\Theta))}{\sigma_T(\Theta)}, \quad (12)$$

where $\sigma_T(\Theta)$ stands for the total particle differential cross section. In the weak-coupling approximation $\sigma_T(\Theta) = \sigma_c(\Theta)$. The ratio

$$\frac{\Theta'(\rho(\Theta))}{\sigma_c(\Theta)} \sim \frac{\delta_c(\Theta)}{\sigma_T(\Theta)}, \quad (13)$$

is always very close to unity for small impact-parameter collisions. Under these circumstances the impact-parameter calculation is adequate. However, it will be shown in Sec. IV that $C$ can be very different from unity for some impact parameters which are experimentally accessible.

Let us now consider case A. In this case, $A_p(l)$ is assumed to be slowly varying for $l > k_0 R_c$. For $l \leq k_0 R_c$ it is assumed that

$$A_p(l) = i G \sin (l - \phi), \quad (14a)$$

where

$$G = 2l^{\frac{1}{2}} (1 - G)^{1/2} \quad (14b)$$

As described in Sec. I, P_L and $\varphi$ are unspecified functions of $l$ and $\nu$ which are supposed to vary slowly enough with $l$ that $G$ and $\exp(\pm i \varphi)$ can be treated as constants in the stationary-phase evaluation of Eq. (2).

Of course, it should be noted that the calculations of Ref. 7 if rainbow scattering occurs. The existing data for H+He collisions do not include measurements near the rainbow angle for $\Gamma_0$; also, for this case $V_p$ is repulsive.
The quantity $\tau$ is given by

$$\tau = \int_{R_0}^{R_e} \mu_d dR - \int_{R_0}^{R_e} \mu_p dR,$$

(15a)

$$\sim -\frac{1}{2} \int_0^{2 \pi \rho^2} dZ \left[ V_p(R) - V_d(R) + \Delta E \right],$$

(15b)

where $R^2 = \rho^2 + Z^2$, $\rho$ and $l$ being related by Eq. (6); $\Delta E$ is the energy defect for the reaction. The approximate relation (15b) exhibits the $v$ and $\rho$ dependence of $\tau$ most clearly; it is a good approximation at kilovolt energies when $\rho$ is small compared to $R_e$.

When Eq. (14a) is used in Eq. (2), the stationary-phase evaluation of Eq. (2) yields the result that

$$f_p(\Theta) = -(k_0/k_p)^{1/2} \left\{ G_k \left( \epsilon \right) e^{i\epsilon_1} e^{i\epsilon_{1a}} - G_p e^{-i\epsilon_2} e^{i\epsilon_{2a}} \right\}. \quad (16)$$

In Eq. (16) the subscripts 1 and 2 on $G$ and $\varphi$ refer to evaluation with $l = l_1$ or $l_2$, where $l_1$ and $l_2$ are solutions of

$$(l/d)(\eta_{1l}^2 + \eta_{2l}^2 + \tau) = (\Theta),$$

(17)

respectively. Once again classical impact parameters $\rho_{1,2}$ are defined in terms of $l_{1,2}$ through Eq. (6). The classical cross sections $\sigma_{1,2}$ are then defined in terms of $\rho_{1,2}$. Finally, the phase angles $\alpha_1$ and $\alpha_2$ can be expressed in the form

$$\alpha_1 = (\eta_{1l}^2 + \eta_{2l}^2 - \tau - (l + 1/2) \Theta - \frac{1}{2} \pi)_{1,2},$$

(18)

$$\alpha_2 = (\eta_{1l}^2 + \eta_{2l}^2 + \tau - (l + 1/2) \Theta - \frac{1}{2} \pi)_{1,2}.$$

The trajectories 1 and 2 can be given an interesting physical interpretation. If J. W. K. B. expressions for the phase shifts $\eta_{1l}^2$ and $\eta_{2l}^2$ are inserted into Eq. (17) along with the formula (15a) for $\tau$, it can be shown that for small-angle scattering trajectory 1 corresponds to a collision in which the system scattered under the influence of $V_d$ until $R_e$ was reached for the first time and thereafter scattered under the influence of $V_p$. Likewise, trajectory 2 corresponds to a collision in which the scattering took place on $V_d$ until $R_e$ was reached the second time and thereafter took place on $V_p$. This result is to be expected on the basis of the p.s.s. method. In case A the transition can occur at $R_e$ when the particles are either approaching or receding; the trajectories described above reflect this fact. It is interference arising from the coherent superposition of the contributions to the transition amplitude at the two passages of $R = R_e$ which gives rise to the oscillations in the capture probability. Strong coupling is not required.

The capture probability $P(\Theta)$ follows directly from Eq. (16). If the impact energy is not too low, and if $R_e$ is large compared to the impact parameters of primary interest, the classical deflection functions $\Theta_1$ and $\Theta_2$ can be well approximated by $\Theta_1$ and $\Theta_2$, and similarly for the cross sections. With the same restrictions on energy and impact parameter, $\alpha_1 \sim \alpha_2$ can be well approximated by $2\tau(\rho_0)$, where $\rho_0$ is defined by Eqs. (11) and (6). Finally, since $G$ and $\varphi$ are slowly varying, we take $G_1 = G_2 = G(\rho_0)$ and $\varphi_1 = \varphi_2 = \varphi(\rho_0)$. The final result for $P(\Theta)$ is then

$$P(\Theta) = \left( \frac{\sigma_0}{\sigma(\rho_0)} \right) G^2 \left\{ (D - 1)^2 + D \sin^2(\tau - \varphi) \right\},$$

(19)

where

$$D = \left( \frac{\sigma_0(\Theta)}{\sigma(\Theta)} \right)^{1/2}. \quad (20)$$

Of special note is the nonoscillatory term in Eq. (19). Since $\sigma = G^2 \sin^2(\tau - \varphi)$, it is seen that for large $D$ the oscillations in $\sigma$ tend to be suppressed in $P$, just as is the case for symmetric resonant collisions. When $D < 1.5$, the nonoscillatory term is negligible and $D$ is close in value to the quantity $C$ introduced in the discussion of case B. In this event cases A and B lead to practically the same relation between $P(\Theta)$ and $G(\rho)$. Values of $C$ and $D$ for $H^+ - He$ collisions are given in Sec. IV. From these it will be seen that for moderate to large impact parameters the scattering corrections to the impact-parameter method can be very large.

III. STRONG-COUPLING THEORY AND COUPLING TO AN ADDITIONAL EXCITED STATE FOR CASE A

The primary defect in the weak-coupling approximation for case A is that it does not allow elastic scattering to take place via the virtual excitation and de-excitation of the final molecular state. For $\Sigma\Sigma$ transitions, the coupled equations of the p.s.s. theory involve derivative coupling and have not yet been solved. However, Stueckelberg has solved the coupled equations which result if the Heitler-London approximation is used for the molecular wave functions and energies. Using Stueckelberg's results we can obtain the form which the differential cross sections take in the strong coupling case. From the formulas on pp. 377, 378, and 400 of Ref. 11, it can be deduced that

$$f_p(\Theta) = -(k_0/k_p)^{1/2} \left\{ P_L^{1/2} (1 - P_L)^{1/2} \theta_1^{1/2} e^{i\epsilon_{1a}} - P_L^{1/2} (1 - P_L)^{1/2} \theta_2^{1/2} e^{i\epsilon_{2a}} \right\}, \quad (21)$$

and

$$f_\theta(\Theta) = (1 - P_L) \theta_1^{1/2} e^{i\epsilon_{1a}} + P_L \theta_2^{1/2} e^{i\epsilon_{2a}}. \quad (22)$$

Here, as before, $P_L$ is the probability of a transition during a single passage of $R = R_e$. In Eq. (21) trajectory 1, $\alpha_1$, and $\theta_1$ are direct analogs, using the Heitler-London potentials, of the corresponding quantities in Eqs. (16)–(18) and in the discussion following Eq. (18); a similar statement applies to trajectory 2, etc. Thus,

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22 In this interpretation it is assumed that the potential discontinuity produced by a jump from $V_d$ to $V_p$ at $R_e$ has a negligible effect on the scattering. For $H^+ - He$ collisions, where $R_e \sim 2.5$, this assumption is very well satisfied for impact energies above 100 eV.

24 As stated in the Introduction, it is not intended that Stueckelberg's expression $P_L = \exp(-2\Theta)$ be used in the equations which follow.
since in Eq. \ref{eq:16} \( G = 2P_L^{1/2}(1-P_L)^{1/2} \), it is seen that
Eq. \ref{eq:21} (based on strong-coupling theory) is completely analogous to Eq. \ref{eq:16} (based on weak-coupling theory) except that \( \psi = 0 \) in Stueckelberg's theory. The effect of the strong coupling manifests itself most directly in Eq. \ref{eq:22}. Here, as would be guessed from the factors \((1-P_L)\) and \(P_L\), trajectory 3, \(a_3\), and \(\tilde{a}_3\) refer to no transitions at either passage of \( R = R_c \) and hence to scattering entirely on \( V_0 \). Likewise, trajectory 4, \(a_4\), and \(\tilde{a}_4\) refer to excitation at the first passage of \( R = R_c \) and de-excitation at the second passage, Thus trajectory 4 refers to scattering on \( V_0 \) for \( R > R_c \) and scattering on \( V_p \) for \( R < R_c \). It is seen from Eq. \ref{eq:22} that strong coupling leads to the possibility of oscillations with scattering angle and impact energy in the elastic-scattering cross section. The oscillations will be most marked when \((1-P_L)\tilde{a}_3^{1/2}\tilde{a}_4^{1/2}\).

If the approximations introduced above Eq. \ref{eq:19} are also used in Eqs. \ref{eq:21} and \ref{eq:22}, one can set \(\tilde{a}_3 = \tilde{a}_4 = \overline{\sigma}_p\), \(a_3 = a_4 = \overline{\sigma}_p\), \(a_1 = a_2\), and \(a_1 = a_0\) in these equations. Equation \ref{eq:21} then leads to the same expression for \(P(\Theta)\) given in Eq. \ref{eq:19}. In addition, with the same approximations, the total particle cross section is given by

\[
\sigma_T = (1-P_L)\overline{\sigma} + P_L\overline{\sigma}_p, \tag{23}
\]

an intuitively reasonable result. It will be observed that with the above approximations, when \(P_L = \frac{1}{2}\), Eqs. \ref{eq:21}–\ref{eq:23} have the same form as those for a symmetric resonant collision.

The preceding discussion shows that strong coupling can manifest itself through oscillations in the elastic differential cross section. Although the discussion is based on the Heitler-London approximation, it is to be expected that the use of the exact molecular wave functions will not change the form of Eqs. \ref{eq:21} and \ref{eq:22}. However, with the exact wave functions, the potentials which described the scattering will not be \(V_0\) and \(V_p\) exactly, since these will be perturbed by the velocity-dependent coupling.

It is not difficult to modify Eqs. \ref{eq:21} and \ref{eq:22} to include the effect of coupling for \(R < R_c\), between \(X_p\) and a neighboring excited state \(X_s\). Suppose, for example, that this coupling is strong only near the distance of closest approach. Let \(P_s(\rho)\) be the impact parameter probability for the transition to \(X_s\) from \(X_p\). Then, using the method of Smith,\(^3\) and supposing \(R_s\) to be large for the same of simplicity, we find

\[
f_\rho(\Theta) = -\left(\frac{k_0}{k}\right)^{1/2} \left( P_L^{1/2}(1-P_L)^{1/2} \right)^{1/2} X_\rho \left[ q \left( a_1 + a_2 \right) \right] - P_L^{1/2}(1-P_L)\overline{\sigma}_p, \tag{24}
\]

\[
f_\Theta(\Theta) = (1-P_L)\overline{\sigma}_p^{1/2} \overline{\sigma}_\rho, \tag{25}
\]

and

\[
f_\delta(\Theta) = \left(\frac{k_0}{k}\right)^{1/2} P_L^{1/2} P_L^{1/2} P_L^{1/2} \overline{\sigma}_p^{1/2} \overline{\sigma}_\rho, \tag{26}
\]

where \(\phi_\rho\), \(\gamma\) are phase factors. In Eq. \ref{eq:26}, \(\overline{\sigma}_p\) is the cross section for scattering on \(V_p\) during the first half of the collision and on \(V_p\) during the second half. The idea behind Eqs. \ref{eq:24}–\ref{eq:26} is that when the potential curve \(V_p\) is traversed between passages of \(R = R_c\), coupling to \(X_s\) changes the amplitude and phase of that part of the wave function associated with \(X_p\), the change in amplitude being determined from probability conservation.\(^4\) The quantities \(P_s\) and \(\overline{\sigma}_p\) can be determined by the impact-parameter method.\(^3\)\(^7\)\(^2\)

From the above formulas, it can be seen that the effect of coupling near the distance of closest approach between \(X_p\) and an additional excited state is to produce a phase shift in the oscillations of \(f_\rho(\Theta)\) and to replace \(\overline{\sigma}_p\) by \((1-P_L)^{1/2}\overline{\sigma}_p\). It is readily seen from Eqs. \ref{eq:19} and \ref{eq:20} that for large \(P_s\) this effective reduction in the value of \(\overline{\sigma}_p\) can either considerably increase or decrease the nonoscillatory contribution to \(P(\Theta)\), depending on the relative values of \(\overline{\sigma}_p\) and \(\overline{\sigma}_s\). In the case of \(H^3\)-\(H\) collisions, Bates and Williams\(^4\) have shown that significant values of \(P_s\) and \(\overline{\sigma}_p\) can arise for certain transitions even at low energies.

The type of coupling discussed above is evidently rather special. However, the method used to treat it can readily be generalized to include other situations. The method does not apply to situations in which more than two states are all strongly interacting over the same range of internuclear separation. The complexity of the system of potential-energy curves for typical diatomic molecules makes it clear that considerable work will be necessary to establish the validity of any particular model for a given collision.

**IV. APPLICATION OF THE THEORY TO \(H^1+H\) COLLISIONS**

In this section we use the results of Secs. II and III to interpret the experiments of Heilig and Everhart\(^8\) on scattering with and without electron capture in \(H^1+H\) collisions.

The data are illustrated in Fig. 1 which shows the experimental electron-capture probability \(P(\Theta)\) plotted versus reciprocal impact velocity for various values of the product of the deflection angle \(\Theta\) and the impact energy \(T\). The interesting "damped" oscillations

\[^{18}\] The above discussion differs slightly from that in Ref. 3, where the states \(1\sigma_g, 2\sigma_g,\) and \(2\pi_g\) correspond to our \(X_n, X_p,\) and \(X_s\). In Ref. 3, \((\epsilon_0/k_0)(\Theta_0(\Theta)\) is taken to be \(P_s(\Theta_0(\Theta) = \frac{1}{2} P_L \overline{\sigma}_p X_\rho + 2\overline{\sigma}_p X_\rho X_\rho + \overline{\sigma}_p X_\rho X_\rho\). The value \(P_s\) is more appropriate because neither excited state is coupled to the \(1\sigma_g\) state and because the \(1\sigma_g\) state has a potential similar to \(1\sigma_g\) for small \(R\). If this choice is used in Ref. 3 the result is to replace \(A_1\) in Eqs. \ref{eq:22} and \ref{eq:24} of that paper by \((1-2\rho)^{1/2}\). This increases the "damping" of the oscillations in \(P(\Theta)\) somewhat, but not enough to materially change the comparison between theory and experiment. Our product \(P_s\) corresponds to \(P_s\) in Ref. 3. The above remarks are in agreement with the work of Bates and Holt (Ref. 17) who reached the same conclusion concerning Ref. 3.


\[^{20}\] The experimental range of \(\Theta\) is about 0.5 to 5.0 deg; the range of \(T\) is about 1 to 200 keV. For small-angle scattering, constant \(P_s\) corresponds to constant distance of closest approach and to approximately constant impact parameter. The value of \(\Theta T\) is the same whether c.m. or laboratory quantities are used.
sions provide a most severe test of the theory, particularly because the impact velocity ranges from 0.2 to 2 a.u., so that adiabatic theory is needed for the low energies, while the Born and Bates\textsuperscript{4} approximations appear most reasonable at the highest energies.

H"ubig and Everhart interpreted the data in terms of the impact-parameter method and showed that an illustrative formula obtained by Bates and Lynn\textsuperscript{27} could not be adapted to the data very well.\textsuperscript{28} A difficulty arose in this analysis because it was not clear which potential function to use in order to relate $\Theta$ and the distance of closest approach $R_e$ in the evaluation of $r$. This uncertainty is exhibited in the inset table in Fig. 1. H"ubig and Everhart decided to determine $R_e(\Theta)$ by averaging the deflection functions for elastic scattering on the ground- and first-excited-state potentials for HeH$^+$. We find [see the discussion of approximations which precedes Eq. (19)] that their intuitive choice, which amounts to using $\tau(a_e(\Theta))$, is a good approximation, except possibly for the smallest values of $\Theta T$.

A second impact-parameter interpretation was given by Lichten,\textsuperscript{29} who proposed the formula

$$P = e^{-\lambda \alpha} [\sin^2((Fa)/2\alpha) - \beta].$$

(27)

In Eq. (27), $\alpha$ is the impact velocity and $v_0$, $\langle Fa\rangle$, and $\beta$ are adjustable parameters. Lichten gave arguments leading to values of $v_0$ and $\langle Fa\rangle$ which, together with the value of $\beta$ from Ref. 10, provided a good fit to the data of Fig. 1 except at high energies, where the formula predicts $P \rightarrow \frac{1}{2}$ instead of $P \rightarrow 0$. This breakdown of Eq. (27) is to be expected. The formula is a typical result of calculations which are based on two-state atomic eigenfunction expansions in which the momentum transferred to the captured electron is neglected.\textsuperscript{30,31} However, an account of momentum transfer is essential at high energies.\textsuperscript{31} It will be shown below that case A applies approximately to H$^+$-He collisions. Thus on the basis of the wave theory [Eq. (19)] formula (27) is also seen to be incorrect whenever $D$ is large, as occurs at large impact parameters. For low energy, small impact-parameter collisions, however, formula (27) has the correct qualitative form.

The oscillatory nature of $P_e(\Theta)$ shown in Fig. 1 suggests that case A applies to H$^+$-He collisions, at least as a first approximation. On this basis $R_e$ was determined from Eqs. (19) and (15b) by requiring that Eq. (19) predict the experimentally observed spacing between the minima in $P_e(\Theta)$ for $\Theta T$ in the range 5-10 keV deg, where the experimental spacing is essentially independent of $\Theta T$.\textsuperscript{31} From Fig. 4 of Ref. 18, the spacing was estimated to be $(0.50 \pm 0.01) \times 10^{-3}$ sec/cm. This led to an experimental value $(2.87 \pm 0.06)$ a.u. for the integral in Eq. (15b). With $\mu = 0.3$ a.u., which corresponds to $\Theta T = 8$ keV deg in Fig. 3, and the potentials $V_{0p}$ described below, $R_e$ was determined

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\textsuperscript{28} It should be kept in mind that the experimental probability $P_e(\Theta)$ includes excitation processes and capture into excited states while the theoretical $P(\Theta)$ refers only to elastic scattering and capture into H(1s). The higher excited states, while not negligible, are not dominant.

\textsuperscript{29} W. Lichten, Phys. Rev. 139, A27 (1965).


\textsuperscript{31} Equation (15b) agrees with Eq. (15a) to about 1% in the range of energies and angles covered by the experimental data.
consistent with each other for $0.8 \leq R \leq 2$, $(R/2)V_p$ was obtained from a graph of $(R/2)V_p$, using the computed values of Michels outside of $(0.8 \leq R \leq 2)$ and making the curve pass smoothly below the computed values of both authors for $(0.8 \leq R \leq 2)$. Again a cubic spline was used to convert the numerical data into a smooth function.

The classical c.m. deflection functions $\Theta_{\phi,p}(\rho)$ were calculated from $V_{\phi,p}$ by the method of Smith\textsuperscript{23} and the capture deflection function $\Theta_c(\rho)$ of Eq. (11) was obtained by averaging $\Theta_\phi$ and $\Theta_p$.\textsuperscript{26} The c.m. differential cross sections $\delta_\phi$, $\delta_p$, and $\delta_c$ were then obtained by numerical differentiation of the deflection functions.

The cross sections are extremely sensitive to variations in the slope of $V_0$ and $V_p$. We believe $\delta_\phi(\Theta)$ to be accurate to within a few percent. Because of uncertainties in our knowledge of $V_p$, $\delta_p(\Theta)$ may be in error of the order of 10% for $\Theta T < 5$ keV deg. As $\Theta T$ is increased beyond 5, the possible error in $\sigma_p$ should decrease from about 5% to 1 or 2%. The deflection angles should be correct to 1 or 2\%.

Figure 3 shows $T \Theta_\phi$, $T \Theta_p$, and $T \Theta_c$ plotted versus $\rho$. For $\Theta T \leq 3$ keV deg, 1-keV results are plotted; for $\Theta T > 3$, 5-keV results are plotted. For small-angle scattering $T \Theta$ is a function only of the distance of closest approach $R_\phi$, and in addition $R_p$ and $\rho$ are equal to within a few percent. The curves can be used for


\textsuperscript{[26]} The averaging process, $\Theta_\phi$ and $\Theta_p$, were both evaluated at the initial c.m. energy. Actually $\Theta_\phi$ should be evaluated at the final c.m. energy. The difference in $\Theta_\phi$ which results thereby is unimportant at the energies for which the experimental data were taken. An analogous statement applies to the cross section $\delta_p$ in the ratio $D$.

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\textsuperscript{23} F. J. Smith, Physica 30, 497 (1964).

\textsuperscript{26} In the averaging process, $\Theta_\phi$ and $\Theta_p$ were both evaluated at the initial c.m. energy. Actually $\Theta_\phi$ should be evaluated at the final c.m. energy. The difference in $\Theta_\phi$ which results thereby is unimportant at the energies for which the experimental data were taken. An analogous statement applies to the cross section $\delta_p$ in the ratio $D$. 

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\textsuperscript{[26]}
angles in the range $0.5 \leq \Theta T \leq 10$ keV with an error of less than 4%.

Figure 4 shows the differential cross sections divided by $T^2$ (c.m.) and plotted versus $\Theta T$. The curves apply to the above-mentioned ranges of angle and energy to 1 or 2%.

The ratios $C$ and $D$ which appear in Eqs. (13) and (20) are shown in Fig. 5. For $\Theta T > 4$ keV deg, $(D-1)/(4D)$ is less than 0.03. In this case the non-oscillatory term in Eqs. (19) is negligible. In addition, since $C$ and $D$ are almost equal for $\Theta T > 4$, case B [Eq. (12)] and case A [Eq. (19)] lead to practically the same result for $P(\Theta)$. For small $\Theta T$ the nonoscillatory term in Eq. (19) becomes increasingly important.

As we said previously, the application of the results to the data of Fig. 1 must be primarily qualitative. Consider first the small impact-parameter collisions, say those for $\Theta T \geq 20$ keV deg. The scattering in these collisions is dominated by the nuclear Coulomb repulsion and consequently, as the calculations show in a quantitative way, the cross sections $\sigma_0$, $\sigma_\rho$, and $\sigma_\tau$ are nearly equal. Their near equality makes the scattering corrections to the impact-parameter method very small. In particular, the nonoscillatory term in Eq. (19) is too small to account for the nonvanishing value of $P_i$ at $v^- = 0.7 \times 10^{-8}$ sec/cm. Thus, it appears that contributions from additional excited states are not negligible here. The quantitative formulas cannot be applied too literally to the data for $\Theta T \geq 20$ because the impact energies are too high for the use of adiabatic theory; for accurate results it would be necessary to include the effects of momentum transfer and at high energies to replace the adiabatic potentials with those of the distorted-wave theory. These changes, however, can hardly alter the basic result that the small impact-parameter scattering is rather insensitive to the state of electronic excitation. Consequently, we conclude that the impact-parameter method is a good approximation for the small impact-parameter collisions. This result is important because the impact-parameter method provides a feasible way of taking momentum transfer, strong coupling, and higher excited states into account. In the wave framework the corresponding calculations would be much more difficult.

Let us consider now the data for moderate to large impact-parameter collisions, say $\Theta T \leq 5$ keV deg. For the most part these data involve impact energies low enough that the p.s.s. approach is appropriate. Because $D$ is large, the scattering corrections to the impact-parameter results are large; so large indeed that it is very unlikely that a more quantitative application of the theory might provide a justification for the impact-parameter approach. We conclude that a wave-theoretic approach is essential to the interpretation of the collisions for $\Theta T \leq 5$.

Once again the quantitative use of our formulas for $P(\Theta)$ would be open to question since the effects of momentum transfer have been neglected and since the model of transitions only at $R_a$, while apparently consistent with the data, may well be an oversimplification. Even so, it seems likely that the nonvanishing values of $P_i(\Theta)$ at $v^- = 1.2 \times 10^{-8}$ sec/cm and $v^- = 1.7 \times 10^{-8}$ sec/cm are due to a combination of scattering effects and additional excitation processes. In this velocity range it can be seen from Fig. 1 that with decreasing $\Theta T$ the oscillations in $\sigma$ are suppressed in $P_i$ in a manner which is qualitatively consistent with Eq. (19) or with the generalization of Eq. (19) which results from coupling to an additional excited state as described in Sec. III. That coupling to such additional excited states can be important even at low energies follows from the work of Bates and Williams\textsuperscript{25} on $H^+\text{He}$ collisions. The potential curves of the two systems are similar enough for small values of $R$ that it seems likely that excited states will also play an important role in $H^+\text{He}$ collisions.

It can be seen that the experimental data just begin to enter the region where scattering effects are really large. It would be of value to extend the measurements to lower values of $\Theta T$ and to lower energies.

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