Diffraction and angular momentum effects in semiclassical atomic scattering theory

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The semiclassical scattering theory of Mott and Massey and Ford and Wheeler is here extended to multichannel scattering as occurs at a crossing or pseudocrossing of the transient molecule formed by the colliding atoms. The generalized theory incorporates both interference and diffraction phenomena, but the emphasis in this work is on diffraction. For small-angle scattering, diffraction effects become broader, not narrower, as the collision energy increases: $\Delta b\Delta\tau \geq \hbar[E_{\rm inc}/(2m)]^{1/2}$ relates the uncertainties in impact parameter b and reduced scattering angle $\tau = E_{\rm inc}\theta$, and determines the range in b required to resolve a structure in the deflection function of height $\Delta\tau$. In the kilovolt range of collision energies, the effects of local maxima and minima in the deflection function are washed out, and the Airy-function approximation of Ford and Wheeler is inappropriate to describe the differential cross section. More generally, it is shown that at keV collision energies the stationary-phase approximation, heretofore essential in the reduction to the semiclassical limit, breaks down in the vicinity of a level crossing. An approximate theorem is proposed which remains valid in this region and elsewhere reduces to the standard stationary-phase approximation. Several illustrative examples are considered. A separate development treats the effect on the differential scattering cross section of a change in electronic angular momentum when electronic excitation occurs.

I. INTRODUCTION

Atom-atom scattering in the low-kilovolt energy range can generally be described in terms of classical deflection under the influence of forces produced by the adiabatic or diabatic interaction potential, somewhat modified by quantum effects. This work deals with two essentially independent classes of effects caused by crossings of molecular energy levels on atomic collisions in this energy range. One topic is diffraction and interference effects in single- and multiple-channel scattering. The other is the effect of changes in the electronic angular momentum on the collision trajectory, and hence on the differential scattering cross section. These two independent topics are incorporated in a single work primarily for economy of presentation.

Where electronic excitation at level crossings is a factor (thus giving rise to multichannel scattering), quantum-mechanical effects due to interference (Stueckelberg oscillations[1-4]) and diffraction (rainbow effects[5] and absorbing disk effects[6,7]) are observable *superimposed on the classical differential cross sections*. By now, interference effects in atomic collisions in the keV range are well understood. On the other hand, diffraction effects in such collisions are not even qualitatively understood. Even the rainbow maximum in the differential scattering cross section, so elegantly treated in Ford and Wheeler,[5] must be reexamined for atomic collisions in the keV energy range. The K^+ on A example of rainbow scattering considered by Ford and Wheeler[8] was for collision energy 0.1 eV. Surprisingly, diffraction effects in atomic collisions become broader, rather than narrower, as the collision energy increases, and the Airy-function approximation by Ford and Wheeler becomes inapplicable for collisions in the keV range. This can be seen from the Heisenberg uncertainty relation $\Delta l\Delta\theta \geq \hbar$, where l is the relative angular momentum of trajectory motion, θ the deflection angle in the center-of-mass frame, and Δl and $\Delta\theta$ the respective uncertainties. For scattering experiments, the relative momentum p is precisely known so that the uncertainty in angular momentum is due solely to the uncertainty in the impact parameter b: $\Delta l = p\Delta b$. Moreover, for small-angle scattering, the quantity that varies as a function of impact parameter only is not θ itself, but $\tau = E\theta$, where $E = p^2/2m$ is the collision energy, which is also known precisely. Thus, in the case of small-angle atomic scattering, the uncertainty relation yields

$$p\Delta b(\Delta\tau/E) \geq \hbar ,$$

or, finally,

$$\Delta b\Delta\tau \geq \hbar[E/(2m)]^{1/2} .$$

Thus, in order to resolve a given structure in the deflection function of size $\Delta\tau$ (such as a local minimum), it must not be confined to a range of impact parameter smaller than $\hbar[E/(2m)]^{1/2}/\Delta\tau$. Clearly, the higher the collision energy, the larger the range of impact parameter needed to resolve that structure. For classic Ford and Wheeler rainbow scattering in a collision at 1 keV, the range of b in which the deflection function must

be essentially quadratic is 100 times larger than for a collision at 0.1 eV. The actual situation is quite the reverse; the relevant minima in atomic collisions at keV energies are due to level crossings and are of the order of a few tenths of an atomic unit in extent, while the minimum in the K^+-A collision considered by Ford and Wheeler was a Van der Waals minimum, which extends for several atomic units. The use of the Airy function, as described by Ford and Wheeler, for atomic collisions in the keV range is not only suspect; it will be shown to be invalid.

A second, independent topic studied in this work is the effect that angular momentum excitation of the electronic state may have on the deflection angle. When electronic excitation occurs, it is possible that the *internal* angular momentum may change in the excitation process. This, of course, must be reflected in an equal and opposite change in the angular momentum of translational motion and, therefore, on the collision trajectory.

Clearly, the most lucid treatment of these quantum effects superimposed on classical scattering theory can be achieved with a quantum-mechanical formulation in which the classical limit of the quantum description is simply and intuitively accessible at each step along the way. Such a description is the semiclassical approximation applied to the Rayleigh-Faxen-Holtzmark partial-wave analysis. First elucidated by Mott and Massey,[9] this approach was expanded and illuminated[5] with several important examples[8] by Ford and Wheeler. In particular, they discussed rainbow scattering, the glory effect, and interference effects. Their formulation was limited, however, to single-channel elastic scattering. In a series of papers, Coffey *et al.*,[1] Smith *et al.*,[2] and Olsen and Smith[3] studied in detail interference effects in multichannel scattering produced by level crossings in atomic collisions, using the He^+-Ne and He^+-Ar systems as examples. Their formulation, based on action integrals rather than a partial-wave analysis, was limited; it could not encompass rainbow scattering and could handle diffraction effects (Smith *et al.*[6] and Baudon *et al.*[7]) only in a qualitative fashion in terms of diffraction by an absorbing disk. Marchi[4] and Kotova[10] developed the semiclassical limit of the partial-wave analysis to include multichannel effects due to level crossings. Marchi's treatment was limited to elastic channels exclusively; Kotova formulated the theory for both elastic and excited channels in the two-states approximation. Ovchinnikova[11] and Kotova and Ovchinnikova[12] applied Kotova's formulation to the threshold behavior of the Stueckelberg interference oscillations, which is a diffraction effect. More recently, Delos and Thorson[13] and Delos[14] developed a semiclassical partial-wave analysis for the two-state system with a level crossing. Although these works did not use the simplifications developed by Mott and Massey[9] and Ford and Wheeler,[5] diffraction effects were included. With this formulation, Delos[14] and Saxon and Olson[15] described rainbow effects in model curve crossing systems resembling the He^{++}+Ne and He^++Ne systems, respectively. In addition, Saxon and Olson incorporated the Airy function of Ford and Wheeler, which would be valid at low collision energies, but not in the kilovolt collision-energy regime.

One of the two principal objectives of the present work is the full generalization of the Ford and Wheeler treatment of the partial-wave analysis in the semiclassical approximation to encompass all multichannel effects which occur at level crossings. There will be nothing new insofar as interference effects are concerned; the main advance will be the systematic inclusion of diffraction effects. This development is presented in Sec. III. For heuristic purposes, a thumbnail summary of the single-channel theory will first be presented in Sec. II, following the notation of Ford and Wheeler[5] insofar as is possible. For convenience, final results will also be expressed in terms of the reduced variables $\rho = \theta \sin\theta \, d\sigma/d\omega$ and $\tau = E\theta$, which have now become standard. Section II also includes an extension of the single-channel theory of Ford and Wheeler to accommodate maxima and minima in the deflection function *as they occur in atomic collision systems*. These are really pseudorainbow effects, and the Airy-function approximation of Ford and Wheeler is inappropriate to describe the collision. For completeness, the true rainbow effect is also discussed as a special case of the general theory.

Section III A presents the multichannel generalization of the semiclassical scattering theory from an intuitive approach, deferring the rigorous derivation to Sec. III B. Although such a presentation may be backward from a logical point of view, it is preferable from a heuristic point of view. Indeed, once one comes to grips with the reality that the Rayleigh-Faxen-Holtsmark theory must be generalized in order to cover multichannel processes, there is hardly any other generalization which can be imagined. In point of fact, the results of Sec. III A were actually written down first, and the formal derivation achieved later, with Sec. III A as a guide. The formal derivation is based on Stueckelberg's partial-wave analysis of collisional excitation of a two-level system in the semiclassical limit,[16] a summary of which can be found in Mott and Massey.[17] A more up-to-date treatment is given by Delos.[14] A brief review of

Stueckelberg's formulation is presented in Secs. III B 1–III B 3. Following, that, Sec. III B 4 describes the further approximation, beyond the semiclassical approximation, required to obtain the standard two-level theory of Landau[18] and Zener.[19] These latter approximations are much less reliable than the approximations inherent in the semiclassical approximation by itself.[20] Stueckelberg's attempt at deriving a connection formula for the more rigorous treatment was incorrect[21]; hence the semiclassical treatment of Sec. III B is presented in terms of the components of a connection matrix T which is best obtained from a numerical solution of the coupled equations across the transition region.

Finally, Sec. IV treats the effects of changes in the angular momentum of the electronic degrees of freedom on the differential scattering cross section. These effects, although not yet observed, may possibly be seen in coincidence experiments as differences between the differential scattering cross sections of atoms which emit left-handed circularly polarized photons and those which emit right-handed photons in a direction perpendicular to the plane of scattering.

II. SINGLE-CHANNEL THEORY

A. Brief review of the semiclassical approximation

For scattering by a single central potential $V(R)$, the differential scattering cross section is given by the square of the scattering amplitude:

$$\frac{d\sigma}{d\omega} = |f(\theta)|^2 , \tag{1}$$

where

$$f(\theta) = (2ki)^{-1} \sum_{l=0}^{\infty} (2l+1)(e^{i2\eta(l)} - 1) \times P_l(\cos\theta) . \tag{2}$$

In atomic units, k is the asymptotic relative momentum $mv(\infty)$, with m the reduced mass, θ the scattering angle in the center-of-mass frame, and $\eta(l)$ the phase shift for the lth partial wave. In the JWKB (i.e., semiclassical) approximation,

$$\eta(l) = \tfrac{1}{4}\pi + \tfrac{1}{2} l\pi - kR_0 + \int_{R_0}^{\infty} [K(R) - k]\, dR , \tag{3}$$

where $K(R)$ is the radial component of the relative momentum at radius R and k is the value of K at infinity:

$$K(R) = [2m(E - V) - (l+\tfrac{1}{2})^2/R^2]^{1/2} , \tag{4a}$$

$$k = K(\infty) = (2mE)^{1/2} , \tag{4b}$$

and R_0 is the classical turning point. An important property of the JWKB phase shift is that the classical deflection function $\Theta(l)$ is given by

$$\Theta(l) = 2\frac{d}{dl}\eta(l) . \tag{5}$$

The deflection function $\Theta(l)$ gives the scattering angle Θ obtained in a classical Newtonian orbital calculation when the incident center-of-mass energy is $k^2/2m$ and the orbital angular momentum is l. In terms of the impact parameter b, which is usually used in classical collision calculations,

$$l = kb . \tag{6}$$

Even for hydrogen on hydrogen at 1 keV incident energy, l is of the order of hundreds of atomic units. Therefore, the sum in (2) can be replaced by an integral and the Legendre polynomial can be replaced by the asymptotic expression

$$P_l(\cos\theta) \simeq [\tfrac{1}{2}(l+\tfrac{1}{2})\pi\sin\theta]^{-1/2} \times \sin[(l+\tfrac{1}{2})\theta + \tfrac{1}{4}\pi] , \tag{7}$$

valid for angles such that $\sin\theta > 1/l$. Expressing the sine in Eq. (7) in terms of complex exponentials, substituting into the expression (2) for $f(\theta)$, and making use of the relation[9] that $\sum(2l+1)P_l(\cos\theta) = 0$ if $\theta \neq 0$ [$2l+1$ is exactly the coefficient of the Legendre-polynomial expansion of $2\delta(\cos\theta - 1)$], (2) becomes

$$f(\theta) = -(2\pi k^2 \sin\theta)^{-1/2} \times \int_0^{\infty} (l+\tfrac{1}{2})^{1/2} [\exp(i\varphi_+) - \exp(i\varphi_-)]\, dl , \tag{8}$$

where

$$\varphi_{\pm} = 2\eta \pm (l+\tfrac{1}{2})\theta \pm \tfrac{1}{4}\pi . \tag{9}$$

The completion of the semiclassical approximation relies on the method of stationary phases; the only significant contribution to integral (8) comes from a small range of l for which either $d\varphi_+/dl = 0$ or $d\varphi_-/dl = 0$. The other phase, which does not exhibit a stationary point, makes a negligible contribution to the integral and can be ignored. An immediate consequence of this fact, taken together with Eq. (5), is that the only significant contribution to $f(\theta)$ (and, therefore, to the differential cross section) at a given angle θ arises from a small range of l (or b) about the value determined by the classical deflection function. Hence the classical limit of the fully quantum-mechanical formulations Eqs. (1) and (2) is established. However, since a finite range of impact parameter, albeit small, does contribute to scattering at a given angle θ, diffraction effects will be observable under appropriate conditions.

B. Generalization of the stationary-phase method

Up to this point, the presentation has been just a review of Refs. 5 and 9. The point of departure is the evaluation of integral (8) to determine the value of the scattering amplitude. The previous treatments expanded whichever phase, φ_+ or φ_-, had the stationary value in a power series about the stationary point. Retaining up to and including quadratic terms for an ordinary point yields the classical scattering cross section formula. When the quadratic term vanishes, the quantun rainbow maximum of Ford and Wheeler is obtained by retaining the cubic term. The classical cross section formula will be valid if the deflection function is essentially linear over the entire range of impact parameters which contribute; the Ford and Wheeler result will be valid if the deflection function is essentially quadratic over the entire range of impact parameters which contribute.

It can be seen from Fig. 1, however, that these criteria are not fulfilled, even in modest energy atomic collisions, when level crossings are involved. The particular case illustrated is the $(Na\text{-}Ne)^+$ collision system at 2-keV incident energy in the laboratory frame (34.2 a.u. in the center-of-mass frame). To make visualization easier, the abscissa is given in units of impact parameter rather than l. Furthermore, for purpose of illustration, it has been assumed that the *adiabatic* energy curve is followed with unit probability. This would give rise to fully elastic scattering for which the single-channel theory is adequate. Figure 1 first of all shows the classical deflection function $\tau = E_{\text{inc}}\theta$ in keV deg, plotted as a function of impact parameter. The range of b which contributes to the scattering at $\tau = 8.75$ keV deg ($\theta = 9.4°$ in the center-of-mass frame) lies between b_1 and b_2 as shown, allowing for oscillations in the integral. This is the range of b for which the phase φ_- differs from the maximum value by less than $\frac{1}{4}\pi$. Note that there are two maxima and one minimum in this overlapping case. The quantity $I(b_m)^2$ is equal to $(2\pi/k)\sin\theta[d\sigma/d\omega]_{b_m}$, where θ is 9.4°, k is the relative momentum, and where the brackets with subscript b_m indicate that this is the

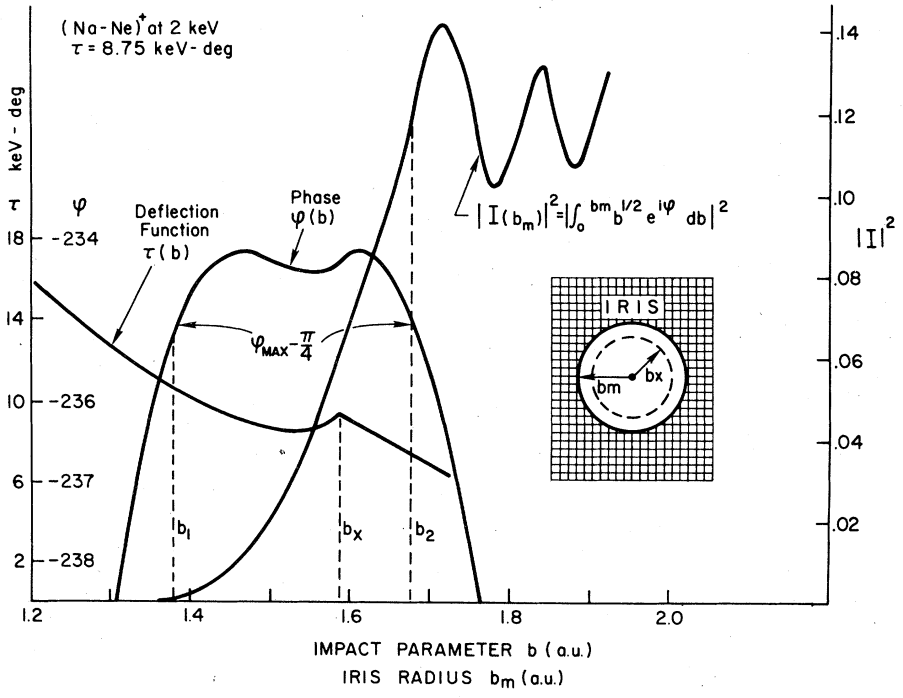

FIG. 1. Classical deflection function τ, the phase φ, and the partial cross section for the adiabatic elastic channel in Na^+-Ne collisions at 2-keV incident energy. All three quantities are plotted as functions of the impact parameter. The phase and partial cross section shown here are for $\tau = 8.75$ keV deg, corresponding to a scattering angle of 9.4° in the laboratory; $I(b_m)^2$ gives the value of $(2\pi/k)\sin\theta\,(d\sigma/d\omega)$ which would be obtained if an absorbing iris were placed in the plane of the target to intercept all incident projectiles with impact parameters greater than b_m. Here, b_2 and b_1 define the range of b within which the phase difference between any two points is less than $\frac{1}{4}\pi$, while b_x gives the impact parameter for which the minimum internuclear separation is just equal to the crossing radius.

differential cross section that *would* be obtained if an absorbing iris with opening of radius b_m were placed in the plane of the target. Thus, as b_m increases (the iris opened), $I(b_m)^2$ shows where the main contribution to the differential cross section comes from. In this figure, b_x is not the level crossing radius itself, but the impact parameter required, at this incident energy, for the classical minimum internuclear separation to be exactly equal to the crossing radius.

Clearly, in such cases the evaluation of integral (8) must not rely on the properties of φ at the stationary point l_0 only; φ is *not* an analytic function and cannot be described in terms of φ and its derivitives evaluated at l_0. Instead, the following approximate theorem is here proposed:

$$\left|\int_0^\infty e^{i\varphi(l)}dl\right| \simeq l_2 - l_1 \tag{10}$$

or, more generally,

$$\left|\int_0^\infty f(l)e^{i\varphi(l)}dl\right| \simeq \int_{l_1}^{l_2} f(l)\,dl\,, \tag{11}$$

where l_1 and l_2 are the extreme values on either side of the stationary-phase point within which the phase does not vary by more than $\frac{1}{4}\pi$

$$|\varphi(l) - \varphi(l')| < \tfrac{1}{4}\pi$$

for all l, l' such that $l_1 \leq l \leq l' \leq l_2$. (12)

It must be stressed that this is not a rigorous and exact theorem and, as such, cannot be proven. It was inferred from many cases and is a good approximation in the particular case illustrated in Fig. 1. The ratio of the approximate cross section obtained from (11) to the exact cross section obtained by full numerical integration of (8) is 1.08. This result is typical; the illustration was selected because it clearly shows the invalidity of a power-series expansion at the stationary-phase point. The theorem reduces exactly to the stationary-phase result in those cases for which l_0 is well within a regular region, so that φ can be well approximated by a quadratic function: $\varphi(l) = \varphi(l_0) + a(l - l_0)^2$. It should be pointed out that the essential concept of this theorem was well understood by Ford and Wheeler. However, in their work they did not quantify the concept, as is done in Eqs. (10)–(12).

Although the semiclassical phase (3) can be used in calculating φ, the differential cross section in the classical region can be expressed entirely in terms of the classical deflection function. This makes it easier to visualize how diffraction effects are superimposed on the classical scattering process. Moreover, in many cases the deflection function is inferred directly from experiment, and the phases are unknown. Writing

$$\varphi(l) - \varphi(l_0) = \int_{l_0}^{l} \frac{d\varphi}{dl}\,dl\,,$$

it follows from (9) that

$$\varphi(l) - \varphi(l_0) = \int_{l_0}^{l} \left(2\frac{d\eta}{dl} \pm \theta\right) dl\,. \tag{13}$$

However, from (5): $2(d\eta/dl) = \Theta(l)$. Moreover, $\theta = \mp\,\Theta(l_0)$; in fact, this equation determines l_0 for given θ. The upper sign should be used for attractive potentials; the lower for repulsive. This phase difference can therefore be written entirely in terms of the deflection function. For either attractive or repulsive scattering,

$$\varphi(l) - \varphi(l_0) = \int_{l_0}^{l} [\Theta(l) - \Theta(l_0)]\,dl\,. \tag{14}$$

The classical limit is easily obtained when the deflection function varies linearly with l. Thus, if

$$\Theta(l) - \Theta(l_0) = (l - l_0)\Theta'(l_0)\,, \tag{15}$$

where $\Theta'(l_0)$ denotes the derivative of the deflection function evaluated at l_0, then from (14),

$$\varphi(l) - \varphi(l_0) = \tfrac{1}{2}\Theta'(l_0)(l - l_0)^2\,. \tag{16}$$

Finding the two values of l for which the phase difference is $\frac{1}{4}\pi$ is an easy matter:

$$l_2 - l_0 = l_0 - l_1 = [\pi/2\Theta'(l_0)]^{1/2}\,,$$

or

$$l_2 - l_1 = [2\pi/\Theta'(l_0)]^{1/2}\,. \tag{17}$$

Finally, using (17) in (8)

$$\frac{d\sigma}{d\omega} = |f(\theta)|^2 = \frac{1}{2\pi k^2 \sin\theta}\Big|(l_0 + \tfrac{1}{2})^{1/2} \times [2\pi/\Theta'(l_0)]^{1/2}\Big|^2 = (l_0 + \tfrac{1}{2})/k^2 \sin\theta\,\Theta'(l_0)\,. \tag{18}$$

Neglecting the $\frac{1}{2}$ relative to l_0, setting $\Theta = \theta$ and $l_0 = kb$, so that $d\theta/dl = (1/k)(d\theta/db)$, the classical expression for the cross section is obtained:

$$\frac{d\sigma}{d\omega} = \frac{b}{\sin\theta\,(d\theta/db)}\,. \tag{19}$$

In terms of the reduced variables ρ and τ, (19) can be rewritten

$$\rho = \theta\sin\theta\,\frac{d\sigma}{d\omega} = \frac{b\tau}{d\tau/db}\,. \tag{19'}$$

It must be stressed that the classical cross section (19) *or* (19′) *is valid only when the classical deflection function varies very nearly linearly with* l (*or* b) *over the full contributing range.* The deflection shown in Fig. 1 is far from linear and

the classical cross section (19) completely invalid.

Finally, with the help of (16) it can be shown that the theorem, Eqs. (10) and (12), essentially contains the physical content of the uncertainty relations. Setting the phase difference in (16) to $\frac{1}{4}\pi$ (or $\hbar\pi/4$ in arbitrary units) and recognizing that

$$(l - l_0)\Theta' = \Theta(l) - \Theta(l_0) = \Delta\theta\,,$$

$$(l - l_0) = \Delta l\,,$$

Equation (16) can be rewritten

$$\tfrac{1}{2}h\pi = \Delta l \Delta\theta\,, \tag{20}$$

again providing that Θ' is for all practical purposes constant over an interval Δl on either side of l_0.

C. Quadratic minimum in the deflection function

Ford and Wheeler treat the special case of a deflection function which is exactly quadratic over the entire contributing range of l. Despite the evidence just presented that this condition does not apply in most atomic collisions at keV energies, it is nevertheless instructive to apply theorem (10)–(12) to this special case. It is important to determine the applicability of the theorem to classically forbidden deflection angles, as occurs when there is an absolute minimum in the deflection function (a lowest value of scattering angle for *any* impact parameter). Such a case arises in multichannel scattering, although the deflection function cannot be characterized as quadratic over a sufficient range of l.

Let l_r, η_r, and θ_r denote the values of the respective quantities at the rainbow minimum. To produce a quadratic deflection function, the phase shift must be of the form

$$\eta = \eta_r + \tfrac{1}{2}\theta_r(l - l_r) + \tfrac{1}{6}q(l - l_r)^3\,, \tag{21}$$

when η and θ_r are positive, as is the case for repulsive scattering. It follows from (5) and (9), which determine Θ and φ, respectively, that

$$\Theta(l) = \frac{2d\eta}{dl} = \theta_r + q(l - l_r)^2\,, \tag{22}$$

$$\varphi_-(l) = 2\eta_r - \theta_r(l_r + \tfrac{1}{2}) + (l + \tfrac{1}{2})(\theta_r - \theta) + \tfrac{1}{3}q(l - l_r)^3 - \tfrac{1}{4}\pi\,. \tag{23}$$

Thus, q, θ_r, and l_r are seen to be parameters which specify the deflection function. Ford and Wheeler define the scaled variables

$$x = q^{-1/3}(\theta_r - \theta)\,, \tag{24a}$$

$$y = q^{1/3}(l - l_r)\,. \tag{24b}$$

In terms of these scaled variables, they obtain for the differential cross section

$$\frac{d\sigma}{d\omega} = \frac{\hbar^2}{p^2}(l_r + \tfrac{1}{2})\frac{2\pi}{\sin\theta}\,q^{-2/3}\mathrm{Ai}^2(x)\,, \tag{25}$$

where

$$\mathrm{Ai}(x) = (2\pi)^{-1}\int_{-\infty}^{+\infty}\exp[i(xy + \tfrac{1}{3}y^3)]\,dy\,. \tag{26}$$

In terms of the scaled variables,

$$\varphi_-(l) - \varphi_-(l_r) = xy + \tfrac{1}{3}y^3\,. \tag{27}$$

Equation (12) states that the range of φ must be $\frac{1}{4}\pi$. In this case φ is monotonic; thus $\varphi(l_2)$ is $\frac{1}{8}\pi$ above $\varphi(l_r)$ and $\varphi(l_1)$ is $\frac{1}{8}\pi$ below, making the total range $\frac{1}{4}\pi$:

$$xy_2 + \tfrac{1}{3}y_2^3 = +\tfrac{1}{8}\pi\,, \tag{28a}$$

$$xy_1 + \tfrac{1}{3}y_1^3 = -\tfrac{1}{8}\pi\,. \tag{28b}$$

From Figs. 1 and 2 it is seen that there is a fundamental difference between the behavior of φ in true rainbow scattering and in the quasirainbow scattering of Sec. II B.

Figure 3 shows a plot of the exact values of the Airy integral from Miller[22] (also tabulated in Ford and Wheeler[5]) compared with the approximate values obtained from Eqs. (10) and (12). The approximation is seen to be good up to about $x = 1.5$. For $x > 2$, the approximation breaks down completely, even having the wrong asymptotic behavior for large values of x. The theorem appears reliable to within an amount 0.03 of the true value; where the Airy integral has values that small, the theorem is invalid. For $x \leq -0.7$, both the theorem and expression (25) become somewhat ambiguous as the cross section evolves into two separate branches.

III. MULTICHANNEL THEORY

In this section the semiquantal theory of scattering is generalized to cover multichannel scattering. To keep this notation as simple as possible, only the two-channel case with positive scattering angle (i.e., repulsive scattering) is considered. The initial molecular state (before the collision) is always taken to be the ground molecular state ϕ_0. After the collision, the molecular state will be a linear combination of ϕ_0 and the excited state ϕ_1. This gives rise to four possible scattering channels, which are illustrated in Fig. 4. The two channels which lead to ϕ_0 after the collision are called the elastic channels and are designated by I and II. The remaining two channels, which lead to ϕ_1 after the collision, are called the excitation channels and are designated by III and IV. Because the overall scattering is repulsive, only the

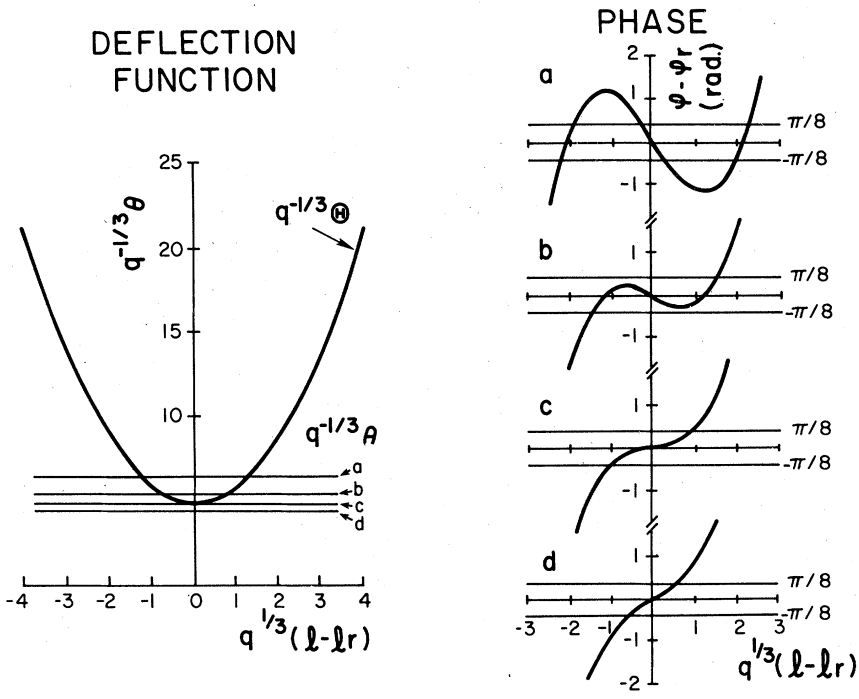

FIG. 2. Deflection function and quantum phases. The drawing on the left depicts a quadratic deflection function in terms of the dimensionless variables x and y of Ford and Wheeler. Four horizontal lines indicate scattering angles labeled, a, b, c, and d. To the right, the quantum phases $\varphi - \varphi_r$ are plotted in radians for each of these scattering angles. The $\pm\frac{1}{8}\pi$ limits defining the range of $\frac{1}{4}\pi$ are indicated. The intersections of each curve $\varphi - \varphi_r$ with these limits define the limiting values l_1 and l_2 for the theorem Eq. (11). It can be seen that for case a, the scattering angle is sufficiently far from the rainbow angle that the cross section decomposes into two separate terms.

phase φ_- need be considered. This is true even if there is a small attractive region in one or more of the scattering channels. For notational simplicity, the minus sign will be suppressed, and the phase simply denoted by φ. In Sec. III A the multichannel theory will be developed in a heuristic, intuitive approach. The rigorous justification will follow in Sec. III B.

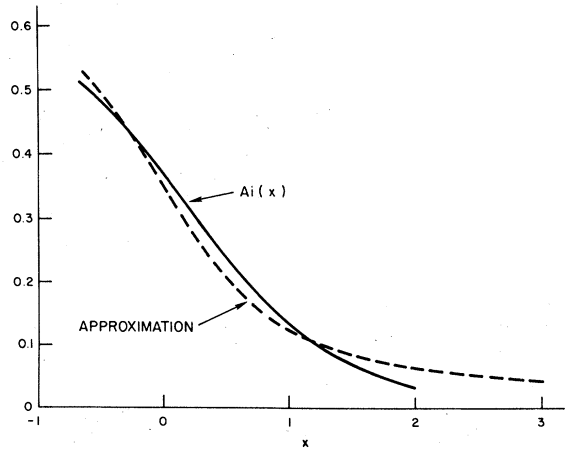

FIG. 3. Airy integral and the approximation from Eq. (10). The exact values of the Airy integral, Eq. (26), taken from Miller[5,22] are compared here with the values which follow from the approximate theorem, Eqs. (10) and (12). The abscissa is the scaled scattering angle variable x defined by Ford and Wheeler, Eq. (24a).

A. Heuristic approach

The salient equations of the single-channel case are Eqs. (8) and (9), along with (3) and (5). From (3), (4a), and (5), note that η and, therefore, Θ are dependent upon the potential. As a consequence, each of these quantities is channel dependent; the distinction between the four channels is precisely the potential curves followed on the trajectory. Moreover, for each of channels III and IV, the potential curve followed during the outgoing portion of the trajectory is different from that followed on the incoming portion. Indeed, the factor 2 which multiplies η in (9) takes into account a contribution from both incoming and outgoing portions of the trajectory, which are identical in the single-channel case. Thus Eq. (9) must be replaced by

$$\varphi_N = \zeta_N + (l+\tfrac{1}{2})\theta - \tfrac{1}{4}\pi\,, \tag{29}$$

where N denotes the channel and ζ_N is the channel phase *development*:

$$\zeta_{\rm I} = (l+\tfrac{1}{2})\pi - 2k_0R_x + 2\int_{R_0}^{R_x} K_0\,dR + 2\int_{R_x}^{\infty}(K_0 - k_0)\,dR\,, \tag{30a}$$

$$\zeta_{\rm II} = (l+\tfrac{1}{2})\pi - 2k_0R_x + 2\int_{R_1}^{R_x} K_1\,dR + 2\int_{R_x}^{\infty}(K_0 - k_0)\,dR\,, \tag{30b}$$

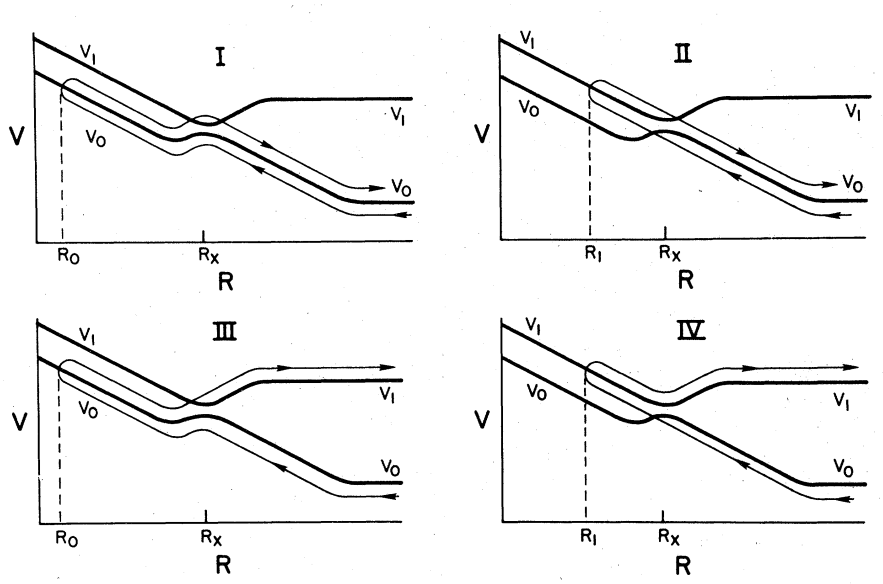

FIG. 4. Four collision channels considered in this work. Channels I and II describe elastic scattering, while III and IV describe inelastic scattering.

$$\zeta_{III} = (l+\tfrac{1}{2})\pi - (k_0+k_1)R_x + 2\int_{R_0}^{R_x} K_0\,dR + \int_{R_x}^{\infty}[(K_0-k_0)+(K_1-k_1)]\,dR \tag{30c}$$

$$\zeta_{IV} = (l+\tfrac{1}{2})\pi - (k_0+k_1)R_x + 2\int_{R_1}^{R_x} K_1\,dR + \int_{R_x}^{\infty}[(K_0-k_0)+(K_1-k_1)]\,dR \tag{30d}$$

In Eqs. (30) the potentials used to calculate the radial components of momentum K_0 and K_1 are $V_0(R)$ and $V_1(R)$; these are the potentials which follow from ϕ_0 and ϕ_1, respectively. Because these two potentials are different, the minimum internuclear separations are also different and are denoted by R_0 and R_1. The limits of integration in Eqs. (30) are easily established from the channel diagrams shown in Fig. 4. As with the single-channel theory, it is easily verified that

$$\Theta_N = \frac{d\zeta_N}{dl}\,. \tag{31}$$

The factor of 2 is not needed here; it is already built into the ζ_N.

With two possible final states, there are two independent scattering amplitudes, f_0 and f_1, each of which is a sum of contributions from two channels:

$$f_0 = (2\pi k_0^2 \sin\theta)^{-1/2}\int_0^{\infty}(l+\tfrac{1}{2})^{1/2}[A_I\exp(i\varphi_I)+A_{II}\exp(i\varphi_{II})]\,dl\,, \tag{32a}$$

$$f_1 = (2\pi k_0 k_1 \sin\theta)^{-1/2}\int_0^{\infty}(l+\tfrac{1}{2})^{1/2}[A_{III}\exp(i\varphi_{III})+A_{IV}\exp(i\varphi_{IV})]\,dl\,. \tag{32b}$$

Each of the complex exponentials in Eqs. (32) is multiplied by its own channel scattering amplitude A_N such that

$$\sum_{N=I}^{IV}|A_N|^2 = 1\,. \tag{33}$$

Thus, $|A_N|^2$ gives the probability that the collision evolved along the Nth channel. Equations (29)–(33) reduce to the single-channel adiabatic elastic scattering results if all A_N vanish except for A_I (the molecular state remains in ϕ_0 throughout the collision); they reduce to the single-channel diabatic elastic results if all A_N vanish except for A_{II} (the molecular state crosses over to ϕ_1 at the pseudocrossing and then returns to ϕ_0 on the outward passage through the pseudocrossing region). There is hardly any other sensible generalization of single-channel theory that could be imagined. All that is needed to complete the scattering calculation are the channel amplitudes A_N. These remain constant, except in the pseudocrossing region, where they can be obtained from Landau-

Zener theory.

As in single-channel theory, the phases for each channel can be obtained directly from the corresponding channel deflection function using Eq. (14):

$$\varphi_N(l) - \varphi_N(l_0) = \int_{l_0}^{l} [\Theta_N(l) - \Theta_N(l_0)]\, dl\,. \qquad (14')$$

This permits diffraction effects to be treated even when the deflection functions are inferred from experiment.

Figure 5 illustrates the diffraction effects associated with a threshold for excitation due to a level crossing in the $(Na\text{-}Ne)^+$ system at 2 keV. A shallow minimum in the deflection function occurs very close to the threshold. At smaller impact parameters, the deflection function exhibits nearly linear behavior, as the screened Coulomb repulsion overwhelms the weak attaction of the attractive molecular energy level (see channel III of Fig. 4). These characteristics are typical. (It should be noted that the particular electronic levels which give rise to this deflection function were at one time considered, but later abandoned in favor of potentials with smaller slopes which yield a deflection function with an even shallower minimum located closer to the threshold. The earlier potential set was chosen for presentation because it illustrates the diffraction effects more clearly.)

Figure 5(a) depicts the classical deflection function. The horizontal bars indicate the range of b about the minimum slope point within which the phase difference between any two points does not exceed $\frac{1}{4}\pi$. The dashed horizontal extensions indicate the additional range of b which *would* have contributed were there not a cutoff at the threshold $b = 1.4$ a.u. Figure 5(b) shows the reduced differential cross section, ρ vs τ, which follows from this deflection function. The solid curve gives the exact differential cross section which follows from channel III, using Eq. (32a). The dashed curve gives the approximate cross section using the theorem of Eqs. (11) and (12). The limiting values of b are those shown in Fig. 5(a).

The theorem does not give the diffraction oscillations produced by the sharp cutoff, but follows the average behavior. The diffraction oscillations will reduce toward this average value if the onset for excitation is spread over a finite range of b. Finally, the dot-dash curve gives the Ford and Wheeler result. The peak is much too high. It occurs at 10 keV deg and arises from the constructive interference of two branches of a parabola, *one of which* (see Fig. 5a) *is not present in this case*. In the classically forbidden region ($\tau < 9.3$), both the theorem of this work and the Ford-Wheeler result are in reasonable agreement with each other,

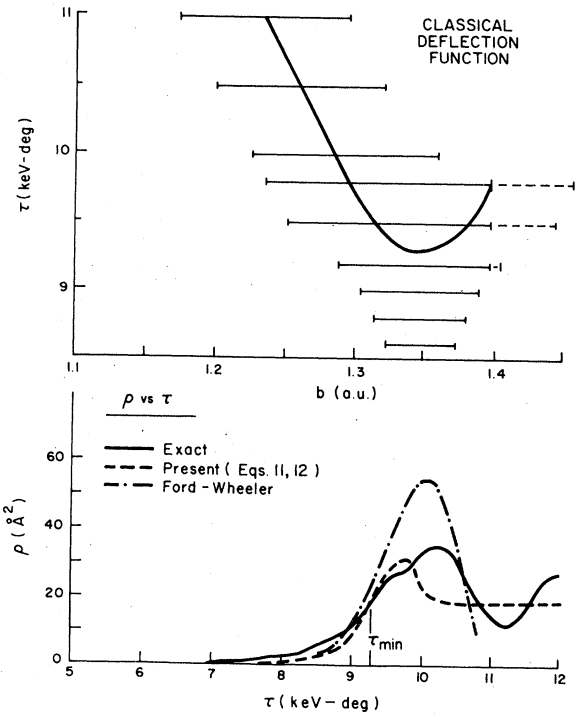

FIG. 5. Classical deflection and differential cross section for inelastic scattering. The upper drawing shows the classical deflection function for channel III for one of the inelastic processes in Na^+-Ne collisions at 2 keV. The solid horizontal bars show the range in impact parameter which contributes to the differential cross section at each angle. The lower drawing shows the differential cross section corresponding to this deflection function plotted in terms of the reduced variables ρ and τ. The solid curve is the exact value from Eq. (32b). The dashed curve gives the approximate cross section using the approximate theorem, Eqs. (11) and (12). The limiting values of b are those shown by the vertical bars above. The dot-dash curve gives the Ford and Wheeler approximation in terms of the Airy integral.

as was established in Sec. II C. They are both considerably below the exact value for a rather subtle reason. The small values which follow from the Ford and Wheeler approximation arise from a near cancellation in the complex integral from the contributions below and above the rainbow value. When one of these contributions is removed, the value of the integral therefore goes up rather than down.

B. Rigorous formulation

In the two-state approximation the wave function Ψ for the entire collision system is a sum of two

terms, one for each molecular state:

$$\Psi = \psi_0 + \psi_1 . \tag{34}$$

Following Stueckelberg's partial-wave analysis, that part of ψ_0 or ψ_1 which describes relative nuclear motion is expanded in terms of Legendre polynomials[16]:

$$\psi_n = \sum_{l=0}^{\infty} \frac{F_n(R,l)}{R} P_l(\mu)\phi_n(\vec{r};\vec{R}) . \tag{35}$$

Here, ϕ_n describes the adiabatic electronic state and the subscript n stands for 0 or 1; k_n is the relative momentum (in atomic units) at infinite internuclear separation when the electronic state is ϕ_n with energy $\mathcal{E}_n$. The variables $\vec{R}$ $(R, \mu = \cos\theta)$ are the relative internuclear coordinates in the center-of-mass frame, while all electronic coordinates are collectively designated by $\vec{r}$. The partial-wave index l denoting the relative angular momentum, is expressed as a parameter in F_n. This will prove convenient when the sum over partial waves is replaced by an integral.

1. Asymptotic conditions

For large values of R, ψ_0 and ψ_1 asymptotically approach[16,17] the following:

$$\psi_0 \to [e^{ik_0 Z} + f_0(\theta)(e^{ik_0 R}/R)]\phi_0 , \tag{36a}$$

$$\psi_1 \to f_1(\theta)(e^{ik_1 R}/R)\,\phi_1 . \tag{36b}$$

The incident beam is taken to be in the electronic ground state. Thus, for the incident-plane-wave part, the electronic state is exclusively ϕ_0. The scattered wave can be in either electronic state, requiring two independent scattering amplitudes to describe the collision. These do not interfere, since the two electronic states are distinguishable. With boundary conditions (36), ψ_0 has both incoming and outgoing radial waves, whereas ψ_1 has only outgoing. The asymptotic forms for $F_n(R,l)$ are

$$\lim_{R\to\infty} F_0 \to k_0^{-1}(l+\tfrac{1}{2})i[a_0(l)e^{ik_0 R} + (-1)^l e^{-ik_0 R}] , \tag{37a}$$

$$\lim_{R\to\infty} F_1 \to k_1^{-1}(l+\tfrac{1}{2})i a_1(l) e^{ik_1 R} , \tag{37b}$$

with $a_0(l)$ and $a_1(l)$ to be determined from the solutions to the Schrödinger equation. Substituting these asymptotic forms for F_n into (35), substituting these in turn into Eqs. (36) [along with the expansion for the plane wave in (36a)], and equating respective coefficients of $e^{ik_n R}$ and $e^{-ik_n R}$ yields for the scattering amplitudes:

$$f_0 = \frac{i}{k_0}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})[1+a_0(l)]P_l(\mu)$$

$$= \frac{i}{k_0}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})a_0(l)P_l(\mu) , \tag{38a}$$

$$f_1 = \frac{i}{k_1}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})a_1(l)P_l(\mu) . \tag{38b}$$

The term $\sum(l+\frac{1}{2})P_l(\mu)$ is equal to zero for all values of μ except at $\mu = 1$ and has therefore been dropped from the final expression in (38a). The scattering amplitudes are undefined at $\mu = 1$ (zero scattering angle), so that the sum which has been dropped rigorously does not contribute to f_0 wherever it is defined.

2. Radial functions

Let

$$H = -(2m)^{-1}\nabla_R^2 + \mathcal{U}(R) + \mathcal{H} , \tag{39}$$

where m is the reduced mass of the collision system, $\mathcal{H}$ the electronic Hamiltonian, and $\mathcal{U}(R)$ the core-core potential, including the nuclear Coulomb repulsion plus the adiabatic potential contribution due to those electrons which are not excited in the collision.

Adiabatic states are employed in (35) to describe the electronic motion of the active electrons. They satisfy the eigenvalue relationship

$$\mathcal{H}\phi_n(\vec{r};\vec{R}) = \mathcal{E}_n(R)\phi_n(\vec{r};\vec{R}) . \tag{40}$$

If necessary, diabatic states can be employed by introducing a unitary transformation $C(R)$ within the two-dimensional space spanned by ϕ_1 and ϕ_2. This has been fully discussed by Smith[23] and will not be repeated here. In this connection, it may be noted that Delos[14] found to his surprise that the adiabatic representation yielded more smoothly varying results than did the diabatic representation at 10-eV incident energy. However, since the behavior is energy dependent, it should not be assumed that the adiabatic representation will also be superior in the keV range. In any event, the adiabatic states are used exclusively in the present work because they are unambiguously defined and simpler to work with.

The scattering event is described by the Schrödinger equation for the entire collision system,

$$(H - E)\Psi = 0 . \tag{41}$$

Substituting the partial-wave expansion (35) for Ψ into (41), multiplying by the electronic state ϕ_ν, and integrating *over electronic coordinates only* yields

$$\sum_l \Big\{[-(2m)^{-1}\nabla_R^2 + (\mathcal{U} + \mathcal{E}_\nu - E)]F_\nu(R,l)P_l(\mu) - \sum_n m^{-1}\Big[\Big(\phi_\nu\Big|\frac{\partial}{\partial R}\Big|\phi_n\Big)_{\vec{r}}\frac{d}{dR} + \frac{1}{R^2}(\phi_\nu|\vec{L}|\phi_n)_{\vec{r}}\cdot\vec{L}$$
$$+ \tfrac{1}{2}(\phi_\nu|\nabla_R^2|\phi_n)_{\vec{r}}\Big]F_n(R,l)P_l(\mu)\Big\} = 0 . \tag{42}$$

The matrix element $(\|)_{\vec{r}}$ denotes an inner product over electronic coordinates only. In (42), the gradient-gradient coupling term has been rewritten using the theorem

$$\vec{\nabla}U\cdot\vec{\nabla}V=\frac{\partial U}{\partial R}\frac{\partial V}{\partial R}+\frac{1}{R^2}(\vec{L}U)\cdot(\vec{L}V), \tag{43}$$

where $\vec{L}$ is the angular momentum operator which acts on the relative internuclear coordinates $\vec{R}$. Equation (42) becomes, after (i) neglecting the term $(\phi_\nu|\nabla_R^2|\phi_n)_{\vec{r}}$, (ii) restricting consideration to the radial coupling term only, and (iii) multiplying (42) by $P_\lambda(\mu)$ and integrating over μ,

$$\left(-\frac{1}{2m}\frac{d^2}{dR^2}+\frac{\lambda(\lambda+1)}{2mR^2}+(\mathcal{U}+\mathcal{E}_\nu-E)\right)F_\nu(R,\lambda)$$
$$-\sum_n\frac{1}{mR^2}\left(\phi_\nu\left|\frac{\partial}{\partial R}\right|\phi_n\right)_{\vec{r}}\frac{dF_n(R,\lambda)}{dR}=0. \tag{44}$$

The rotational-coupling term is not considered here because it is inconsisent with an expansion solely in terms of Legendre polynomials. A full expansion in terms of all spherical harmonics would be required if the rotational-coupling term were retained. In physical terms, a $\sigma\to\pi$ transition produces an azimuthal thrust, perpendicular to the plane of motion. This aspect will be discussed further in Sec. IV.

The adiabatic potentials $V_\nu(R)$ used in Eqs. (30) are the sum of the core-core potential plus the energy $\mathcal{E}_\nu$ of the active electrons in state ϕ_ν:

$$V_\nu(R)=\mathcal{U}(R)+\mathcal{E}_\nu(R). \tag{45}$$

In this section the radial component of the relative momentum at internuclear separation R is denoted by K_ν and is a function of l as well as R.

$$K_\nu(R,l)=\{2m[E-V_\nu(R)]-l(l+1)/R^2\}^{1/2}, \tag{46}$$

with

$$k_\nu=K_\nu(R=\infty). \tag{47}$$

In the two-state approximation, Eqs. (44) can be rewritten

$$\left(\frac{d^2}{dR^2}+K_0^2\right)F_0(R,l)-2M_{01}\frac{dF_1}{dR}=0, \tag{48a}$$

$$\left(\frac{d^2}{dR^2}+K_1^2\right)F_1(R,l)-2M_{10}\frac{dF_0}{dR}=0, \tag{48b}$$

where $M_{\nu n}$ denotes the coupling matrix element

$$M_{\nu n}(R)=\left(\phi_\nu\left|\frac{\partial}{\partial R}\right|\phi_n\right)_{\vec{r}}. \tag{49}$$

The diagonal matrix elements M_{00} and M_{11} are both equal to zero. Because $(\phi_\nu|\phi_n)_{\vec{r}}=\delta_{\nu n}$, independent of R, it is seen that for electronic functions ϕ_n which are real,

$$M_{\nu n}+M_{n\nu}=\frac{\partial}{\partial R}(\phi_\nu|\phi_n)_{\vec{r}}=0. \tag{50}$$

Equation (50) is also valid if the ϕ_n are complex, provided that the complex parts are independent of R [e.g., $\exp(i\Lambda\phi)$]. With this generalization, Eq. (50) is valid for all useful states. From (50) it follows that

$$M_{00}=M_{11}=0, \tag{51a}$$

$$M_{01}=-M_{10}. \tag{51b}$$

Equations (48) differ from those of Marchi[4] and Olson and Smith[3] in that derivative coupling terms (i.e., involving dF_n/dR) are obtained here, whereas Refs. 3 and 4 consider only nonderivative coupling terms. It will be seen that derivative coupling terms lead to Landau-Zener (LZ) equations with a different velocity dependence than is ordinarily assumed. The LZ transitions obtained here are independent of the relative velocity.

3. *Semiclassical approximation*

The semiclassical approximation, otherwise called the JWKB approximation, is obtained by expressing the radial functions F_n for each electronic state and partial wave as a sum of an inward and outward propagating wave with hopefully slowly varying amplitudes:

$$F_n=K_n^{-1/2}\left[c_n\exp\left(-i\int_{R_n}^R K_n\,dR\right)\right.$$
$$\left.+d_n\exp\left(+i\int_{R_n}^R K_n\,dR\right)\right]. \tag{52}$$

It is understood that F_n, K_n, c_n, and d_n are all functions of R and l. By carrying out the differentiations, it can be verified that

$$\frac{d}{dR}c_n\exp\left(-i\int_{R_n}^R K_n\,dR\right)$$
$$=(c_n'-iK_nc_n)\exp\left(-i\int_{R_n}^R K_n\,dR\right) \tag{53a}$$

$$\left(\frac{d^2}{dR^2}+K_n^2\right)c_n\exp\left(-i\int_{R_n}^R K_n\,dR\right)$$
$$=(c_n''-2iK_nc_n'-iK_n'c_n)\exp\left(-i\int_{R_n}^R K_n\,dR\right), \tag{53b}$$

where the prime denotes differentiation with respect to R. Analogous expressions can be derived for the outgoing wave. The important simplifying assumption in the semiclassical approximation is the neglect of all terms of order K'/K. The derivatives of $K_n^{-1/2}$ are of order K'/K and are neglected. In the semiclassical approximation Eq. (48) becomes

$$K_0^{-1/2}(c_0'' - 2iK_0c_0')\exp\left(-i\int_{R_0}^{R}K_0\,dR\right) - 2M_{01}K_1^{-1/2}(c_1' - iK_1c_1)\exp\left(-i\int_{R_1}^{R}K_1\,dR\right) = 0\,, \tag{54a}$$

$$K_1^{-1/2}(c_1'' - 2iK_1c_1')\exp\left(-i\int_{R_1}^{R}K_1\,dR\right) - 2M_{10}K_0^{-1/2}(c_0' - iK_0c_0)\exp\left(-i\int_{R_0}^{R}K_0\,dR\right) = 0\,, \tag{54b}$$

$$K_0^{-1/2}(d_0'' + 2iK_0d_0')\exp\left(+i\int_{R_0}^{R}K_0\,dR\right) - 2M_{01}K_1^{-1/2}(d_1' + iK_1d_1)\exp\left(+i\int_{R_1}^{R}K_1\,dR\right) = 0\,, \tag{55a}$$

$$K_1^{-1/2}(d_1'' + 2iK_1d_1')\exp\left(+i\int_{R_1}^{R}K_1\,dR\right) - 2M_{10}K_0^{-1/2}(d_0' + iK_0d_0)\exp\left(+i\int_{R_0}^{R}K_0\,dR\right) = 0\,. \tag{55b}$$

In obtaining Eqs. (54) and (55), the terms with negative exponentials, which describe the incoming waves, are separately set equal to zero as were the outgoing wave terms, with the positive complex exponentials. Actually, substitution of (52) into (48) yields only two equations. The sum of the left-hand sides of (54a) and (55a) combined is equal to zero, as is the sum of the left-hand sides of (54b) and (55b). Setting incoming-wave and outgoing-wave terms separately equal to zero is consistent with the semiclassical approximation; there is no appreciable interaction between incoming and outgoing waves except at the classical turning points R_0 and R_1. Mathematically, a transition from one term to another occurs only when the integrands in the exponents are equal or nearly equal, as is well known from Landau-Zener-Stueckelberg theory: $K_\nu - K_n \ll 1$ in atomic units. This cannot happen when the signs of the exponents are opposite. In fact, $K_\nu + K_n$ is of the order of 1000. Thus, incoming and outgoing waves decouple. It must, however, be stressed that although the decoupling of incoming and outgoing waves is based on the same mathematical effect that is used in LZ theory, it is really part of the semiclassical approximation and remains valid even when the further approximations made in the Landau-Zener theory fail. An important exception occurs when the level crossing occurs very near the classical turning point. In that case, Eqs. (48) should be solved directly in the critical region.

In the neighborhood of a classical turning point R_n the behavior of F_n is given by[9]

$$F_n = A_nK_n^{-1/2}\sin\left(\int_{R_n}^{R}K_n\,dR + \frac{\pi}{4}\right)$$

$$= 0.5A_nK_n^{-1/2}\left[\exp\left(i\int_{R_n}^{R}K_n\,dR\right) + i\exp\left(-i\int_{R_n}^{R}K_n\,dR\right)\right]\exp(-\tfrac{1}{4}i\pi) \quad \text{for } R > R_n \tag{56a}$$

$$F_n = 0.5A_nK_n^{-1/2}\exp\left(-\int_{R}^{R_n}|K_n|dR\right) \quad \text{for } R < R_n\,, \tag{56b}$$

where A_n is a constant.

4. *Reduction to the Landau-Zener theory*

The semiclassical approximation was achieved by neglecting terms of the order K_n'/K_n. The reduction to the LZ theory is achieved by further neglecting terms of order c_n'/K_n, c_n''/K_n, d_n'/K_n, and d_n''/K_n. This latter approximation is not always valid, since the coefficients c_n and d_n change very rapidly in a very small radial interval (the level-crossing region). Indeed it is well known that LZ theory often yields poor results in atomic collisions at keV energies and should be used with caution. When these terms are neglected, Eqs. (54) and (55) reduce to

$$K_0^{1/2}c_0' = -MK_1^{1/2}c_1\exp(i\alpha)\,, \tag{57a}$$

$$K_1^{1/2}c_1' = MK_0^{1/2}c_0\exp(-i\alpha)\,, \tag{57b}$$

$$K_0^{1/2}d_0' = -MK_1^{1/2}d_1\exp(-i\alpha)\,, \tag{58a}$$

$$K_1^{1/2}d_1' = MK_0^{1/2}d_0\exp(i\alpha)\,, \tag{58b}$$

where

$$\alpha = \int_{R_0}^{R}K_0\,dR - \int_{R_1}^{R}K_1\,dR\,, \tag{59}$$

and

$$M = M_{01} = -M_{10}\,. \tag{60}$$

The coefficients c_n and d_n change appreciably only in the level-crossing region $R_x - \frac{1}{2}\delta < R < R_x + \frac{1}{2}\delta$; outside this region the coefficients remain essentially constant. Inside the crossing region, $K_1 \simeq K_0 = mv_R$, where v_R is the approximate radial velocity. Therefore the LZ equations can, without

loss of accuracy, be replaced by

$$v_R c_0' = \dot{c}_0 = v_R M c_1 \exp(i\alpha)\,, \tag{61a}$$

$$v_R c_1' = \dot{c}_1 = -v_R M c_0 \exp(-i\alpha)\,, \tag{61b}$$

$$v_R d_0' = \dot{d}_0 = v_R M d_1 \exp(-i\alpha)\,, \tag{62a}$$

$$v_R d_1' = \dot{d}_1 = -v_R M d_0 \exp(i\alpha)\,. \tag{62b}$$

These clearly yield velocity-independent transition probabilities. To complete the reduction to the textbook version of the LZ equations,[24] it is necessary to make a Taylor expansion of K_n as given by (4a), considering $2mE-(l+\frac{1}{2})^2/R^2$ to be the dominant term, which is valid away from the classical turning point. Making the approximation

$$\frac{[2mE-(l+\frac{1}{2})^2/R^2]^{1/2}}{m} \simeq v_R = \frac{dR}{dt}\,, \tag{63}$$

it follows that

$$\alpha \simeq \int_{R_0}^{R} (V_1 - V_0)\,dt - \int_{R_1}^{R_0} K_1\,dR\,. \tag{64}$$

The second term on the right-hand side of (64) is a constant term, which is generally neglected in the straight-line approximation. Approximation (63) is also consistent with the straight-line approximation.

Smith[23] reports both a velocity-dependent derivative coupling term for the Landau-Zener equations, as obtained above, plus a velocity-independent, anti-Hermitian coupling term which he claims to be important only at very low velocities. This latter coupling term can be seen as the c_n' term on the right-hand sides of Eqs. (54) and (55), consistent with Smith. However, these terms must be neglected along with the c_m'' terms on the left-hand sides for consistent reduction to the Landau-Zener equations. Smith assigns a wider meaning to "Landau-Zener model" than the strict textbook definition used in this work [closer to Eqs. (54) and (55)], so the difference is purely semantic.

5. *Channel amplitudes*

Let the transition region be the interval $R_x-\frac{1}{2}\delta<R<R_x+\frac{1}{2}\delta$ and let the coupling between the amplitudes on the outgoing trajectory be denoted by the matrix equation

$$\begin{pmatrix} d_0(R_x+\frac{1}{2}\delta) \\ d_1(R_x+\frac{1}{2}\delta) \end{pmatrix} = \begin{pmatrix} U_{00} & U_{01} \\ U_{10} & U_{11} \end{pmatrix} \begin{pmatrix} d_0(R_x-\frac{1}{2}\delta) \\ d_1(R_x-\frac{1}{2}\delta) \end{pmatrix}. \tag{65}$$

The transition matrix U can be obtained by solving the full semiclassical equations (55) or the LZ approximations to these equations, Eqs. (62). In either case, the coupling matrix for the passage through the coupling region on the incoming portion of the trajectory is given by

$$\begin{pmatrix} c_0(R_x+\frac{1}{2}\delta) \\ c_1(R_x+\frac{1}{2}\delta) \end{pmatrix} = \begin{pmatrix} U_{00}^* & U_{01}^* \\ U_{10}^* & U_{11}^* \end{pmatrix} \begin{pmatrix} c_0(R_x-\frac{1}{2}\delta) \\ c_1(R_x-\frac{1}{2}\delta) \end{pmatrix}. \tag{66}$$

This can be seen by taking the complex conjugates of Eqs. (54a) and (54b). The resulting equations for c_0^* and c_1^* are identical to (55a) and (55b) and are therefore solved by the same coupling matrix U. Taking the complex conjugate (not the adjoint) of the linear connecting equations yields Eqs. (66). This result also holds for the LZ approximation to the full semiclassical equations. It may be parenthetically noted that the reason for the complex conjugate in (66), rather than the full adjoint, stems from the fact that the coupling matrices are defined in an unorthodox manner. The coupling matrices for both incoming and outgoing cases give the values of the coefficients at $R_x+\frac{1}{2}\delta$ in terms of their values at $R_x-\frac{1}{2}\delta$, which is not in sequential order along the trajectory.

In the region $R<R_x-\frac{1}{2}\delta$, the coefficients c_n and d_n for all practical purposes remain constant. Moreover, c_0 and d_0 are connected by Eq. (56a), which gives the behavior of F_0 at the classical turning point R_0. Similarly, c_1 and d_1 are connected by (56a) at the turning point R_1.

$$\begin{aligned} F_0(R_x-\tfrac{1}{2}\delta) = {} & 0.5A_0 K_0^{-1/2}(R_x-\tfrac{1}{2}\delta) \\ & \times[i\exp(-i\beta_0)+\exp(+i\beta_0)] \\ & \times\exp(-\tfrac{1}{4}i\pi)\,, \end{aligned} \tag{67a}$$

$$\begin{aligned} F_1(R_x-\tfrac{1}{2}\delta) = {} & 0.5A_1 K_1^{-1/2}(R_x-\tfrac{1}{2}\delta) \\ & \times[i\exp(-i\beta_1)+\exp(+i\beta_1)] \\ & \times\exp(-i\pi/4)\,, \end{aligned} \tag{67b}$$

where

$$\beta_0 = \int_{R_0}^{R_x-\delta/2} K_0\,dR\,, \tag{68a}$$

$$\beta_1 = \int_{R_1}^{R_x-\delta/2} K_1\,dR\,. \tag{68b}$$

From (67a) and (68a) it is seen that

$$-ic_0(R_x-\tfrac{1}{2}\delta) = d_0(R_x-\tfrac{1}{2}\delta) = 0.5A_0\exp(-\tfrac{1}{4}i\pi)\,, \tag{69a}$$

$$-ic_1(R_x-\tfrac{1}{2}\delta) = d_1(R_x-\tfrac{1}{2}\delta) = 0.5A_1\exp(-\tfrac{1}{4}i\pi)\,, \tag{69b}$$

where the constants A_0 and A_1 have yet to be determined by the asymptotic conditions (37a) and (37b) as $R\to\infty$. Inserting (69a) and (69b) into (65) and (66) yields

$$c_0(R_x+\tfrac{1}{2}\delta) = (U_{00}^*A_0 + U_{01}^*A_1)\exp(+\tfrac{1}{4}i\pi) \tag{70a}$$

$$c_1(R_x+\tfrac{1}{2}\delta) = (U_{10}^*A_0 + U_{11}^*A_1)\exp(+\tfrac{1}{4}i\pi) \tag{70b}$$

$$d_0(R_x+\tfrac{1}{2}\delta)=(U_{00}A_0+U_{01}A_1)\exp(-\tfrac{1}{4}i\pi) \tag{70c}$$

$$d_1(R_x+\tfrac{1}{2}\delta)=(U_{10}A_0+U_{11}A_1)\exp(-\tfrac{1}{4}i\pi) \tag{70d}$$

The coefficients c_n and d_n remain constant from $R_x+\frac{1}{2}\delta$ to $R=\infty$. Comparing, at some large value of R, the exact semiclassical expressions (52) for F_0 and F_1, using the coefficient given by Eqs. (70), with the asymptotic forms (37), it follows that

$$k_0^{-1}(l+\tfrac{1}{2})i(-1)^l\exp(-ik_0R)$$
$$=\tfrac{1}{2}\exp(\tfrac{1}{4}i\pi)k_0^{-1/2}(U_{00}^*A_0+U_{01}^*A_1)$$
$$\times\exp\left(-i\int_{R_0}^{R}K_0\,dR\right), \tag{71a}$$

$$k_0^{-1}(l+\tfrac{1}{2})ia_0\exp(ik_0R)$$
$$=\tfrac{1}{2}\exp(-\tfrac{1}{4}i\pi)k_0^{-1/2}(U_{00}A_0+U_{01}A_1)$$
$$\times\exp\left(i\int_{R_0}^{R}K_0\,dR\right), \tag{71b}$$

$$0=\tfrac{1}{2}\exp(\tfrac{1}{4}i\pi)k_1^{-1/2}(U_{10}^*A_0+U_{11}^*A_1)$$
$$\times\exp\left(-i\int_{R_1}^{R}K_1\,dR\right), \tag{71c}$$

$$k_1^{-1}(l+\tfrac{1}{2})ia_1\exp(ik_1R)$$
$$=\tfrac{1}{2}\exp(-\tfrac{1}{4}i\pi)k_1^{-1/2}(U_{10}A_0+U_{11}A_1)$$
$$\times\exp\left(i\int_{R_1}^{R}K_1\,dR\right). \tag{71d}$$

The four equations (71) can be solved for a_0, a_1, A_0, and A_1 in terms of the matrix elements U_{ij}. It follows from (71c) that

$$A_1=-A_0U_{10}^*/U_{11}^*. \tag{72}$$

Substituting this result into (71a) yields

$$A_0=(U_{11}^*/|U^*|)(2l+1)k_0^{-1/2}i^l\exp(i\gamma_0), \tag{73}$$

where

$$\gamma_n=\int_{R_n}^{\infty}(K_n-k_n)\,dR-k_nR_n+\tfrac{1}{2}(l+\tfrac{1}{2})\pi \tag{74}$$

and $|U^*|$ is the determinant of the matrix U_{ij}^*. In (74), k_nR has been rewritten as $k_nR_n+\int_{R_n}^{R}k_n\,dR$. With this substitution, the upper limit R in the integral can be permitted to go to infinity, since $K_n(R)=k_n$ for large values of R and the integrand becomes zero. Furthermore, γ_n includes a term $\frac{1}{2}(l+\frac{1}{2})\pi$, so that $\exp(i\gamma_n)$ absorbs part of the factor $i(-1)^l$ on the left-hand side of Eq. (71a). As written in this way, $2\gamma_0=\zeta_I$ of Eq. (30a). With A_0 and A_1 given by (73) and (72), Eqs. (71b) and (71d) can be solved for a_0 and a_1, respectively:

$$a_0=-\exp(2i\gamma_0)(U_{11}^*U_{00}-U_{01}U_{10}^*)/|U^*|, \tag{75a}$$

$$a_1=-(k_1/k_0)^{1/2}\exp(i\gamma_0+i\gamma_1)$$
$$\times(U_{11}^*U_{10}-U_{11}U_{10}^*)/|U^*|. \tag{75b}$$

It can be established that Eqs. (54) and (55) each preserve probability, as is to be expected. Consequently, the transition matrix U is unitary; i.e., $(U^*)^{-1}=U$ which yields the following relations between the components:

$$\frac{1}{|U^*|}\begin{pmatrix}U_{11}^* & -U_{10}^*\\ -U_{01}^* & U_{00}^*\end{pmatrix}=\begin{pmatrix}U_{00} & U_{01}\\ U_{10} & U_{11}\end{pmatrix}. \tag{76}$$

With the help of (76), the complex-conjugated matrix elements in (75) can be eliminated and Eqs. (75) more compactly written in the form

$$a_0(l)=-\exp(2i\gamma_0)(U_{00}^2+U_{01}^2), \tag{77a}$$

$$a_1(l)=-(k_1/k_0)^{1/2}$$
$$\times\exp(i\gamma_0+i\gamma_1)(U_{00}U_{10}+U_{01}U_{11}). \tag{77b}$$

The matrix elements U_{01} and U_{10} which couple the coefficients d_0 and d_1 across the transition region are, in general, complex. This fact arises from the mismatch between the phases of the radial wave functions associated with the two states in the crossing region. Each matrix element can be approximately factored into a real amplitude and a unitary complex factor by defining a transition matrix which couples $d_n\exp(i\int_{R_n}^{R_x}K_n dR)$ across the transition region. Defining a new set of amplitudes

$$D_n(R)=d_n(R)\exp\left(i\int_{R_n}^{R_x}K_n\,dR\right), \tag{78}$$

which differ from the original amplitudes by constant unitary factors and defining the transition matrix T which couples these amplitudes across the transition region:

$$\begin{pmatrix}D_0(R_x+\frac{1}{2}\delta)\\ D_1(R_x+\frac{1}{2}\delta)\end{pmatrix}=\begin{pmatrix}T_{00} & T_{01}\\ T_{10} & T_{11}\end{pmatrix}\begin{pmatrix}D_0(R_x-\frac{1}{2}\delta)\\ D_1(R_x-\frac{1}{2}\delta)\end{pmatrix}, \tag{79}$$

it is found that for all practical purposes, T is real in the Landau-Zener approximation. This can be seen by substituting (78) into the Landau-Zener approximations, Eqs. (62), which then become:

$$D_0'=MD_1\exp(-i\epsilon), \tag{80a}$$

$$D_1'=-MD_0\exp(+i\epsilon), \tag{80b}$$

where

$$\epsilon=\int_{R}^{R_x}(K_1-K_0)\,dR. \tag{81}$$

In the vicinity of the crossing, $K_1 - K_0$ is small and moreover, the crossing region itself is small. Consequently, over the entire range of interest ϵ is small and $\exp(i\epsilon)$ can be approximated by unity. The resulting equations are then real and yield real solutions

$$D_0 = \cos\{M[R - (R_x - \tfrac{1}{2}\delta] + (\text{phase constant})\}, \quad (82a)$$

$$D_1 = -\sin\{M[R - (R_x - \tfrac{1}{2}\delta)] + (\text{phase constant})\}. \quad (82b)$$

By comparing (65) with (78), it is seen that

$$U_{01} = T_{01} \exp i\left(\int_{R_1}^{R_x} K_1\, dR - \int_{R_0}^{R_x} K_0\, dR\right), \quad (83a)$$

$$U_{10} = T_{10} \exp i\left(\int_{R_0}^{R_x} K_0\, dR - \int_{R_1}^{R_x} K_1\, dR\right), \quad (83b)$$

$$U_{00} = T_{00}, \quad (83c)$$

$$U_{11} = T_{11}. \quad (83d)$$

Substituting these results into Eqs. (77) yields

$$-a_0(l) = T_{00}^2 \exp(i\zeta_{\mathrm{I}}) + T_{01}^2 \exp(i\zeta_{\mathrm{II}}), \quad (84a)$$

$$-(k_0/k_1)^{1/2} a_1(l) = T_{00}T_{10} \exp(i\zeta_{\mathrm{III}}) + T_{01}T_{11} \exp(i\zeta_{\mathrm{IV}}), \quad (84b)$$

where the phase developments ζ_N have been defined in Eqs. (30).

Defining

$$T_{00}^2 = A_{\mathrm{I}}, \quad (85a)$$

$$T_{01}^2 = A_{\mathrm{II}}, \quad (85b)$$

$$(k_1/k_0)^{1/2} T_{00}T_{10} = A_{\mathrm{III}}, \quad (85c)$$

$$(k_1/k_0)^{1/2} T_{01}T_{11} = A_{\mathrm{IV}}, \quad (85d)$$

substituting (84) and (85) into expressions (38a) and (38b) for the scattering amplitudes, using the asymptotic form (7) for the Legendre polynomials, and replacing the sum over l by an integral yields Eqs. (32a) and (32b), which are precisely the equations heuristically obtained in A. In Eqs. (32), only φ_-, given by Eq. (29), has been retained, so that the results are valid for the repulsive scattering case.

IV. ANGULAR MOMENTUM CONSIDERATIONS

It was established in Sec. II that under conditions appropriate for semiclassical scattering, the contribution to the differential scattering cross section at angle θ arises from a small range of partial waves (or impact parameters). It was further shown in Sec. III that the contribution due to the Nth channel comes from the range centered about the value of l determined by $\theta = d\zeta_N/dl$. This value was claimed to be the one predicted by classical scattering theory for the set of incoming and outgoing potentials which define the Nth channel. That assertion is the topic of this section, and it will be shown to be almost, but not exactly, true. In order to be rigorously valid, it is necessary that the internuclear forces are exactly radial; in that case, l is a constant of the motion and there is no coupling between channels. This cannot be correct; it would, for example, exclude excitation of one of the colliding atoms from an initial s to a final p state. Any change of angular momentum of the internal degrees of freedom (i.e., the electrons) must, of course, be balanced by an equal and opposite change in the angular momentum l of translation motion of the collision trajectory. The source of the problem is not hard to find. The electronic angular momentum is not a constant of the motion in the two-center problem, so that electronic angular momentum *can* change during the collision. However, the recoil of the internuclear axis is neglected in adiabatic molecular theory. This neglect is equivalent to taking the center of mass for the entire system to be the same as the center of mass of the nuclei. At low collision energies, this approximation will be seen to cause no difficulties; it becomes important only at higher collision energies.

When the trajectory cannot be described in terms of a potential, it is necessary to revert to Newton's second law: $\vec{F} = m\vec{a}$. A force can always be defined so long as (i) a classical trajectory is applicable and (ii) the electronic state changes adiabatically, with excitation occurring only at level crossings (or pseudocrossings), where discontinuities or uncertainties in energy are inconsequential. Both the radial component of the scattering force and the torque must be taken into consideration, since changes in angular momentum imply the existence of a torque. It must be noted that "angular momentum excitation" as here used, is different from "rotational excitation." Rotational excitation refers to a change in the component of angular momentum along the internuclear axis. Such a change (e.g., $\sigma \to \pi$) produces a thrust in the azimuthal direction and will not be measurable in scattering experiments, which average over the azimuthal direction. To affect the scattering angle requires a change in the component of angular momentum perpendicular to the plane of scattering. This component is not a constant of motion in adiabatic theory.

In what follows, the classical orbits will be calculated in the center-of-mass frame. With m denoting the reduced mass of the system, the angular momentum of relative motion is

$$l = mR^2\dot{\theta} \,. \tag{86}$$

Let $V(R)$ be the potential energy due to the nuclear Coulomb force plus the screening force produced by those electrons not excited in the collision (i.e., behave completely adiabatically), and let $\vec{F}(R,v,t) = \hat{R}F_R + \hat{\theta}F_\theta$ be the force exerted by those electrons which are excited in the collision. From the Newtonian equations of motion,

$$F_R - \frac{\partial V}{\partial R} = m\ddot{R} - mR\dot{\theta}^2 \,, \tag{87a}$$

$$T = RF_\theta = \frac{dl}{dt} = mR^2\ddot{\theta} + 2mR\dot{R}\dot{\theta} \,. \tag{87b}$$

Since only the trajectory is desired, that is, R as a function of θ, Eqs. (87) are transformed so that θ is the independent variable rather than t. With this transformation,

$$F_R - \frac{\partial V}{\partial R} = \frac{F_\theta}{R}\frac{dR}{d\theta} + \frac{l^2}{mR^4}\left[-\frac{2}{R}\left(\frac{dR}{d\theta}\right)^2 + \frac{d^2R}{d\theta^2} - R\right] \,, \tag{88a}$$

$$F_\theta = (2mR^3)^{-1}\frac{d}{d\theta}l^2 \,. \tag{88b}$$

The standard procedure, at this point, is to make the transformation of the dependent variable[25]

$$u = 1/R \,. \tag{89}$$

With this transformation, the orbital equations become:

$$\frac{d^2u}{d\theta^2} + \frac{1}{l}\frac{dl}{d\theta}\frac{du}{d\theta} + u = -\frac{m}{l^2}\left(\frac{dV}{du} + \frac{F_R}{u^2}\right) \,, \tag{90a}$$

$$\frac{u^3}{2m}\frac{dl^2}{d\theta} = F_\theta \,. \tag{90b}$$

After multiplying (90a) by $l^2du/d\theta$, it can be put in the form

$$\frac{d}{d\theta}\left\{l^2\left[\left(\frac{du}{d\theta}\right)^2 + u^2\right] + 2m\left[V(u) + U_t(u) + \Omega_t\right]\right\} = 0 \,, \tag{91}$$

where t stands for the incoming or outgoing portions of the trajectory and U_t is the internal (i.e., electronic) energy. This is different, in general, for incoming and outgoing portions of the trajectory. Finally, Ω, which is also path dependent, is defined so that

$$\frac{d\Omega}{d\theta} = -\frac{u^2}{2m}\frac{dl^2}{d\theta} \,. \tag{92}$$

Clearly, Ω cannot be obtained from (92) unless u is known as a function of θ. Thus Ω is path dependent. However, if the change of l occurs in a narrow region about some value u_x, Ω is an approximate perfect differential:

$$\Omega \approx -(u_x^2/2m)(l^2 - l_0^2) \,. \tag{93}$$

A first integral is obtained by integrating Eq. (91) over θ. The constant of integration, determined from the initial conditions, is $l_0^2/b^2 = k_0^2 = 2mE_0$, provided that the datum, or zero of energy, is chosen such that $V + U_0 = 0$ at $u = 0 (R = \infty)$. Solving this result for $du/d\theta$ yields a separable equation which is solved by quadratures:

$$\begin{aligned}\theta &= \pi - \int_0^{u_m}\{[A(E_0 - W_{in} - \Omega_{in}) - u^2]^{-1/2} \\ &\qquad + [A(E_0 - W_{out} - \Omega_{out}) - u^2]^{-1/2}\}\,du \,, \\ &= \pi - \int_0^{u_m}\{[b^{-2} - u^2 - A(W_{in} + \Omega_{in})]^{-1/2} \\ &\qquad + [b^2 - u^2 - A(W_{out} + \Omega_{out})]^{-1/2}\}\,du \,,\end{aligned} \tag{94}$$

where the W_t are the overall molecular potentials for the two states:

$$W_t(u) = V(u) + U_t(u) \tag{95}$$

and

$$A = 2m/l^2 \simeq 2m/l_0^2 \,. \tag{96}$$

For the small changes in angular momentum of relative motion caused by electronic excitation (one or two units in several hundred or even thousands), the difference between l^2 and l_0^2 can be neglected insofar as the constant A is concerned. The major effect of these changes is incorporated in Ω.

The torque produces a negligible deflection. In the region of minimum internuclear separation where most of the deflection takes place, F_θ is longitudinal and causes no deflection. Nevertheless, it can have an important effect on the deflection, since it accounts for some fraction of the change in internal energy required by the potentials W_t via the Ω terms in Eq. (94). In essence, that work which is done by the torque is not done by the radial force, implying a smaller radial force and, therefore, a smaller deflection. By conservation of total angular momentum of the entire collision system, the change Δl in the angular momentum of translational motion must be equal to $-\Delta l_e$, the negative of the change in angular momentum of electronic motion. Taking Δl_e to be small compared with l, it follows that

$$\Delta\Omega \simeq u_x^2 l\Delta l_e/m = bu_x^2\Delta l_e(2E_0/m)^{1/2} \,, \tag{97}$$

producing a shift in the ρ vs. τ reduced differential scattering cross section proportional to $E_0^{1/2}$. Remember that Δl_e is the change of the component of electronic angular momentum perpendicular to the plane of the trajectory.

In the special case in which the angular momentum is constant, Ω, which is zero initially, remains zero throughout the collision. Thus, from (94),

$$\Theta = \pi - \int_0^{u_m} \left[\left(\frac{(E_0 - W_{in})2m}{l^2} - u^2 \right)^{-1/2} + \left(\frac{(E_0 - W_{out})2m}{l^2} - u^2 \right)^{-1/2} \right] du . \quad (98)$$

Apart from the small difference between l^2 and $(l+\frac{1}{2})^2$, these results are the same as those which follow from Eq. (31):

$$\Theta_N = \frac{d\zeta_N}{dl},$$

with the ζ_N given by Eqs. (30). The essence of the proof is given below:

$$\frac{\partial}{\partial l} \int_{R_a}^{R_b} K \, dR = \frac{\partial}{\partial l} \int_{u_a}^{u_b} [2m(E-W) - (l+\tfrac{1}{2})^2 u^2]^{1/2} \frac{-du}{u^2} = \int_{u_a}^{u_b} \frac{(l+\frac{1}{2})\, du}{[2m(E-W) - (l+\frac{1}{2})^2 u^2]^{1/2}}.$$

Finally,

$$\frac{\partial}{\partial l} \int_{R_a}^{R_b} K \, dR = - \int_{u_b}^{u_a} \left(\frac{2m(E-W)}{(l+\frac{1}{2})^2} - u^2 \right)^{-1/2} du . \quad (99)$$

The limits in (99) have been interchanged with an accompanying change in sign. If the appropriate potentials required by Eqs. (30) (W_0 for K_0 and W_1 for K_1) are used in the two regions $0 < u < u_x$ and $u_x < u < u_{max}$, the results are those summarized in (98), provided that $l + \frac{1}{2}$ is approximated by l.

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[1]D. Coffey, Jr., D. C. Lorents, and F. T. Smith, Phys. Rev. 187, 201 (1969).
[2]F. T. Smith, H. H. Fleischmann, and R. A. Young, Phys. Rev. A 2, 379 (1970).
[3]R. E. Olson and F. T. Smith, Phys. Rev. A 3, 1607 (1971).
[4]R. P. Marchi, Phys. Rev. 183, 185 (1969).
[5]K. W. Ford and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 259 (1959).
[6]F. T. Smith, R. P. Marchi, W. Aberth, D. C. Lorents, and O. Heinz, Phys. Rev. 161, 31 (1967).
[7]J. Baudon, M. Barat, and M. Abignoli, J. Phys. B 3, 207 (1970).
[8]K. W. Ford and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 287 (1959).
[9]N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 2nd ed. (Clarendon, Oxford, 1949), Chaps. II and VII, Secs. 3–5.
[10]L. P. Kotova, Zh. Eksp. Teor. Fiz. 55, 1375 (1968) [Sov. Phys. JETP 28, 719 (1969)].
[11]M. Ya. Ovchinnikova, Zh. Eksp. Teor. Fiz. 59, 1795 (1970) [Sov. Phys. JETP 32, 974 (1971)].
[12]L. P. Kotova and M. Ya. Ovchinnikova, Zh. Eksp. Teor. Fiz. 60, 2026 (1971)[Sov. Phys. JETP 33, 1092 (1971)].
[13]J. B. Delos and W. R. Thorson, Phys. Rev. A 6, 728 (1972).
[14]J. B. Delos, Phys. Rev. A 9, 1626 (1974).
[15]R. P. Saxon and R. E. Olson, Phys. Rev. A 12, 830 (1975).
[16]E. C. G. Stueckelberg, Helv. Phys. Acta 5, 369 (1932).
[17]Reference 9, Chap. VIII, Secs. 6.1 and 6.2.
[18]L. Landau, Phys. Z. Sowjetunion 2, 46 (1932).
[19]C. Zener, Proc. R. Soc. London A 137, 696 (1932).
[20]D. R. Bates, Proc. R. Soc. London A 257, 22 (1960).
[21]W. R. Thorson and S. A. Boorstein, in *Fourth International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers* (Science Bookcrafters, Hastings-on-Hudson, 1965), p. 218.
[22]J. C. P. Miller, *The Airy Integral* (Cambridge University, London, 1946), Vol. B.
[23]F. T. Smith, Phys. Rev. 179, 111 (1969).
[24]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, translated by J. B. Sykes and J. S. Bell (Addison-Wesley, Reading, Mass., 1965), Sec. 87.
[25]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1953), Chap. 3, Sec. 5.