change sign along $\vec{r}_t$, while if $\partial\Theta/\partial b$ is negative $\partial x_2/\partial x_2'$ changes sign once and only once (the reader may convince himself of this by drawing trajectories). Putting it all together in a formula gives Eq. (4.8).

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[1]K. W. Ford and J. A. Wheeler, Ann. Phys. (N. Y.) 7, 259 (1959); R. G. Newton, Scattering Theory of Waves and Particles (McGraw-Hill Book Company, Inc., New York, 1966), Chap. 18. For further development of the theory and extensive applications see especially the excellent articles by R. B. Bernstein, Advan. Chem. Phys. 10, 75–134 (1966); and R. B. Bernstein and J. T. Muckerman, Advan. Chem. Phys. 12, 389–486 (1967).

[2]R. P. Feynman, Rev. Mod. Phys. 20, 367 (1948); R. P. Feynman and A. R. Hibbs, Quantum Mechanics and Path Integrals (McGraw-Hill Book Company, Inc., New York, 1965). For a different approach to a time-dependent semiclassical scattering theory see S. A. Lebedeff, Phys. Rev. 165, 1399 (1968).

[3]The calculation in the Appendix is the simplest we could find. There are others: E. W. Montroll, Comm. Pure Appl. Math. 5, 415 (1952); I. M. Gel'fand and A. M. Yaglom, Usp. Mat. Nauk. II, 77 (1956) [English transl.: J. Math. Phys. 1, 48 (1960)]; P. Pechukas and J. C. Light, J. Chem. Phys. 44, 3897 (1966).

[4]See any book which includes a discussion of time-dependent scattering theory; for instance, R. G. Newton, Ref. 1.

[5]The argument is correct provided the potential falls off faster than $1/r$. In the case of Coulomb scattering it is still this "large impact parameter" path which gives the incident wave, but that wave of course is no longer $\exp(i\vec{k}\cdot\vec{r})$.

[6]L. D. Landau and E. M. Lifshitz, Mechanics (Addison-Wesley Publishing Company, Inc., Reading, Mass., 1960).

[7]Equations (5.5) and (5.6) are derived from the relation

$$\partial\chi/\partial b = -\hbar k b\partial\Theta/\partial b.$$

Notice that $d\Theta/db$ changes sign at b_r; this leads to the equation for $\bar{n}$.

[8]For an example of this phenomenon see E. A. Mason and L. Monchick, J. Chem. Phys. 41, 2221 (1964).

[9]Since $|\theta-\theta_g| \ll 1$ the behavior of S in directions perpendicular to the circle will be essentially independent of ϕ.

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Time-Dependent Semiclassical Scattering Theory. II. Atomic Collisions

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We derive "classical" equations for the relative motion of two atoms as their insides make a given quantum transition. The classical changes in relative energy and angular momentum associated with this description just balance the corresponding quantum changes in internal energy and angular momentum for the transition involved. The work is based on a generalization of Hamilton's principle, suggested in a natural way by Feynman's formulation of quantum mechanics; the semiclassical scattering theory which emerges is, in essence, a justification and extension of the impact-parameter method. Applications to low-energy atomic collisions are discussed briefly.

I. INTRODUCTION

In the preceding paper,[1] referred to below as I, the standard semiclassical theory of scattering by a potential was derived in a rather novel way, from a stationary phase approximation to Feynman's representation of the quantum-mechanical propagator for the problem. One thinks of generalizations. For instance, consider an electronically adiabatic collision between two molecules, resulting in rotational-vibrational excitation or chemical rearrangement. One could describe the collision by combining the semiclassical propagator for all the nuclei in their Born-Oppenheimer potential with semiclassical wave functions for the rotational-vibrational states of

the molecules before and after collision. Formally, this would be a straightforward extension of the work of I.

A fundamentally different problem obtains if one is interested in electronically diabatic processes, since it is in general not a good idea to consider electrons as classical particles. The problem is then one of describing semiclassically the relative motion of the colliding atoms or molecules while their insides undergo a quantum transition. That is, one has to find an appropriate way to mix quantum and classical mechanics. This is the problem we discuss here. We speak of atomic collisions, but the extension to electronically diabatic collisions of molecules is straightforward, if complicated.

In Sec. II we derive a path-integral representation of the reduced propagator for motion of the colliding atoms while their insides make a specified quantum transition. Section III discusses the semiclassical approximation to this propagator, obtained by a stationary phase evaluation of the path integral. In Sec. IV we discuss properties of the "classical" paths about which one expands, and in particular show that this mixture of classical and quantum mechanics is consistent in the sense that energy and angular momentum are conserved. An expression for the semiclassical scattering amplitude is derived in Sec. V.

In Sec. VI we consider briefly a few applications of the formalism. At high energies one is generally content to use the impact-parameter method, in which the atomic nuclei are imagined to move past each other on straight lines with constant velocity. This treatment neglects the reaction of the quantum transition involved back on the relative motion of the atoms; the theory of this paper, which is specifically concerned with that reaction, may be regarded as a low-energy extension of the impact-parameter method. We indicate the various types of "classical" atomic motion which one would expect in a low-energy collision in which only two molecular electronic states participate.

A number of papers on semiclassical theories of inelastic scattering have appeared recently, among which we mention the work of Cross[2] on generalizing the Schiff approximation, the studies of the eikonal approximation by Wilets and Wallace[3] and Chen and Watson,[4] and a paper by Bates and Holt[5] on a WKB-type formalism. Our ideas, however, are closest to those of F. T. Smith and his co-workers at Stanford,[6] and in fact in their studies of the scattering of noble-gas ions by noble-gas atoms they have anticipated several of the results of Sec. VI.[6]

II. THE REDUCED PROPAGATOR

We consider the collision of two atoms in their center-of-mass frame. Let $\vec{r}$ be the relative position vector of their individual centers of mass, and let x be the totality of internal coordinates (including spin). We split the Hamiltonian into kinetic energy of relative motion and everything else,

$$H = p^2/2\mu + h(\vec{r}, x) \equiv H_0 + h, \tag{2.1}$$

and assume that h depends only on $\vec{r}$, not on the conjugate momentum $\vec{p}$.

Suppose we are interested in a collision which takes the atoms from internal state α to internal state β, assumed to be eigenstates of the internal Hamiltonian

$$h_0(x) = \lim_{r \to \infty} h(\vec{r}, x). \tag{2.2}$$

To describe the collision it is not necessary to know the full propagator

$$K(\vec{r}''x''t'' \mid \vec{r}'x't') \equiv \langle \vec{r}''x'' \mid e^{-iH(t''-t')/\hbar} \mid \vec{r}'x' \rangle; \tag{2.3}$$

we need only the "reduced" propagator

$$K_{\beta\alpha}(\vec{r}''t'' \mid \vec{r}'t') = \int\int dx''dx' \varphi_\beta^*(x'') K(\vec{r}''x''t'' \mid \vec{r}'x't') \varphi_\alpha(x')$$

$$\equiv \langle \vec{r}''\beta \mid e^{-iH(t''-t')/\hbar} \mid \vec{r}'\alpha \rangle \ . \tag{2.4}$$

We will make a semiclassical approximation to $K_{\beta\alpha}$ by analogy with the work of I, so the first problem is to derive a path-integral representation of $K_{\beta\alpha}$.

Notice that

$$\langle \vec{r}''\beta \mid e^{-iH(t''-t')/\hbar} \mid \vec{r}'\alpha \rangle \equiv \int \cdots \int d\vec{r}_1 \cdots d\vec{r}_{n-1} \langle \vec{r}''\beta \mid e^{-iH\epsilon/\hbar} \mid \vec{r}_{n-1} \rangle$$

$$\times \langle \vec{r}_{n-1} \mid e^{-iH\epsilon/\hbar} \mid \vec{r}_{n-2} \rangle \tag{2.5}$$

$$\times \cdots \langle \vec{r}_1 \mid e^{-iH\epsilon/\hbar} \mid \vec{r}'\alpha \rangle, \quad \epsilon = (t''-t')/n,$$

and that for small ϵ, $|\vec{r}_j - \vec{r}_{j-1}|$,

$$\langle \vec{r}_j | e^{-iH\epsilon/\hbar} | \vec{r}_{j-1} \rangle \cong \langle \vec{r}_j | e^{-iH_0\epsilon/\hbar} | \vec{r}_{j-1} \rangle e^{-ih(\vec{r}_j, x)\epsilon/\hbar}$$

$$= (\mu/2\pi i\hbar\epsilon)^{\frac{3}{2}} \exp[i\mu(\vec{r}_j - \vec{r}_{j-1})^2/2\hbar\epsilon] e^{-ih(\vec{r}_j, x)\epsilon/\hbar}. \tag{2.6}$$

The appropriate representation of $K_{\beta\alpha}$ is therefore (see I)

$$K_{\beta\alpha}(\vec{r}''t''|\vec{r}'t') = \int_{\vec{r}'t'}^{\vec{r}''t''} d\vec{r}_t \exp\{iS_0[\vec{r}_t]/\hbar\} T_{\beta\alpha}[\vec{r}_t], \tag{2.7}$$

where

$$T_{\beta\alpha}[\vec{r}_t] = \lim_{\epsilon \to 0} \langle \beta | e^{-ih_{t''}\epsilon/\hbar} e^{-ih_{t''-\epsilon}\epsilon/\hbar} \cdots e^{-ih_{t'+\epsilon}\epsilon/\hbar} | \alpha \rangle, \quad h_t \equiv h(\vec{r}_t, x) \tag{2.8}$$

is the amplitude for the transition $\alpha \to \beta$ as the atoms pass each other on the path $\vec{r}_t$, and

$$S_0[\vec{r}_t] = \int_{t'}^{t''} dt \tfrac{1}{2}\mu \dot{\vec{r}}_t^{\,2} \tag{2.9}$$

is the action functional for relative motion.

Calculating $T_{\beta\alpha}$ is the standard quantum-mechanical problem of the response of a bound system to a time-dependent force – in this case, the force between the passing atoms; we assume it can be solved, in whatever approximation seems reasonable, and concentrate on evaluating the path integral (2.7). For future use, we introduce two solutions $\alpha_{tt'}$, $\beta_{tt''}$ of Schrödinger's equation

$$(i\hbar\partial_t - h_t)(\ldots) = 0 \tag{2.10}$$

with boundary conditions $\alpha_{t't'} = \alpha$, $\beta_{t''t''} = \beta$. Then

$$T_{\beta\alpha}[\vec{r}_t] = (\beta, \alpha_{t''t'}) = (\beta_{tt''}, \alpha_{tt'}), \tag{2.11}$$

independent of t.

III. SEMICLASSICAL APPROXIMATION

The transition amplitude $T_{\beta\alpha}$ is a complex functional of $\vec{r}_t$. We base the semiclassical approximation to the reduced propagator $K_{\beta\alpha}$ on the assumption that the magnitude of $T_{\beta\alpha}$ varies much more slowly with path than does its phase.[7] It is natural, then, to consider a stationary phase approximation to Eq. (2.7): We expand the phase to second order about "classical" paths $\bar{\vec{r}}_t$ where

$$\delta(S_0[\bar{\vec{r}}_t] + \hbar \operatorname{Im} \ln T_{\beta\alpha}[\bar{\vec{r}}_t]) = 0. \tag{3.1}$$

Since[8] $$\delta T_{\beta\alpha}[\vec{r}_t] = -(i/\hbar) \int_{t'}^{t''} dt (\beta_{tt''}, \delta h_t \alpha_{tt'}), \tag{3.2}$$

the "classical" equation of motion reads

$$\mu \ddot{\bar{\vec{r}}}_t = \operatorname{Re}[(\beta_{tt''}, -\partial_{\vec{r}} h\, \bar{\alpha}_{tt'})/(\bar{\beta}_{tt''}, \bar{\alpha}_{tt'})]; \tag{3.3}$$

that is, $\bar{\vec{r}}_t$ is a Newtonian path in the time-dependent potential

$$V(\vec{r}, t) = \operatorname{Re}[(\bar{\beta}_{tt''}, h(\vec{r}, x)\bar{\alpha}_{tt'})/(\bar{\beta}_{tt''}, \bar{\alpha}_{tt'})]. \tag{3.4}$$

Note that since this potential in fact depends on the path $\bar{\vec{r}}_t$ which we are trying to calculate, Eq. (3.3) is much less useful than Newton's equation in classical mechanics and in general must be solved iteratively. That is, one guesses a path, calculates $\alpha_{tt'}$, $\beta_{tt''}$ along it, solves (3.3) to find a new path, and continues until the process converges or one runs out of patience. Note also that the variational principle (3.1) is not of Lagrangian form, which leads to a certain amount of unpleasantness (see Sec. IV).

The properties of the paths defined by Eqs. (3.1) or (3.3) will be considered in more detail in the follow-

ing section; we want to dispense first with the formal problem of defining the semiclassical approximation to Eq. (2.7). The calculation follows closely that of I; again for notational simplicity we drop the bar which distinguishes "classical" paths.

Consider the second-order variation in the phase of $T_{\beta\alpha}$,

$$\delta^2(\hbar\,\mathrm{Im}\ln T_{\beta\alpha}[\vec{r}_t]) = -\delta\int_{t'}^{t''} dt\,\mathrm{Re}[(\beta_{tt''},\delta h_t\alpha_{tt'})/(\beta_{tt''},\alpha_{tt'})]$$

$$= -\mathrm{Re}\int_{t'}^{t''} dt\frac{(\beta_{tt''},\delta^2 h_t\alpha_{tt'})}{(\beta_{tt''},\alpha_{tt'})} - \mathrm{Re}\int_{t'}^{t''} dt\left(\frac{(\delta\beta_{tt''},\delta h_t\alpha_{tt'})+(\beta_{tt''},\delta h_t\delta\alpha_{tt'})}{(\beta_{tt''},\alpha_{tt'})}\right.$$

$$\left. -\frac{(\beta_{tt''},\delta h_t\alpha_{tt'})[(\delta\beta_{tt''},\alpha_{tt'})+(\beta_{tt''},\delta\alpha_{tt'})]}{(\beta_{tt''},\alpha_{tt'})^2}\right) \tag{3.5}$$

But to the extent that the phase of $T_{\beta\alpha}$ varies much more rapidly with path than does its magnitude, we must have

$$\delta\beta_{tt''}\cong i\phi_t\beta_{tt''},\quad \delta\alpha_{tt''}\cong i\chi_t\alpha_{tt''}, \tag{3.6}$$

where ϕ_t, χ_t are real numbers, and Eq. (3.5) reduces to

$$\delta^2(\hbar\,\mathrm{Im}\ln T_{\beta\alpha}) = -\mathrm{Re}\int_{t'}^{t''} dt\frac{(\beta_{tt''},\delta^2 h_t\alpha_{tt'})}{(\beta_{tt''},\alpha_{tt'})} = -\frac{1}{2}\int_{t'}^{t''} dt\sum_{i,j}\frac{\partial^2 V(\vec{r},t)}{\partial x_i\partial x_j}\delta x_i\delta x_j. \tag{3.7}$$

The normalizing path integral is then

$$\int_{0t'}^{0t''} d\vec{\eta}_t\exp\left\{\frac{i}{\hbar}\int_{t'}^{t''} dt\left[\frac{\mu\dot{\vec{\eta}}_t^{\,2}}{2}-\frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V_t}{\partial x_i\partial x_j}\right)\eta_{it}\eta_{jt}\right]\right\},\quad \vec{\eta}_t=\vec{r}_t-\bar{\vec{r}}_t, \tag{3.8}$$

of the same form as that evaluated in I. We find that the semiclassical approximation to the reduced propagator is

$$K_{\beta\alpha}(\vec{r}''t''|\vec{r}'t')=\sum[\mu^3/(2\pi i\hbar)^3|\partial\vec{r}_{t''}/\partial\dot{\vec{r}}_{t'}|]^{1/2}\exp\{iS_0[\vec{r}_t]/\hbar-\tfrac{1}{2}n\pi i\}T_{\beta\alpha}[\vec{r}_t], \tag{3.9}$$

the sum taken over all "classical" paths from $(\vec{r}'t')$ to $(\vec{r}''t'')$, $|\partial\vec{r}_{t''}/\partial\dot{\vec{r}}_{t'}|$ the Jacobian of final position with respect to initial velocity in the potential $V(\vec{r},t)$, and n equal to the number of zero characteristic values of $|\partial\vec{r}_t/\partial\dot{\vec{r}}_{t'}|$ in the interval $t'<t<t''$. Again to the same approximation as Eq. (3.6), $|\partial\vec{r}_{t''}/\partial\dot{\vec{r}}_{t'}|$ in the potential $V(\vec{r},t)$ is equal to $|\partial\vec{r}_{t''}/\partial\dot{\vec{r}}_{t'}|$ for paths calculated according to the variational principle (3.1).

The semiclassical approximation to the scattering amplitude implied by Eq. (3.9) will be derived below. Here we remark that this approximation will automatically satisfy the principle of detailed balancing, which states in essence that for a real Hamiltonian H, one can interchange initial and final positions in the propagator

$$K(\vec{r}''x''t''|\vec{r}'x't')=K(\vec{r}'x't''|\vec{r}''x''t'). \tag{3.10}$$

Equation (3.10) is equivalent to

$$K_{\beta\alpha}(\vec{r}''t''|\vec{r}'t')=K_{\alpha^*\beta^*}(\vec{r}'t''|\vec{r}''t'), \tag{3.11}$$

where α^*, β^* are the complex conjugates of the states α and β. That the semiclassical approximation to $K_{\beta\alpha}$ satisfies Eq. (3.11) follows immediately from the relations

$$T_{\beta\alpha}[\vec{r}_t]=T_{\alpha^*\beta^*}[\vec{r}_{t''+t'-t}],\quad S_0[\vec{r}_t]=S_0[\vec{r}_{t''+t'-t}], \tag{3.12}$$

which in turn are obvious from Eqs. (2.8) and (2.9).

IV. CHARACTERISTICS OF THE "CLASSICAL" PATHS

Given initial and final conditions $(\alpha\vec{r}'t')$, $(\beta\vec{r}''t'')$, Eq. (3.1) defines a set of "classical" paths for the atoms. In this section we investigate to what extent these paths furnish a sensible description of the collision.

First, consider the change with time of the

classical relative energy and angular momentum. From Eq. (3.3) we can derive the conservation laws

$$\frac{d}{dt}\left(\frac{\mu\dot{\vec{r}}_t^{\,2}}{2}+\mathrm{Re}\frac{(\beta_{tt'''},h_t\alpha_{tt'})}{(\beta_{tt'''},\alpha_{tt'})}\right)=0, \tag{4.1a}$$

$$\frac{d}{dt}\left(\mu\vec{r}_t\times\dot{\vec{r}}_t+\mathrm{Re}\frac{(\beta_{tt'''},\vec{J}_{\mathrm{int}}\alpha_{tt'})}{(\beta_{tt'''},\alpha_{tt'})}\right)=0, \tag{4.1b}$$

where $\vec{J}_{\mathrm{int}}$ is the operator for internal angular momentum,

$$\vec{J}_{\mathrm{int}}=\vec{J}-\vec{J}_{\mathrm{rel}}=\vec{J}+i\hbar\vec{r}\times\partial_{\vec{r}}.$$

To prove Eqs. (4.1) we notice that $(\beta_{tt''},\alpha_{tt'})$ is independent of t and that

$$\frac{d}{dt}(\beta_{tt'''},O_t\alpha_{tt'})=\left(\beta_{tt'''},\frac{[O_t,h_t]}{i\hbar}\alpha_{tt'}\right)+(\beta_{tt'''},(\partial_t O_t)\alpha_{tt'}), \tag{4.2}$$

where O_t is any operator. Equation (4.1a) then follows from Eq. (3.3), since

$$(\partial_t h_t)\equiv\partial_t h(\vec{r}_t,x)=\partial_{\vec{r}}h\cdot\dot{\vec{r}}_t. \tag{4.3}$$

Similarly, since h commutes with the total angular momentum operator $\vec{J}$, we have

$$[\vec{J}_{\mathrm{int}},h]=[h,\vec{J}_{\mathrm{rel}}]=i\hbar\vec{r}\times\partial_{\vec{r}}h, \tag{4.4}$$

and Eqs. (4.2) and (3.3) then imply Eq. (4.1b).

The interpretation of these conservation laws is quite simple. Suppose the endpoints $(\vec{r}'t')$, $(\vec{r}''t'')$ are outside the region of interaction, so that $h_{t'}=h_{t''}=h_0(x)$. Then Eq. (4.1a) becomes

$$\tfrac{1}{2}\mu\dot{\vec{r}}_{t'}^{\,2}+\epsilon_\alpha=\tfrac{1}{2}\mu\dot{\vec{r}}_{t''}^{\,2}+\epsilon_\beta; \tag{4.5}$$

that is, the change in *classical* relative energy along the path $\vec{r}_t$ just balances the change in *quantum* internal energy in the transition at which we are looking. Similarly, if α and β are both eigenstates of, say, the z component of internal angular momentum, then

$$(\mu\vec{r}_{t'}\times\dot{\vec{r}}_{t'})_z+J_{z\alpha}=(\mu\vec{r}_{t''}\times\dot{\vec{r}}_{t''})_z+J_{z\beta}. \tag{4.6}$$

There is, then, a certain consistency in this formal mixing of classical and quantum mechanics: The classical description of relative motion correctly reflects the quantum change in internal state.

Another important aspect of the collision process which should be described correctly by any semiclassical theory is the asymptotic free-particle behavior of the collision partners: Before and after collision we should find that the atoms move with constant velocity, along the free-particle continuation of their paths through the region of interaction. That is, if $\vec{r}_t$ is the "classical" path from $(\vec{r}'t')$ to $(\vec{r}''t'')$, where $\vec{r}'$ and $\vec{r}''$ are outside the region of interaction, and if $\tau'\langle t',\tau''\rangle t''$, we should find that the "classical" path from $(\vec{r}'-\dot{\vec{r}}_{t'}(t'-\tau'),\tau')$ to $(\vec{r}''+\dot{\vec{r}}_{t''}(\tau''-t''),\tau'')$ is

$$\begin{aligned}&\vec{r}''+\dot{\vec{r}}_{t''}(t-t''), && t''\le t\le\tau'';\\ &\vec{r}_t, && t'\le t\le t'';\\ &\vec{r}'-\dot{\vec{r}}_{t'}(t'-t), && \tau'\le t\le t'.\end{aligned} \tag{4.7}$$

Assume that this is so. Then since $h(\vec{r}_t,x)=h_0(x)$ for $t\le t'$ or $t\ge t''$, we find that

$$\begin{aligned}\alpha_{t\tau'}&=\exp[-i\epsilon_\alpha(t'-\tau')/\hbar]\alpha_{tt'},\\ \beta_{t\tau''}&=\exp[-i\epsilon_\beta(t''-\tau'')/\hbar]\beta_{tt''},\end{aligned} \tag{4.8}$$

and the path (4.7) does in fact satisfy the equation of motion (3.3).

We have finally to consider the difficulties which arise because the variational principle (3.1) is non-Lagrangian. One has as a consequence no guarantee that a particle which starts with definite position and momentum will end up somewhere definite: There may be points $\vec{r}_1''$, $\vec{r}_2''$ such that the initial velocities of the respective "classical" paths from $(\vec{r}'t')$ to $(\vec{r}_1''t'')$ and $(\vec{r}_2''t'')$ are identical. This is perhaps to be expected: The transition $\alpha\to\beta$ and the attendant transfer of energy and angular momentum can take place, roughly speaking, anytime during the collision (for a practical example see Sec. VI). In ordinary potential scattering the impact parameter may be a many-valued function of scattering angle; in this theory there is the additional complication that the scattering angle may be a many-valued function of impact parameter.

It is interesting to consider an example for which this pathological behavior of the formalism can be exactly and explicitly exhibited. Consider a particle interacting in one dimension with an oscillator fixed at the origin, through a term linear in the oscillator coordinate,

$$H=\frac{p_r^{\,2}}{2m_r}+\frac{p_x^{\,2}}{2m_x}+\frac{m_x\omega^2x^2}{2}+\left(\frac{2m_x\omega}{\hbar}\right)^{\frac{1}{2}}V(r)x \tag{4.9}$$

with $V(r)=V$, $-a\le r\le+a$,

$=0$, otherwise. (4.10)

Suppose we are interested in a transition from the

nth to $n+1$st vibrational state of the oscillator. The transition amplitude $T_{n+1,n}[r_t]$ can be calculated exactly for any r_t.[9] The details are not fascinating, and we give only the results. Since $V(r)$ is constant in each of the regions $r<-a$, $-a<r<+a$, and $r>+a$, a "classical" path from $r'<-a$ to $r''>+a$ is characterized by three velocities, v_1, v_2, v_3. If E is the initial relative energy, we find that

$$\tfrac{1}{2}m_r v_2^2 = E - \tfrac{1}{2}\hbar\omega - (2V^2/\hbar\omega)\sin^2(\omega a/v_2),$$
$$\tfrac{1}{2}m_r v_1^2 = E, \quad \tfrac{1}{2}m_r v_3^2 = E - \hbar\omega. \tag{4.11}$$

For small V (weak interactions), Eq. (4.11) says that the particle loses half a quantum of energy to the oscillator as it enters the region of interaction and the other half as it leaves. This is a sensible result. However, as V increases at fixed E other solutions appear, and for strong enough interaction one finds an infinity of "classical" paths (v_1, v_2, v_3) through the potential!

In the equation for v_2, the velocity of the particle as it passes through the region of interaction, $\frac{1}{2}\hbar\omega$ is half the energy transferred to the quantum-mechanical oscillator during the collision. It is a curious fact that

$$(2V^2/\hbar\omega)\sin^2(\omega a/v_2) \tag{4.12}$$

is just half the energy transferred to a *classical* oscillator, initially at rest, by a particle passing through with velocity v_2.[10] Make of it what you will.

V. THE SEMICLASSICAL SCATTERING AMPLITUDE

Let $\Psi^+_\alpha(\vec{r}x;\vec{k})$ be the scattering wave function for collision of two atoms in internal state α with relative momentum $\hbar\vec{k}$. The part of Ψ^+_α which describes scattering into internal state β is evidently

$$\psi^+_{\beta\alpha}(\vec{r},\vec{k}) = \int dx\, \varphi^*_\beta(x)\Psi^+_\alpha(\vec{r}x;\vec{k}) \tag{5.1}$$

with asymptotic form as $r\to\infty$,

$$\psi^+_{\beta\alpha}(\vec{r},\vec{k}) \cong e^{i\vec{k}\cdot\vec{r}}\delta_{\beta\alpha} + f_{\beta\alpha}(\hat{r},\vec{k})e^{ik'r}/r, \tag{5.2}$$

which defines the corresponding scattering amplitude $f_{\beta\alpha}$. Here k' is the magnitude of the final-state wave vector $\vec{k}'=k'\hat{r}$, determined by conservation of energy, $E(\vec{k}\alpha)=E(\vec{k}'\beta)$ where $E(\vec{k}\alpha)=\hbar^2k^2/2\mu+\epsilon_\alpha$ and so on.

The scattering wave function Ψ^+_α is that state of the system which in the infinite past was the free state

$$e^{i\vec{k}\cdot\vec{r}}\varphi_\alpha(x)e^{-iE(\vec{k}\alpha)t/\hbar}; \tag{5.3a}$$

that is,

$$\Psi^+_\alpha(\vec{r}x;\vec{k}) = \lim_{t'\to-\infty}\int d\vec{r}'dx'K(\vec{r}x0|\vec{r}'x't')\times e^{i\vec{k}\cdot\vec{r}'}\varphi_\alpha(x')e^{-iE(\vec{k}\alpha)t'/\hbar} \tag{5.3b}$$

and

$$\psi^+_{\beta\alpha}(\vec{r},\vec{k}) = \lim_{t'\to-\infty}\int d\vec{r}'K_{\beta\alpha}(\vec{r}0|\vec{r}'t')\times e^{i\vec{k}\cdot\vec{r}'}e^{-iE(\vec{k}\alpha)t'/\hbar} \tag{5.3c}$$

The limit (5.3c) is equivalent to

$$\psi^+_{\beta\alpha}(\vec{r},\vec{k}) = \lim_{t'\to-\infty}\left(\frac{2\pi i\hbar|t'|}{\mu}\right)^{\frac{3}{2}}K_{\beta\alpha}(\vec{r}0|\vec{r}'t')\times e^{i\vec{k}\cdot\vec{r}'}e^{-iE(\vec{k}\alpha)t'/\hbar}, \tag{5.4a}$$

where $|\vec{r}'-\hbar\vec{k}t'/\mu| = O(1);$ (5.4b)

the proof is exactly as in I.

From Eq. (5.4b) and the results of Sec. III it is clear that the semiclassical approximation to $\psi^+_{\beta\alpha}(\vec{r};\vec{k})$ will be a sum of contributions from the various "classical" orbits which pass through $\vec{r}$ and have velocity $\hbar\vec{k}/\mu$ in the distant past. The contribution from one of these trajectories, say, $\vec{r}_t$ with

$$\vec{r}_0=\vec{r}, \quad \lim_{t'\to-\infty}\dot{\vec{r}}_{t'}=\hbar\vec{k}/\mu,$$

is

$$\lim_{t'\to-\infty}\left(\frac{|t'|^3}{|\partial\vec{r}_0/\partial\dot{\vec{r}}_{t'}|_{\dot{\vec{r}}_{t'}}}\right)^{1/2}T_{\beta\alpha}[\vec{r}_t]\times\exp\left\{i\int_{\vec{r}_{t'}}^{\vec{r}_0}\vec{p}\cdot d\vec{r}/\hbar - \int_{t'}^{0}d\tau\, p^2/2\mu - \tfrac{1}{2}n\pi i + i\vec{k}\cdot\vec{r}_{t'} - \frac{iE(\vec{k}\alpha)t'}{\hbar}\right\}, \tag{5.5}$$

where $\vec{p}$ is the classical relative momentum $\mu\dot{\vec{r}}_t$ and all integrals are taken along $\vec{r}_t$. The calculation of the asymptotic form of (5.5) for large r goes through essentially as in I. We find that

$$\lim_{t'\to-\infty}\left(\frac{|t'|^3}{|\partial\vec{r}_0/\partial\dot{\vec{r}}_{t'}|_{\dot{\vec{r}}_{t'}}}\right)^{1/2} \cong r^{-1}[(k/k')\sigma_{\beta\alpha}(\hat{r},\vec{k})]^{1/2}, \quad \text{as } r\to\infty, \tag{5.6}$$

where $\sigma_{\beta\alpha}(\hat{r},\vec{k})$ is the classical differential cross section for scattering into direction $\hat{r}$ calculated from the paths defined in Sec. III and the factor

k/k' appears because (see I and the conservation theorem of Sec. IV)

$$\frac{dr}{dz}=\frac{dr/dt}{dz/dt}=\frac{k'}{k}\,. \tag{5.7}$$

The contribution of the trajectory $\vec{r}_t$ to the scattering amplitude is then

$$f_{\beta\alpha}(\hat{r},\vec{k})=[(k/k')\sigma_{\beta\alpha}(\hat{r},\vec{k})]^{1/2} \\ |T_{\beta\alpha}(\hat{r},\vec{k})|\exp\{i\chi_{\beta\alpha}(\hat{r},k)\}, \tag{5.8}$$

where $|T_{\beta\alpha}(\hat{r},\vec{k})|$ is the magnitude of the transition amplitude along the "classical" path leading into $\hat{r}$ in the infinite future and having velocity $\hbar\vec{k}/\mu$ in the infinite past, and the phase $\chi\beta\alpha$ is

$$\chi_{\beta\alpha}(\hat{r},\vec{k})=\lim_{\substack{\vec{r}''\to\hat{r}(\infty)\\ \vec{r}'\to\hat{k}(-\infty)}}\int_{\vec{r}'}^{\vec{r}''}\frac{\vec{p}}{\hbar}\cdot d\vec{r}-k'\hat{r}\cdot\vec{r}''+\vec{k}\cdot\vec{r}' \\ -\tfrac{1}{2}n\pi i+\phi_{\beta\alpha}(\hat{r},\vec{k})\,, \\ \phi_{\beta\alpha}(\hat{r},\vec{k})=\lim_{\substack{t''\to+\infty\\ t'\to-\infty}}\frac{E(\vec{k}\alpha)(t''-t')}{\hbar} \\ -\int_{t'}^{t''}dt(\mu\dot{\vec{r}}_t^{\,2}/2\hbar)+\operatorname{Im}\ln T_{\beta\alpha}[\vec{r}_t]. \tag{5.9}$$

That the limits in Eq. (5.9) exist is a consequence of the energy conservation relation found in Sec. IV.

The total amplitude for scattering in direction $\hat{r}$ and into state β is the sum of (5.8) over all "classical" paths with the proper initial and final velocities. The quantum-mechanical differential cross section for scattering into $(\hat{r},\beta)$ is given by[11]

$$(k'/k)|f_{\beta\alpha}(\hat{r},\vec{k})|^2\,; \tag{5.10}$$

if there is only one "classical" path which contributes this becomes simply

$$\sigma_{\beta\alpha}(\hat{r},\vec{k})|T_{\beta\alpha}(\hat{r},\vec{k})|^2. \tag{5.11}$$

The interpretation is transparent: The cross section for scattering in a given direction and with a given quantum transition is simply the classical cross section for scattering of the atoms in that direction times the probability for the quantum transition. If more than one path contributes to scattering in a given direction one has of course the possibility of interference in the inelastic differential cross section; if these paths are close together in function space, in the sense discussed in I, then one will see rainbow and/or glory effects in the inelastic scattering. The semiclassical theory of these effects can be worked out completely by analogy to that of I.

VI. EXAMPLES

Equations (5.8)–(5.11) complete the formal development of the theory. One has two problems: that of calculating the transition amplitudes $T_{\beta\alpha}$, and that of finding the "classical" paths which determine the angular dependence of scattering. The first problem is central to the usual impact-parameter calculations, in which the atoms are imagined to pass each other along free-particle trajectories, and it is already hard enough. The additional complication of considering the reaction of the quantum transition back on the relative motion of the atoms should be contemplated only in cases where the effect is likely to be large; that is, in low-energy atomic collisions (relative energies $\lesssim 100$ eV). In this section we discuss the nature of the "classical" paths for such low-energy collisions in the case when only two "molecular" electronic states participate.

First, a digression. We have based our formalism on Eq. (2.1), the decomposition of the center-of-mass Hamiltonian into relative energy of the centers of mass of the separated atoms and internal energy. We have, therefore, a semiclassical description of the motion of the centers of mass of the atoms as they collide. This is satisfactory from a formal point of view, but in practice it is a little silly: We are really interested in a semiclassical description of the motion of the individual atomic nuclei. If the theory can be reformulated to give such a description, then it can be applied not only to pure excitation processes but also to electron exchange and transfer problems. The reformulation is not difficult, but one pays a price: The definition of initial and final internal states α and β becomes more complicated.

To see how it goes, let $\vec{r}$ be the vector between the two nuclei, $\vec{x}_i$ the position vector of the ith electron with respect to the center of mass of the two nuclei, and $\vec{p}$ and $\vec{p}_i$ the corresponding conjugate momenta. Then the electrostatic Hamiltonian, in the center of mass frame, can be written

$$H=p^2/2\mu+h(\vec{r},x)\,, \tag{6.1}$$

where μ is the reduced mass of the two nuclei and

$$h(\vec{r},x)=\sum\frac{p_i^2}{2m}+\frac{(\sum\vec{p}_i)^2}{2(m_1+m_2)}-\sum\frac{Z_1e^2}{|x_i-\mu\vec{r}/m_1|}-\sum\frac{Z_2e^2}{|x_i+\mu\vec{r}/m_2|}+\frac{Z_1Z_2e^2}{r}+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{x}_i-\vec{x}_j|}, \tag{6.2}$$

where m is the electron mass, (m_1Z_1) and (m_2Z_2) are the mass and charge of the two nuclei.

Now suppose we are interested in the collision of two atoms with relative momentum $\hbar\vec{k}$ and with N_1, N_2 electrons, respectively, in internal state

$$\psi(X,\sigma)=\varphi_1(\{\vec{X}_{i1}\sigma_i\})\varphi_2(\{\vec{X}_{j2}\sigma_j\}), \tag{6.3}$$

where $\vec{X}_{i1}$, for instance, is the position vector with respect to nucleus 1 of the ith electron around it. Then if $\vec{R}$ is the vector between the centers of mass of the two atoms, the appropriate incoming state is

$$\begin{aligned}\Psi_{\text{in}}&=\mathcal{A}[e^{i\vec{k}\cdot\vec{R}}\psi(X,\sigma)]\\&=e^{i(\mu/\mu_{\text{in}})\vec{k}\cdot\vec{r}}\,\mathcal{A}\left\{\exp\left[i\vec{k}\cdot\left(\frac{m}{m_1+N_1m}\sum\vec{x}_{i1}-\frac{m}{m_2+N_2m}\sum\vec{x}_{j2}\right)\right]\right.\\&\left.\times\varphi_1(\{\vec{x}_{i1}-\mu\vec{r}/m_1,\sigma_i\})\varphi_2(\{\vec{x}_{j2}+\mu\vec{r}/m_2,\sigma_j\})\right\},\end{aligned} \tag{6.4}$$

where $\mathcal{A}$ is the electron antisymmetrizer and $\mu_{\text{in}}=[(m_1+N_1m)^{-1}+(m_2+N_2m)^{-1}]^{-1}$ is the reduced mass of the separated atoms. Similarly, if we are interested in the cross section for formation of atoms with relative momentum $\hbar\vec{k}'$ and with N_1', N_2' electrons, respectively, in internal state

$$\psi'(X',\sigma')=\psi_1'(\{\vec{X}_{i1}',\sigma_i'\})\varphi_2'(\{\vec{X}_{j2}',\sigma_j'\}) \tag{6.5}$$

and if $\vec{R}'$ is the vector between the centers of mass of the two atoms, the appropriate outgoing state is

$$\begin{aligned}\Psi_{\text{out}}&=\mathcal{A}[e^{i\vec{k}'\cdot\vec{R}'}\psi'(X',\sigma')]\\&=e^{i(\mu/\mu_{\text{out}})\vec{k}'\cdot\vec{r}}\,\mathcal{A}\left\{\exp\left[i\vec{k}'\cdot\left(\frac{m}{m_1+N_1'm}\sum\vec{x}_{i1}-\frac{m}{m_2+N_2'm}\sum\vec{x}_{j2}\right)\right]\right.\\&\left.\times\varphi_1'(\{\vec{x}_{i1}-\mu\vec{r}/m_1,\sigma_i\})\varphi_2'(\{\vec{x}_{j2}+\mu\vec{r}/m_2,\sigma_j\})\right\}.\end{aligned} \tag{6.6}$$

From Eqs. (6.1), (6.4), and (6.6) it is clear that the semiclassical formalism will go through as we have presented it provided we define the initial and final internal states as

$$\begin{aligned}\alpha&=\mathcal{A}\left\{\exp\left[i\vec{k}\cdot\left(\frac{m}{m_1+N_1m}\sum\vec{x}_{i1}-\frac{m}{m_2+N_2m}\sum\vec{x}_{j2}\right)\right]\varphi_1\varphi_2\right\},\\\beta&=\mathcal{A}\left\{\exp\left[i\vec{k}'\cdot\left(\frac{m}{m_1+N_1'm}\sum\vec{x}_{i1}-\frac{m}{m_2+N_2'm}\sum\vec{x}_{j2}\right)\right]\varphi_1'\varphi_2'\right\}.\end{aligned} \tag{6.7}$$

That is, we define "classical" paths for the atomic nuclei by the variational principle

$$\delta\left(\int_{t'}^{t''}dt\,\tfrac{1}{2}\mu\dot{\vec{r}}_t^{\,2}+\hbar\,\text{Im}\ln T_{\beta\alpha}[\vec{r}_t]\right)=0 \tag{6.8}$$

using now the reduced mass μ of the nuclei and states α and β which depend on the initial and final relative momenta.

Notice that α and β in this formalism are no longer precise eigenstates of the internal Hamiltonian

$$\lim_{r\to\infty}h(\vec{r},x),$$

even for $\vec{k}=0$; this is the price one pays for fixing attention on the nuclei of the atoms instead of on their centers of mass. However, one usually drops the second term of (6.2), getting the Born-Oppenheimer electronic Hamiltonian, and to the same accuracy replaces the atomic states φ_1, φ_1', φ_2, φ_2' by their

infinitely-heavy-nucleus approximation. The internal states α and β are then eigenstates of

$$\lim_{r\to\infty} h(\vec{r},x)$$

provided one can ignore the phase factors dependent on $\vec{k}$ and $\vec{k}'$. For high-energy electron transfer collisions this is not possible,[12] but at relative energies below 100 eV it is fine since the wavelength associated with electron momentum $(m/m_1)\hbar\vec{k}$ is much longer than an atomic radius.

Suppose now that $\alpha_{\vec{r}}, \beta_{\vec{r}}$ are the normalized eigenstates of $h(\vec{r},x)$,

$$h(\vec{r},x)\alpha_{\vec{r}}(x) = \epsilon_\alpha(r)\alpha_{\vec{r}}(x), \quad h(\vec{r},x)\beta_{\vec{r}}(x) = \epsilon_\beta(r)\beta_{\vec{r}}(x) \tag{6.9}$$

which go to the states α, β as $r\to\infty$. In considering a transition from α to β at low energy, one has to distinguish two possibilities, that the potential energy curves ϵ_α and ϵ_β come close together at some r_0 or that they do not. If they do not, we anticipate that the collision will be nearly adiabatic; that is, that the states $\alpha_{tt'}, \beta_{tt''}$ will be approximately

$$\begin{aligned}\alpha_{tt'} &\cong \exp[-(i/\hbar)\textstyle\int_{t'}^{t} d\tau\, \epsilon_\alpha(r_\tau)]\,\alpha_{\vec{r}_t} + \text{small correction},\\ \beta_{tt''} &\cong \exp[-(i/\hbar)\textstyle\int_{t''}^{t} d\tau\, \epsilon_\beta(r_\tau)]\,\beta_{\vec{r}_t} + \text{small correction}.\end{aligned} \tag{6.10}$$

We imagine then that the effective potential in which the nuclei find themselves moving while the electrons make the transition from state α to β will be some mixture of the ϵ_α and ϵ_β curves, looking like ϵ_α before collision and like ϵ_β after collision. This is in fact what comes out of the formalism; substituting Eq. (6.10) in Eq. (3.4) we find that to first order the effective potential is

$$V(r,t) = c_\alpha(t)\epsilon_\alpha(r) + c_\beta(t)\epsilon_\beta(r), \tag{6.11a}$$

where

$$\begin{aligned}c_\alpha(t) &= \mathrm{Re}\{\exp[-(i/\hbar)\textstyle\int_{t'}^{t} d\tau\, \epsilon_\alpha(r_\tau)]\,(\beta_{tt''}, \alpha_{\vec{r}_t})/(\beta_{tt''}, \alpha_{tt'})\}\\ c_\beta(t) &= \mathrm{Re}\{\exp[-(i/\hbar)\textstyle\int_{t''}^{t} d\tau\, \epsilon_\beta(r_\tau)](\beta_{\vec{r}_t}, \alpha_{tt'})/(\beta_{tt''}, \alpha_{tt'})\}\end{aligned} \tag{6.11b}$$

and, to first order,

$$c_\alpha(t) + c_\beta(t) = 1 \tag{6.12}$$

by Eq. (6.10). Furthermore, it is easy to see that

$$c_\alpha(t) \underset{t\to t'}{\longrightarrow} 1, \quad c_\beta(t) \underset{t\to t'}{\longrightarrow} 0; \quad c_\alpha(t) \underset{t\to t''}{\longrightarrow} 0, \quad c_\beta(t) \underset{t\to t''}{\longrightarrow} 1 \tag{6.13}$$

so the mathematical picture corresponds to our physical idea about what is going on.

In practice it is still necessary to determine the mixing coefficients c_α, c_β by the iterative procedure of guessing a path, calculating c_α, c_β along it by, say, first-order perturbation theory, solving the equations of motion to find a new path, and so on.

Now consider a pseudocrossing, $\epsilon_\alpha(r_0) \cong \epsilon_\beta(r_0)$ for some r_0, and a path $\vec{r}_t$ which cuts the pseudocrossing at times t_1 and t_2, $r_{t_1} = r_{t_2} = r_0$. We no longer have a nearly adiabatic situation: There is appreciable possibility of a change from electronic state $\alpha_{\vec{r}}$ to $\beta_{\vec{r}}$ as the internuclear separation passes through r_0. We assume with Landau and Zener[13] that a change in electronic state is possible over such a small region around r_0 that its amplitude depends only on the internuclear position and velocity $\vec{r}$, $\dot{\vec{r}}$ at the pseudocrossing. Let $t_{\alpha\alpha}$, $t_{\beta\beta}$, $t_{\beta\alpha}$, and $t_{\alpha\beta}$ be the four possible transition amplitudes at a pseudocrossing.[14] Then the total transition amplitude $T_{\beta\alpha}[\vec{r}_t]$ is approximately

$$\begin{aligned}T_{\beta\alpha}[\vec{r}_t] = {} & t_{\beta\beta}(\vec{r}_{t_2}, \dot{\vec{r}}_{t_2}) t_{\beta\alpha}(\vec{r}_{t_1}, \dot{\vec{r}}_{t_1}) \exp[-(i/\hbar)\textstyle\int_{t_1}^{t''} d\tau\, \epsilon_\beta(r_\tau) - (i/\hbar)\int_{t'}^{t_1} d\tau\, \epsilon_\alpha(r_\tau)]\\ & + t_{\beta\alpha}(\vec{r}_{t_2}, \dot{\vec{r}}_{t_2}) t_{\alpha\alpha}(\vec{r}_{t_1}, \dot{\vec{r}}_{t_1}) \exp[-(i/\hbar)\textstyle\int_{t_2}^{t''} d\tau\, \epsilon_\beta(r_t) - (i/\hbar)\int_{t'}^{t_2} d\tau\, \epsilon_\alpha(r_\tau)]\,.\end{aligned} \tag{6.14}$$

That is, $T_{\beta\alpha}$ is a sum of two terms, reflecting the possibility that the electronic state changes at either the first or second crossing through r_0. Since the two amplitudes describe distinct physical situations, we make a semiclassical approximation to each term of $K_{\beta\alpha}$ separately, and neglect the phases of the amplitudes t since the transitions they describe occur essentially instantaneously. Then from Eqs. (6.14) and (3.1) it is clear that for given impact parameter b and relative energy E the nuclei move either in potential $\epsilon_\alpha(r)$ up to the first crossing through r_0 and then in potential $\epsilon_\beta(r)$, or in potential $\epsilon_\alpha(r)$ up to the second crossing and then in potential $\epsilon_\beta(r)$. Let $\Theta_{1,2}(b,E)$ be the deflection angles for the two possibilities and $\epsilon'_\alpha(r)=\epsilon_\alpha(r)-\epsilon_\alpha(\infty)$, $\epsilon'_\beta(r)=\epsilon_\beta(r)-\epsilon_\alpha(\infty)$. We have

$$\begin{aligned}\Theta_1(b,E)&=\pi-b\int_{r_0}^{\infty}dr\,r^{-2}\left(1-\frac{\epsilon'_\alpha(r)}{E}-\frac{b^2}{r^2}\right)^{-\frac{1}{2}}-b\int_{r_0}^{\infty}dr\,r^{-2}\left(1-\frac{\epsilon'_\beta(r)}{E}-\frac{b^2}{r^2}\right)^{-\frac{1}{2}}\\&\quad-2b\int_{r_{\min,\beta}}^{r_0}dr\,r^{-2}\left(1-\frac{\epsilon'_\beta(r)}{E}-\frac{b^2}{r^2}\right)^{-\frac{1}{2}}\\\Theta_2(b,E)&=(\ldots)-2b\int_{r_{\min,\alpha}}^{r_0}dr\,r^{-2}\left(1-\frac{\epsilon'_\alpha(r)}{E}-\frac{b^2}{r^2}\right)^{-\frac{1}{2}}.\end{aligned}\tag{6.15}$$

The semiclassical scattering amplitude is

$$\begin{aligned}f_{\beta\alpha}(\hat{r},\vec{k})&=\sum|(k/k')b/(\sin\theta\,d\Theta_1/db)|^{\frac{1}{2}}e^{i\chi_1(b,E)}|t_{\beta\beta}(2)t_{\beta\alpha}(1)|\\&\quad+\sum|(k/k')b/(\sin\theta\,d\Theta_2/db)|^{\frac{1}{2}}e^{i\chi_2(b,E)}|t_{\beta\alpha}(2)t_{\alpha\alpha}(1)|,\end{aligned}\tag{6.16}$$

the sum being over all impact parameters which lead to scattering in the direction $\hat{r}$. In the differential cross section there is now the possibility of interference between two paths with different impact parameters *and* different effective potential.

The total cross section for scattering into state β is

$$\begin{aligned}\sigma(\beta,E)&=\int d\hat{r}\,(k'/k)|f_{\beta\alpha}(\hat{r},\vec{k})|^2\\&\cong 2\pi\int_0^{b_0}b\,db[|t_{\beta\beta}(2)|^2|t_{\beta\alpha}(1)|^2+|t_{\beta\alpha}(2)|^2|t_{\alpha\alpha}(1)|^2]\end{aligned}\tag{6.17}$$

if the interference pattern in the differential cross section is "dense" enough to be averaged over. Here b_0 is the impact parameter for which the distance of closest approach in the potential $\epsilon'_\alpha(r)$ is equal to the pseudocrossing distance r_0. Now consider the part of the semiclassical cross section for elastic scattering contributed by impact parameters less than b_0; to the same approximation this is

$$\sigma(\alpha,E)\cong 2\pi\int_0^{b_0}b\,db[|t_{\alpha\beta}(2)|^2|t_{\beta\alpha}(1)|^2+|t_{\alpha\alpha}(2)|^2|t_{\alpha\alpha}(1)|^2].\tag{6.18}$$

Sum the two; one gets

$$\begin{aligned}\sigma(\alpha,E)+\sigma(\beta,E)\cong 2\pi\int_0^{b_0}b\,db[&|t_{\alpha\beta}(2)|^2|t_{\beta\alpha}(1)|^2+|t_{\beta\beta}(2)|^2|t_{\beta\alpha}(1)|^2]+[|t_{\alpha\alpha}(2)|^2|t_{\alpha\alpha}(1)|^2\\&+|t_{\beta\alpha}(2)|^2|t_{\alpha\alpha}(1)|^2],\end{aligned}\tag{6.19}$$

where each transition element is evaluated along the "classical" trajectory with impact parameter b which passes through the sequence of potentials indicated by its subscripts. Now since the classical path for the sequence $(\alpha\to\beta\to\alpha)$ is identical with the path for $(\alpha\to\beta\to\beta)$ up to the second crossing, and since the transition amplitude depends only on internuclear position and velocity at the crossing, we have in the two-state approximation

$$\begin{aligned}|t_{\alpha\beta}(2)|^2|t_{\beta\alpha}(1)|^2+|t_{\beta\beta}(2)|^2|t_{\beta\alpha}(1)|^2&=|t_{\beta\alpha}(1)|^2,\\|t_{\alpha\alpha}(2)|^2|t_{\alpha\alpha}(1)|^2+|t_{\beta\alpha}(2)|^2|t_{\alpha\alpha}(1)|^2&=|t_{\alpha\alpha}(1)|^2.\end{aligned}\tag{6.20}$$

Similarly, the classical path $(\alpha\to\beta)$ is identical to that for $(\alpha\to\alpha)$ up to the first crossing, so

$$|t_{\beta\alpha}(1)|^2+|t_{\alpha\alpha}(1)|^2=1 \tag{6.21}$$

and $$\sigma(\alpha,E)+\sigma(\beta,E)=\pi b_0^{\,2}. \tag{6.22}$$

In other words, to this approximation we have a kind of "conservation of total cross section" in a system with both elastic and inelastic processes.[15]

Notice that in this two-state theory one has a formula analogous to (6.16) for the concurrent elastic scattering amplitude

$$f_{\alpha\alpha}(\hat{r},\vec{k})=\sum|b/(\sin\theta\, d\Theta_1/db)|^{\frac{1}{2}}\, e^{i\chi_1(b,E)}|t_{\alpha\beta}(2)t_{\beta\alpha}(1)|+\sum|b/(\sin\theta\, d\Theta_2/db)|^{\frac{1}{2}}\, e^{i\chi_2(b,E)}|t_{\alpha\alpha}(2)t_{\alpha\alpha}(1)|, \tag{6.23}$$

where Θ_1 is the deflection function in a potential equal to $\epsilon'_\alpha(r)$ for $r>r_0$ and $\epsilon'_\beta(r)$ for $r<r_0$, while Θ_2 is the deflection function in the potential $\epsilon'_\alpha(r)$ for all r. One then expects curve-crossing oscillations in the differential cross section for elastic scattering, even at energies below the threshold for inelastic processes.[16]

We have finally to discuss the case of symmetric electron transfer. Let g_r, u_r be the electronic eigenstates which are respectively even and odd in the spatial coordinates of the transferred electron. Then the initial state α, representing an electron around one of the nuclei, is, say,

$$\text{(a)}\ \alpha=\lim_{r\to\infty}\frac{1}{\sqrt{2}}(g_{\vec{r}}+u_{\vec{r}}),\quad \text{while (b)}\ \beta=\lim_{r\to\infty}\frac{1}{\sqrt{2}}(g_{\vec{r}}-u_{\vec{r}}). \tag{6.24}$$

If the g and u potential curves are well separated for finite r, the individual electronic states will change adiabatically with time, so that

$$\alpha_{t''t'}\cong 2^{-1/2}\{\exp[-(i/\hbar)\int_{t'}^{t''}d\tau\,\epsilon_g(r_\tau)]g_{\vec{r}_{t''}}+2^{-1/2}\exp[-(i/\hbar)\int_{t'}^{t''}d\tau\,\epsilon_u(r_\tau)]u_{\vec{r}_{t''}}\} \tag{6.25}$$

and
$$T_{\beta\alpha}[\vec{r}_t]=\tfrac{1}{2}\{\exp[-(i/\hbar)\int_{t'}^{t''}dt\,\epsilon_g(r_t)]-\exp[-(i/\hbar)\int_{t'}^{t''}dt\,\epsilon_u(r_t)]\},$$
$$T_{\alpha\alpha}[\vec{r}_t]=\tfrac{1}{2}\{\exp[-(i/\hbar)\int_{t'}^{t''}dt\,\epsilon_g(r_t)]+\exp[-(i/\hbar)\int_{t'}^{t''}dt\,\epsilon_u(r_t)]\}. \tag{6.26}$$

The situation is formally the same as with curve crossing. One has two distinct sets of classical paths for the nuclei, which according to Eqs. (6.26) and (3.1) are classical paths in the potentials $\epsilon'_g(r)=\epsilon_g(r)-\epsilon_g(\infty)$ and $\epsilon'_u(r)=\epsilon_u(r)-\epsilon_u(\infty)$. The amplitudes for scattering with and without electron transfer are

$$f_{\beta\alpha}(\hat{r},\vec{k})=\tfrac{1}{2}\sum|b/(\sin\theta)d\Theta_g/db|^{\frac{1}{2}}\, e^{i\chi_g(b,E)}-\tfrac{1}{2}\sum|b/(\sin\theta)d\Theta_u/db|^{\frac{1}{2}}\, e^{i\chi_u(b,E)}, \tag{6.27a}$$

$$f_{\alpha\alpha}(\hat{r},\vec{k})=\tfrac{1}{2}\sum|b/(\sin\theta)d\Theta_g/db|^{\frac{1}{2}}\, e^{i\chi_g(b,E)}+\tfrac{1}{2}\sum|b/(\sin\theta)d\Theta_u/db|^{\frac{1}{2}}\, e^{i\chi_u(b,E)}, \tag{6.27b}$$

where the sum is over all impact parameters leading to scattering in the direction $\hat{r}$ in either of the two potentials. Equations (6.27) have in fact been used very successfully by F. T. Smith and his colleagues to interpret scattering data on low-energy electron transfer.[17]

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Compton Scattering From a Bound System of Two Charged Particles*

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With reference to a previous paper by Fronsdal, the expression for Compton scattering on the fundamental state of the hydrogen atom is derived, taking into account the effect of the proton motion. An example of its extension to an inelastic case is shown. The result is discussed in connection with some problems of interpretation of the formalism of the infinite-component wave functions.

1. INTRODUCTION

The formalism of the infinite-component wave functions has often been proposed and used in recent years to describe systems having internal degrees of freedom.[1,2] One of the problems arising in this formulation is to show as clearly as possible the connection between the new mathematical techniques and the older ones. The system most commonly studied in this connection is the hydrogen atom, since there the older formulation is completely clear and the newer formulation can be built up explicitly. In particular, Fronsdal[3] recently used this formalism to calculate the scattering of photons by bound electrons without using the dipole approximation, but still keeping the proton mass infinite. Here we wish to go a step further and study the effect of the finite mass of the proton, which allows recoil effects and interaction of the proton with real photons. The main reason for including these effects is not that the finite-mass effect is important experimentally, but to study, in a concrete example, how one can describe, in the frame of the infinite-component formalism, the interaction of a composite system in which both the components interact. In particular, we shall see that the requirement of locality for the interaction Lagrangian is no longer valid and that some weaker condition should be substituted. The paper is, in a broad sense, a continuation of Ref. 3, although its particular purpose led us to choose a different starting point, i.e., we use the classical Schrödinger formulation and introduce the infinite-component functions after the problem has been completely formulated.