the peak indicate that it is a separate line and not a series limit. It also falls at the energy expected for the transition of the $3d'(^3P)$ state into the ^4S continuum. This transition is forbidden in LS coupling, but the presence of this peak (which was well verified in many runs) probably indicates a breakdown of LS coupling. This is not surprising since Codling *et al.*[14] have observed such a breakdown in neon.

The only other feature of the spectrum observed between 0.5 and 18 eV is the hump just above 4 eV. This could represent the series limit for the transitions from the $ns\sigma^3\Sigma_u^-$ and $nd\pi^3\Pi_u$ molecular states into the $^2\Sigma_g^-$ continuum. Codling and Madden[15] have observed these excited states in the absorption spectrum in the 500–600 Å region and by their broadened, asymmetric nature deduce that they are auto-ionizing. These levels converge on the $c^4\Sigma_u^-$ state of O_2^+ which is 4.26 eV above the $^2\Sigma_g^-$ limit. This energy is consistent with our interpretation of the hump as this series limit. However, none of the individual lines from this series of transitions could be observed. Evidently most of the auto-ionization observed in this experiment occurs after dissociation of the oxygen molecule.

That the lines reported here are from atomic oxygen is further verified by the fact that we observe the same line spectrum using carbon dioxide as a target gas.

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Eikonal Method in Atomic Collisions. I*

L. WILETS AND S. J. WALLACE†
University of Washington, Seattle, Washington
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A complete and systematic quantal description of atomic collisions is developed employing the eikonal method. The lowest-order approximation involves the solution of the time-dependent Schrödinger equation for the electrons in the rectilinear trajectories of the atomic nuclei. The differential scattering amplitude (and hence the differential cross section) for the various reaction channels is expressed as a Fraunhofer integral, over the impact parameter, of the asymptotic state amplitudes. This completely avoids the ambiguities involved in obtaining an effective interatomic potential. Higher-order corrections are exhibited. However, the lowest-order approximation not only is valid at high energies, but penetrates deeply into the adiabatic regime, probably down to 100 eV. Numerical calculations will be presented in a later paper.

I. INTRODUCTION

THE assumption of a classical trajectory for the nuclei in atomic collisions has long been known to be a good approximation at energies above tens or hundreds of electron volts, although there has always remained an ambiguity as to the precise method of determining the trajectory. In recent years, several papers have been addressed to the question of treating the mechanics of the nuclei by such means as the solution of a classical differential equation using an average internuclear potential,[1,2] and by the construction of wave packets centered about a classical trajectory.[3] The methods developed have served mainly to define the energies at which the impact parameter approximation (rectilinear trajectory for the nuclei) is valid.

The rectilinear trajectory is used extensively to calculate amplitudes $a(b)$ for the various electronic transitions at fixed impact parameter b. The attendant differential cross sections $f(\Theta)$ are generally predicted by means of assigning a correspondence $\Theta(b)$. The perpendicular impulse could be calculated, according to well-known techniques, from the expectation value of the perpendicular component of force. This last point is fraught with ambiguity. In a calculation where the nuclear trajectory is treated classically and the electrons are treated quantum mechanically, it is not possible (except in the adiabatic limit) to separate uniquely the electronic configurations associated with the various excitation processes until the collision is completed. One can only calculate a mean trajectory for all processes. (In practice, it is popular to use a Coulomb or shielded Coulomb classical trajectory.) In

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† Permanent address: Boeing Company, Seattle, Wash.
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order to remove such ambiguities it is necessary to have a completely quantal description of the collision process.

A complete and systematic, fully quantal description is available for slow collisions in the form of the adiabatic expansion, such as has been utilized by Bates.[4,5] The beginning point for that analysis is the set of adiabatic wave functions $U_k(r,R)$ satisfying the eigenvalue equation

$$[H_e(\mathbf{r},\mathbf{p};\mathbf{R})-\epsilon_k(\mathbf{R})]U_k(\mathbf{r};\mathbf{R})=0, \quad (1)$$

where H_e (as defined, for example, in Sec. III B) is the electronic part of the Hamiltonian. The nuclear kinetic energy has been ignored at this point. The U_k can be chosen to be a complete orthonormal set of functions in the electronic coordinates $\mathbf{r}$, depending parametrically on the internuclear coordinate $\mathbf{R}$. In complete generality, the wave function can be expanded:

$$\Psi(\mathbf{r},\mathbf{R})=\sum_k F_k(\mathbf{R})U_k(\mathbf{r};\mathbf{R}). \quad (2)$$

The projectile velocity is an appropriate expansion parameter, and to lowest order the F_k satisfy

$$[-(1/2M)\nabla_R^2+\epsilon_k(\mathbf{R})-E]F_k(\mathbf{R})=0. \quad (3)$$

The above equation describes elastic scattering; higher-order corrections admix excited states as well as correct the elastic amplitudes. The dimensionless adiabatic parameter is actually $\xi_{ad}=\hbar v/(a\Delta E)$, where v is the projectile velocity, a is a characteristic collision length, and ΔE is a characteristic energy spacing. When the parameter approaches unity, the expansion fails; thus pseudocrossings of energy levels require special consideration, since their occurrence can severely limit the range of the approximation.

The present paper approaches the problem from the large velocity, massive projectile end. A completely quantal description is again available, through a generalization of the eikonal method, which also preserves the simplicity of the rectilinear trajectory for the analysis of the electronic processes. We refer to the eikonal "method" or "representation" rather than "approximation" because higher-order corrections can be displayed systematically.

The eikonal method has a time-honored history in optics and was introduced into potential scattering of a particle by Moliere.[6] Glauber[7] developed the method for high-energy scattering and also included some discussion of its applicability to atomic collisions. The method is similar to the three-dimensional WKB method of Bates and Holt.[8]

One of the advantages of the present work is simplicity. The basis functions employed are obtained from calculations based on straight-line trajectories which are becoming progressively more available in the literature. We demonstrate that there is phase information in the electronic functions which can be used to obtain reaction cross sections with little extra effort and free of the ambiguities associated with a classical trajectory.

The beginning point of the analysis is the complete wave equation

$$[-\nabla_R^2/2M+H_e(\mathbf{r},\mathbf{p};\mathbf{R})-E]\Psi(\mathbf{r};\mathbf{R})=0, \quad (4)$$

where M is the reduced mass of the nuclei. Atomic units are used ($\hbar=m=e=1$). Writing Ψ as $e^{iMvZ}\psi$ reduces the equation to

$$\left[-\frac{\nabla_R^2}{2M}-iv\frac{\partial}{\partial Z}+H_e(\mathbf{r},\mathbf{p};\mathbf{R})\right]\psi(\mathbf{r};\mathbf{R})=0, \quad (5)$$

where $E=\frac{1}{2}Mv^2$ and the target ground-state energy is taken to be zero. Our definitions of E and M result in v being slightly different from the projectile velocity since the electron kinetic energy in nuclear center-of-mass coordinates must be accounted. Equation (5) may be solved by temporarily dropping the part of ∇_R^2 associated with motion perpendicular to the projectile motion

$$\left[-\frac{1}{2M}\frac{\partial^2}{\partial Z^2}-iv\frac{\partial}{\partial Z}+H_e(\mathbf{r},\mathbf{p};\mathbf{R})\right]\psi(\mathbf{r};\mathbf{R})=0, \quad (6)$$

where ψ here depends parametrically on $\mathbf{b}$. This form is not the standard impact parameter method (which identifies $Z=vt$) because of the presence of the term $-(1/2M)\partial^2/\partial Z^2$; however, this term does provide a means of including higher-order corrections in the analysis from the outset.

The standard impact parameter wave equation is simply obtained from (5) or (6) by letting the mass M become infinite while v remains finite:

$$\left[-iv\frac{\partial}{\partial Z}+H_e(\mathbf{r},\mathbf{p};\mathbf{R})\right]\psi(\mathbf{r};\mathbf{R})=0. \quad (7)$$

There are, plausibly, two expansion parameters which must be small in this procedure, The first of these is the ratio of the nuclear wavelength to the atomic size; this must be small if the concept of a classical trajectory has any utility. The second is the ratio of the electronic energy to the projectile kinetic energy. This must be small if the trajectory is to be treated as rectilinear.

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These parameters are expressed as

$$\xi_1=(Mva)^{-1},$$
$$\xi_2=\epsilon/\tfrac{1}{2}Mv^2,$$

where a is a characteristic collision length and ϵ is a characteristic electron energy. In atomic units, $a\sim 1$ and $\epsilon\sim\frac{1}{2}$. This gives

$$\xi_1\sim(Mv)^{-1},\quad \xi_2\sim(Mv^2)^{-1}.$$

Note that both parameters contain M^{-1}. For $v>1$, both parameters are very small ($<10^{-3}$ for H^+-H). In pressing the method to low velocity, it is ξ_2 which will concern us.

ξ_2 is of the order of unity when the projectile center-of-mass energy is of the order of the electron energy (i.e., the order of 10 eV). This is to be contrasted with the adiabatic expansion parameter which is of the order of unity when the projectile velocity is of the order of the electron velocity. (For H^+-H, this is 25 keV in the laboratory system.) The eikonal method, which we develop here, is thus not only complementary to the adiabatic method, but penetrates deeply into the (low-energy) region of the latter.

We briefly review the eikonal method for potential scattering, Sec. II, and formulate the method to lowest order for an atomic collision process with a stationary target in Sec. III. Back scattering and nuclear identity are discussed in Secs. IV and V.

A subsequent paper, in preparation, will present numerical calculations utilizing available impact parameter amplitudes.

II. POTENTIAL SCATTERING

In the eikonal *approximation* for potential scattering, the wave function through the interaction region is approximated by

$$\Psi(\mathbf{R})\propto\exp\left[i\int^{Z}k(X,Y,Z')dZ'\right],\tag{8}$$

where $k(\mathbf{R})$ is the local wave number of the particle

$$k^2(\mathbf{R})/2M=E-V(\mathbf{R}).\tag{9}$$

The integral for the phase is taken over the rectilinear trajectory dZ', keeping the impact parameter $\mathbf{b}=(X,Y)$ fixed. Beyond the interaction region, the wave function does not, in fact, satisfy the wave equation,[9] but the phase information contained in Ψ can be used to continue the wave function properly. This is accomplished by the artifice of introducing a Fraunhofer surface to the right of the interaction region. By Kirchoff's theorems, one can express the wave function to the right of the surface in terms of an integral over the surface:

$$\begin{aligned}\Psi(\mathbf{R})\underset{R\to\infty}{\longrightarrow}&-(1/4\pi R)e^{iKR}\int e^{-iKb\sin\Theta\cos\Phi}\\&\times\hat{n}\cdot[\nabla_{R'}\Psi(\mathbf{R}')+iK\hat{R}\Psi(\mathbf{R}')]da'\\&=(e^{iKR}/R)\left\{-iK\cos^2(\tfrac{1}{2}\Theta)\int_0^\infty bdb\,J_0(qb)a(b)\right\}\\&\equiv(e^{iKR}/R)f(\Theta),\end{aligned}\tag{10}$$

where here we have defined

$$q\equiv K\sin\Theta,$$
$$a(b)\equiv\exp\left[i\int^{Z_0}dz'\,k(\mathbf{b},z')\right],$$
$$K\equiv k(R=\infty)=(2ME)^{1/2}.$$

The last form is valid for spherically or axially symmetric potentials.

Note that for $\xi_2=V/E\ll 1$, we may expand

$$\begin{aligned}\Psi(\mathbf{R})&\propto\exp\left[i\int^{Z}k(\mathbf{b},Z')dZ'\right]\\&\approx e^{iKZ}\exp\left[-i\int^{Z}V(k,Z')\frac{dZ'}{v}\right]\\&\equiv e^{iKZ}\psi(\mathbf{R}),\end{aligned}\tag{11}$$

where $v=K/M$.

This last form satisfies the differential equation $iv\partial\psi/\partial Z=V\psi$ and suggests generalization to scattering from a system with internal degrees of freedom, for example an atomic collision. An example revealing the utility of the eikonal method for atomic collisions is afforded by analysis of Coulomb scattering. Here in lowest order the wave function satisfies $iv\partial\psi/\partial Z=(1/R)\psi$ and we calculate the amplitude to be

$$\begin{aligned}\psi(\mathbf{R})\underset{R\to\infty}{\longrightarrow}a(b)&=\exp\left[-\frac{2i}{v}\int_b^\infty\frac{dR}{(R^2-b^2)^{1/2}}\right]\\&=(b/2)^{2i/v}e^{(2i/v)\gamma_E},\end{aligned}\tag{12}$$

where γ_E is Eulers constant and an infinite phase factor has been ignored. The scattering amplitude is obtained from (10) and the scattering cross section is given by

$$\begin{aligned}\frac{d\sigma}{d\Omega}&=|f_{\mathrm{Coul}}(\Theta)|^2=[K\cos^2(\tfrac{1}{2}\Theta)]^2\left(\frac{2}{vq^2}\right)^2\\&=\frac{1}{E^2(2\sin\frac{1}{2}\Theta)^4}.\end{aligned}\tag{13}$$

The cross section (but not the amplitude) is exact, even though ξ_2 need not be small.

[9] We note that

$$\left(\frac{1}{2M}\frac{\partial^2}{\partial Z^2}+K^2\right)\Psi=0,\quad\text{but}\quad\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}\right)\Psi\neq 0.$$

III. INFINITE-MASS TARGET

A. Asymptotic Conditions

We consider first a simple but physically important system. This consists of a fixed (infinite-mass) atomic target and a projectile of finite mass M. Only one electron on the target is considered. Such a system could describe muon or positron scattering from a hydrogen atom, where we regard the proton as much heavier than the muon or positron. Proton-hydrogen scattering requires equal target-projectile masses.

The Hamiltonian for the system is

$$H=-(1/2M)\nabla_R^2-(1/2m)\nabla^2+V(\mathbf{r},\mathbf{R}). \quad (14)$$

For a proton on a (fixed-nucleus) hydrogen atom, for example,

$$V(\mathbf{r},\mathbf{R})=-1/r-1/|\mathbf{r}-\mathbf{R}|+1/R, \quad (15)$$

where $\mathbf{R}$ and $\mathbf{r}$ are the projectile and electron coordinates referred to the target.

The electron-target system, in the absence of the projectile, has a complete set of eigenstates satisfying

$$[-(1/2m)\nabla^2-1/r]\phi_k(\mathbf{r})=\epsilon_k\phi_k(\mathbf{r}), \quad (16)$$

with k standing for the set of quantum numbers (n,l,m).

The projectile-electron system (neglecting the target interaction) is described by

$$H=-(1/2M)\nabla_R^2-(1/2m)\nabla^2-1/|\mathbf{r}-\mathbf{R}|. \quad (17)$$

Here it is convenient to introduce relative and center-of-mass coordinates,

$$\mathbf{r}'=\mathbf{r}-\mathbf{R},$$
$$\mathbf{S}=(M\mathbf{R}+m\mathbf{r})/(M+m), \quad (18)$$

so that the Hamiltonian becomes

$$H=-[1/2(M+m)]\nabla_s^2-(1/2\mu)\nabla'^2+v(\mathbf{r}'), \quad (19)$$

where $\mu=mM/(m+M)$. The Hamiltonian is separable, and we can immediately write the most general solution to the projectile-electron system as

$$\bar{G}_k(\mathbf{S})\bar{\phi}_k(\mathbf{r}'), \quad (20)$$

where the functions satisfy

$$[-(1/2\mu)\nabla'^2+v(\mathbf{r}')]\bar{\phi}_k(\mathbf{r}')=\bar{\epsilon}_k\bar{\phi}_k(\mathbf{r}'),$$
$$-\nabla_s^2\bar{G}_k(\mathbf{S})=\bar{K}^2\bar{G}_k(\mathbf{S}), \quad (21)$$

with $\bar{K}^2/2(M+m)=E-\bar{\epsilon}_k$.

At large separations between the projectile and target, the most general wave function can thus be written in the form

$$\Psi(\mathbf{r},\mathbf{R})\underset{R\to\infty}{\longrightarrow}\sum_k G_k(\mathbf{R})\phi_k(\mathbf{r})+\sum_k \bar{G}_k(\mathbf{S})\bar{\phi}_k(\mathbf{r}'), \quad (22)$$

where G_k satisfies

$$-\nabla_R^2G_k(\mathbf{R})=K^2G_k(\mathbf{R}), \quad (23)$$

with $K^2/2M=E-\epsilon_k$.

The expansion in (22) is actually overcomplete as regards continuum states of the electron. This is not a serious difficulty, but we will direct our attention primarily to discrete states.

The "initial" state is described by a plane-wave projectile and the target in a ground atomic state ϕ_0. We can choose the zero of energy so that $\epsilon_0=0$, and define a velocity v so that $E=\frac{1}{2}Mv^2$. The solution we seek is of the form

$$\Psi\underset{R\to\infty}{\longrightarrow}e^{iMvZ}\phi_0(\mathbf{r})+\text{outgoing waves}. \quad (24)$$

B. Rectilinear Trajectory Representation

We now turn our attention to the solution of the rectilinear trajectory problem, where $\mathbf{R}$ may be *regarded* as a classical variable

$$\mathbf{R}(\tau)=\mathbf{b}+\mathbf{v}\tau, \quad (25)$$

with $\mathbf{v}=v\hat{z}$, $\mathbf{b}\cdot\mathbf{v}=0$, and $\mathbf{b}$ fixed. The variable $\tau=Z/v$ is used here instead of t in order to emphasize the distinction between its role and that of real time. The corresponding Schrödinger equation is

$$\left[i\frac{\partial}{\partial\tau}-H_e(\mathbf{r},\mathbf{p};\mathbf{R}(\tau))\right]\psi_\alpha(\mathbf{r};\mathbf{b},\tau)=0, \quad (26a)$$

where $H_e=-(2m)^{-1}\nabla^2+V(\mathbf{r},\mathbf{R})$.

Because $\mathbf{R}$ is related to $(\mathbf{b},\tau)$ uniquely by (25), we may equally well set

$$\psi_\alpha(\mathbf{r};\mathbf{b},\tau)\equiv\psi_\alpha(\mathbf{r};\mathbf{R}). \quad (26b)$$

The $\psi_\alpha(\mathbf{r};\mathbf{b},\tau)$ for all impact parameters $\mathbf{b}$ define the wave functions $\psi_\alpha(\mathbf{r};\mathbf{R})$ for all $\mathbf{R}$, and $\psi_\alpha(\mathbf{r};\mathbf{R})$ satisfies (7).

As in the adiabatic method the above differential equation defines a set of basis states $\psi_\alpha\leftrightarrow|\alpha\rangle$ which are complete and which may be chosen to be orthonormal in the electronic coordinates.

$$\langle\alpha|\alpha'\rangle=\int\psi_\alpha^*(\mathbf{r};\mathbf{R})\psi_{\alpha'}(\mathbf{r};\mathbf{R})d^3r=\delta_{\alpha,\alpha'}. \quad (27)$$

The orthonormality is obvious in the asymptotic limit $Z\to-\infty$ since the ψ_α go to the separated-atom solutions; it is preserved for arbitrary Z by the unitarity of the state transition matrix $U(\tau_2,\tau_1)$. The index α may specify the initial electronic configuration. We will be interested in the state, say $\alpha=0$, where ψ_0 reduces to the atomic ground state for $Z\to-\infty$ [Eq. (24)]. For large positive Z, however, the wave function is given to lowest order in m/M by

$$\psi_0(\mathbf{r};\mathbf{R})\underset{Z\to\infty}{\longrightarrow}\sum a_k(\mathbf{b})\phi_k(\mathbf{r})e^{-i\epsilon_kZ/v}$$
$$+\sum_k\bar{a}_k(\mathbf{b})\phi_k(\mathbf{r}-\mathbf{R})e^{-imvz}e^{-i(\epsilon_k+\frac{1}{2}mv^2)Z/v}, \quad (28)$$

where ϵ_k is the atomic hydrogen energy ($\epsilon_0=0$ by choice); $a_k(b)$ and $\bar{a}_k(b)$ are the amplitudes for the possible direct and electron transfer processes; and the ϕ_k are hydrogenic functions for electrons of mass m. Coupled state calculations for these amplitudes have recently been made, for example, by Gallaher and Wilets,[10] and others.

C. Solution of the Full Wave Function

The solution to the complete Schrödinger equation $H\Psi=\frac{1}{2}Mv^2\Psi$, with H corresponding to the Hamiltonian (11), is now expanded in terms of the ψ_α:

$$\Psi(\mathbf{r},\mathbf{R})=\sum_\alpha F_\alpha(\mathbf{R})\psi_\alpha(\mathbf{r};\mathbf{R}). \tag{29}$$

This is substituted into the Schrödinger equation and the orthonormality properties of the ψ_α are utilized to obtain

$$\begin{aligned}[-\nabla_R^2/2M-\tfrac{1}{2}Mv^2]F_\alpha(\mathbf{R})&\\ =\sum_{\alpha'}[(1/M)\langle\alpha|\boldsymbol{\nabla}_R|\alpha'\rangle\cdot\boldsymbol{\nabla}_R-\langle\alpha|H_e|\alpha'\rangle&\\ +(1/2M)\langle\alpha|\nabla_R^2|\alpha'\rangle]F_{\alpha'}(\mathbf{R}).&\end{aligned} \tag{30}$$

The above equation is exact. We may solve it in a variety of ways, subject to the asymptotic condition (24) which requires

$$F_\alpha(\mathbf{R})\underset{R\to\infty}{\longrightarrow}\delta_{\alpha,0}e^{iMvZ}+\text{outgoing waves}. \tag{31}$$

We also know that in the limit of infinite mass M the Schrödinger equation simplifies to the form (7), i.e., the straight-line trajectory. This suggests the following (presumably asymptotic) expansion:

$$\begin{aligned}F_\alpha(\mathbf{R})&=e^{iMvZ}[F_\alpha^{(0)}+(1/M)F_\alpha^{(1)}+(1/M^2)F_\alpha^{(2)}+\cdots]\\ &=e^{iMvZ}\sum_{j=0}^{\infty}\frac{F_\alpha^{(j)}}{M^j}.\end{aligned} \tag{32}$$

Since we are working in atomic units, $M^{-1}=m/M$ suffices as a nondimensional expansion parameter. In the expansion v (not E) is regarded as fixed. We substitute this back into Eq. (30) to obtain

$$\begin{aligned}\sum_j\left(-\frac{\nabla_R^2}{2M}-iv\frac{\partial}{\partial Z}\right)\frac{F_\alpha^{(j)}}{M^j}&\\ =\sum_{j,\alpha'}\left[\langle\alpha|iv\frac{\partial}{\partial Z}-H_e|\alpha'\rangle+(1/M)\langle\alpha|\boldsymbol{\nabla}_R|\alpha'\rangle\cdot\boldsymbol{\nabla}_R\right.&\\ \left.+(1/2M)\langle\alpha|\nabla_R^2|\alpha'\rangle\right]\frac{F_{\alpha'}^{(j)}}{M^j}.&\end{aligned} \tag{33}$$

The result simplifies by virtue of the defining equation (7) for ψ_α; the first term on the right-hand side vanishes. Arranging by orders of M^{-1}, we obtain a set of recursion relations among the $F_\alpha^{(j)}$ in which the jth equation is

$$\begin{aligned}-iv\frac{\partial F_\alpha^{(j)}}{\partial Z}&=\tfrac{1}{2}\nabla_R^2F_\alpha^{(j-1)}\\ &+\sum_{\alpha'}(\langle\alpha|\boldsymbol{\nabla}_R|\alpha'\rangle\cdot\boldsymbol{\nabla}_R+\tfrac{1}{2}\langle\alpha|\nabla_R^2|\alpha'\rangle)F_{\alpha'}^{(j-1)}.\end{aligned} \tag{34}$$

These are sufficient conditions to satisfy (26) and we exhibit the lowest orders.

M^0 Order

$$-iv\frac{\partial F_\alpha^{(0)}}{\partial Z}=0. \tag{35a}$$

To satisfy our boundary condition at $Z\to-\infty$, we set

$$F_\alpha^{(0)}=\delta_{\alpha,0}. \tag{35b}$$

This procedure omits reflections; however, for atomic collisions the omission is not serious. The reflections may be included as will be shown in Sec. IV.

M^{-1} Order

The solution for $F_\alpha^{(0)}$ leads to an equation for $F_\alpha^{(1)}$

$$-iv\frac{\partial F_\alpha^{(1)}}{\partial Z}=\langle\alpha|\tfrac{1}{2}\nabla_R^2|0\rangle \tag{36a}$$

with the solution

$$F_\alpha^{(1)}=\frac{i}{v}\int_{-\infty}^{Z}dZ'\,\langle\alpha|\tfrac{1}{2}\nabla_{R'}^2|0\rangle. \tag{36b}$$

The expansion may be carried further (to any desired order) but soon becomes complicated. To lowest order the wave function is simply a plane wave times the straight-line trajectory electronic function

$$\Psi=e^{iMvZ}\psi_0(\mathbf{r};\mathbf{R}). \tag{37}$$

The first correction terms contain a factor $(Mv)^{-1}$ and are given by

$$i\tfrac{1}{2}(Mv)^{-1}e^{iMvZ}\sum_\alpha\left[\int dZ'\,\langle\alpha|\nabla_{R'}^2|0\rangle\right]\psi_\alpha(\mathbf{r};\mathbf{R}). \tag{38}$$

We use the defining equation for the ψ_α to expand the correction term (36b) in the following manner:

$$\begin{aligned}M^{-1}F_\alpha^{(1)}=-\frac{\epsilon_\alpha}{2Mv^2}-\frac{i}{2Mv^3}\int dZ'\,\langle\alpha|H_e^2|0\rangle&\\ +\frac{i}{2Mv}\int dZ'\,\langle\alpha|\nabla_b^2|0\rangle,&\end{aligned} \tag{39}$$

[10] L. Wilets and D. F. Gallaher, Phys. Rev. **147**, 13 (1966); D. F. Gallaher and L. Wilets, *ibid.*, this issue **169**, 139 (1968).

where we define $\epsilon_\alpha=\langle\alpha|H_e|0\rangle$ and have made use of

$$\frac{\partial\epsilon_\alpha}{\partial Z}=\langle\alpha|\frac{\partial H_e}{\partial Z}|0\rangle. \tag{40}$$

The internuclear "potential" ϵ_α is a tube beyond the target in the "shadow" of the interaction region. The second term in (39) may be viewed as a correction to the internuclear wave number by means of rewriting it as follows:

$$-\frac{i}{2Mv^3}\int dZ'\,\langle\alpha|H_e^2|0\rangle \rightarrow \exp\left(-\frac{i}{2Mv^3}\int dZ'\,\langle\alpha|H_e^2|0\rangle\right)-1. \tag{41}$$

This form is valid through the interaction region and pulls in higher-order corrections as well. Using Eq. (41) we write out the $\alpha=0$ part of the wave function (to order M^{-1}) as follows:

$$\begin{aligned}e^{iMvZ}F_0\psi_0 &=\sum_k\left\{\exp\left[iMv\int dZ'\left(1-\frac{\epsilon_k}{Mv^2}-\frac{\langle 0|H_e^2|0\rangle}{2(Mv^2)^2}\right)\right]a_k(b)\phi_k\right.\\ &\quad+\exp\left[iMv\int dZ'\left(1-\frac{\epsilon_k}{Mv^2}-\frac{\frac{1}{2}mv^2}{Mv^2}-\frac{\langle 0|H_e^2|0\rangle}{2(Mv^2)^2}\right)\right]\\ &\quad\left.\times\bar{a}_k(b)\bar{\phi}_k e^{-imvz}\right\}+\frac{\epsilon_0}{2Mv^2}e^{iMvZ}\psi_0\\ &\quad+\frac{i}{2Mv}\left[e^{iMvZ}\int dZ'\,\langle\alpha|\nabla_b^2|0\rangle\right]\psi_0.\end{aligned} \tag{42}$$

This expression shows how the internuclear wave number is corrected for the Q of the reaction. The nuclear recoil terms emerge from ψ_0 and are first order in ξ_2. Equation (41) contributes a second-order correction. The third term in Eq. (39) produces corrections due to the average energy transferred to the nuclei perpendicular to the rectilinear trajectory.

At this point our motivation for suggesting a modified impact parameter calculation, Eq. (6), is clarified. The first-order corrections in such a calculation would simply be the third term of Eq. (39).

The above results are remarkable. They suggest that the lowest-order wave function, Eq. (37), is a very accurate prescription for the total quantum-mechanical wave function at moderate energies. This is deceiving, but in a rectifiable way. For large values of R, our solution should be of the asymptotic form (28). In fact for large impact parameters b, ψ_0 reduces to the initial atomic state ϕ_0.

D. Introduction of a Fraunhofer Screen

We can avoid the above complications by using our knowledge of the exact solutions to the wave equation for large R. This suggests dividing the space into two parts. The separation is accomplished by inserting an imaginary screen to the right of the interaction region at some distance Z_0 (see Fig. 1). The region to the right of the screen is assumed to be free of interactions involving *both* the projectile and the target, and will be called simply the "outside" region. The left-hand region will be called the "inside" region.

In the outside region we choose wave functions to be linear combinations of

$$G_k(\mathbf{R})\phi_k(\mathbf{r}) \tag{43}$$

and

$$\bar{G}_k(\mathbf{S})\bar{\phi}_k(\mathbf{r}') \tag{44}$$

depending upon whether the electron remains with the target or travels with the projectile; the latter is called electron transfer scattering. For definiteness, we can consider continuum states as belonging to the former type (and ignore the lack or orthogonality between target continuum states and projectile bound states).

Both the $G(\mathbf{R})$ and the $\bar{G}(\mathbf{S})$ satisfy homogeneous wave equations in the outside region. By Kirchoff's theorem, we can determine the functions everywhere to the right of Z_0 from an integral over the "screen." At large distances, the expression is

$$G(\mathbf{R})\underset{R\to\infty}{\longrightarrow}-(1/4\pi R)e^{iKR}\oint e^{-iKb\sin\Theta\cos\Phi} \times\hat{n}\cdot[\nabla_{R'}G(\mathbf{R}')+iK\hat{R}G(\mathbf{R}')]da' \tag{45}$$

and a similar expression holds for $\bar{G}(\mathbf{S})$.

It is now a matter of decomposing the inside wave functions [which to lowest order are $e^{iKZ}\psi_0(\mathbf{r};\mathbf{R})$] into the noninteracting form given in Eq. (22). This permits an identification of the G and $\bar{G}$ associated with appropriate electron states.

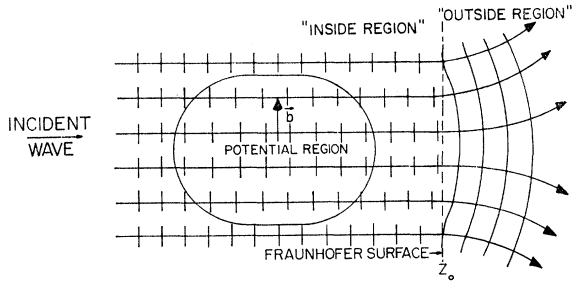

FIG. 1. The incident wave is described by a set of rectilinear trajectories with fixed b (horizontal lines). The vertical lines represent the wave fronts and indicate the phase information inherent in the set of rectilinear functions in the inside region. The wave function is continued in the outside region by means of an imaginary Fraunhofer screen which is placed a distance Z_0 past the interaction region.

In what follows we will consider the target and projectile nuclei to be point particles of charge $+e$. This is done only to simplify the charge transfer scattering.

E. Differential Cross Sections

The electron-on-target states are easier to consider, because they are immediately of the form $G_k(\mathbf{R})\phi_k(\mathbf{r})$, with

$$G_k(\mathbf{R})=a_k(\mathbf{b})e^{i(Mv-\epsilon_k/v)Z}=a_k(\mathbf{b})e^{iKZ}, \quad Z\sim Z_0, \tag{46}$$

where here

$$K=K_k=Mv-\epsilon_k/v\simeq[(\tfrac{1}{2}Mv^2-\epsilon_k)2M]^{1/2}. \tag{47}$$

Note that Eq. (47) shows that, to the order of the calculation (M^{-1}), the projectile wave number K is properly corrected for the Q of the reaction.

Let us consider the initial state of the target to be an s state. The reaction should be independent of the φ direction; that is, it should depend only on $|\mathbf{b}|$. This does not mean that the final ψ's have only $m=0$ components, and actual calculations yield appreciable $m\neq 0$ components. Let Φ be the nuclear azimuthal coordinate; this defines the plane of the collision for the semiclassical calculation. In terms of the relative electronic coordinate $\varphi'=\varphi-\Phi$ the wave function can be written

$$\sum_k a_k(|\mathbf{b}|)e^{iKZ}\phi_{nlm}(r,\theta,\varphi') =\sum_k a_k(|\mathbf{b}|)e^{iKZ}e^{-im\Phi}\phi_{nlm}(r,\theta,\varphi). \tag{48}$$

This yields, finally, the identification

$$G_k(\mathbf{R})=a_k(b)e^{iKZ}e^{-im\Phi} \tag{49}$$

for the inside solution.

We are now in a position to evaluate the asymptotic value of $G_k(\mathbf{R})$ for the electron-on-target final states. Substitution of (49) into (45) and separation of the incident and scattered waves gives

$$\begin{aligned} G_k(\mathbf{R}) \underset{R\to\infty}{\longrightarrow} & e^{iKZ}\delta_{k,0}-iKe^{iKZ_0}(e^{iKR}/R)\cos^2(\tfrac{1}{2}\Theta)\int_0^\infty bdb \\ &\times(a_k(b)-\delta_{k,0})\int_0^{2\pi}\frac{d\Phi}{2\pi}e^{-iKb\sin\Theta\cos\Phi}e^{-im\Phi} \\ =& e^{iKZ}\delta_{k,0}+K(-i)^{m+1}(e^{iK(R+Z_0)}/R)\cos^2(\tfrac{1}{2}\Theta) \\ &\times\int_0^\infty bdb\,(a_k(b)-\delta_{k,0})J_m(Kb\sin\Theta) \\ \equiv & (e^{iK(R+Z_0)}/R)f_k(\Theta)+e^{iKZ}\delta_{k,0}, \end{aligned} \tag{50}$$

where

$$\begin{aligned} f_k(\Theta)=&K\cos^2(\tfrac{1}{2}\Theta)(-i)^{m+1}\int_0^\infty bdb \\ &\times(a_k(b)-\delta_{k,0})J_m(qb), \\ q=&K\sin\Theta. \end{aligned} \tag{51}$$

The cross section is given by

$$\frac{d\sigma_k}{d\Omega}=\frac{v_k}{v}|f_k(\Theta)|^2. \tag{52}$$

For electron transfer, the result to lowest order is equally simple, with $\bar{a}_k(b)$ replacing $a_k(b)$. Higher-order correction terms due to nuclear recoil and due to the first-order correction terms $F_\alpha^{(1)}$ of Sec. III C may be displayed systematically but are cumbersome. We omit further development of these terms since, as with expansions in general, the utility of the method depends on our not having to actually calculate them. However, in the spirit of Eq. (42) we remark that the projectile wave number K (or $\bar{K}$ for electron transfer) and velocity v_k (or $\bar{v}_k$) which appears in Eqs. (51) and (52) may be replaced by the known asymptotic values for improved accuracy at no additional complexity.

The above expression has the familiar Fraunhofer diffraction form, and arises in a wide variety of scattering and reaction problems. It generally emerges out of calculations valid only for small-angle scattering, as is presumably also the case here. According to "folklore," the extension to large-angle scattering can be effected experimentally by ignoring the factor $\cos^2(\frac{1}{2}\Theta)$ and replacing $\sin\Theta$ by Θ in the argument of the Bessel function, although most theorists would prefer to replace the $\sin\Theta$ by $2\sin\frac{1}{2}\Theta$.

IV. BACK SCATTERING

For strong interactions, we may include reflections by solving Eq. (30) in successive orders where the right-hand side is taken to be of higher order. Thus, in lowest order we get

$$[-\nabla_R^2/2M-\tfrac{1}{2}Mv^2]F_\alpha^{(0)}(R)=0. \tag{53}$$

The solution which satisfies our boundary condition at $Z\to-\infty$ is

$$F_\alpha^{(0)}=\delta_{\alpha,0}e^{iMvZ}. \tag{54}$$

The next-order equation is obtained by substitution of Eq. (54) into the right side of Eq. (30).

$$\begin{aligned} &[-\nabla_R^2/2M-\tfrac{1}{2}Mv^2]F_\alpha^{(1)} \\ &\quad=\langle\left\{\alpha|iv\frac{\partial}{\partial Z}-H_e|0\rangle+\frac{1}{2M}\langle\alpha|\nabla_R^2|0\rangle\right\}e^{iMvZ} \\ &\quad=\frac{1}{2M}\langle\alpha|\nabla_R^2|0\rangle e^{iMvZ}. \end{aligned} \tag{55}$$

The last step follows from Eq. (7). The solution to (55) is written with the aid of the Green's function

$$G(\mathbf{R},\mathbf{R}')=\frac{1}{4\pi}\frac{e^{iMv|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}, \qquad [-\nabla_R^2-(Mv)^2]G(\mathbf{R},\mathbf{R}')=\delta(\mathbf{R}-\mathbf{R}'). \tag{56}$$

The solution to (55) is

$$F_\alpha^{(1)}=\frac{1}{4\pi}\int d^3R'\frac{e^{iMv|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\langle\alpha|\frac{\nabla_{R'}^2}{2M}|0\rangle e^{iMvZ'}. \quad (57)$$

We note at this point that the lowest-order solution (54) must yet be continued by means of a Fraunhofer screen. The first-order correction (57) is, however, already properly continued into the scattering region by use of the appropriate Green's function. At large distances from the target, the correction term simplifies to

$$F_\alpha^{(1)}\underset{R\to\infty}{\longrightarrow}\frac{e^{iMvR}}{R}\frac{1}{4\pi}\int dZ'\int_0^{2\pi}d\Phi\int_0^\infty bdb \times e^{-iMvb\sin\Theta\cos\Phi}e^{iMv(1-\cos\Theta)Z'}\langle\alpha|\frac{\nabla_{R'}^2}{2M}|0\rangle. \quad (58)$$

The matrix element $\langle\alpha|\nabla_{R'}^2|0\rangle$ contains terms proportional to $e^{-im\Phi}$ where m ranges over all electronic states included. This is the only dependence of the matrix element on the azimuthal angle, thus the above integral over Φ may be performed for each such term.

$$F_\alpha^{(1)}\underset{R\to\infty}{\longrightarrow}\sum_m\frac{e^{iMvR}}{R}\tfrac{1}{2}(-i)^m\int_0^\infty bdb\,J_m(qb) \times\int dZ'\,e^{iMv(1-\cos\Theta)Z'}\langle\alpha,m|\frac{\nabla_{R'}^2}{2M}|0\rangle, \quad (59)$$

where we denote by $\langle\alpha,m|\nabla_{R'}^2|0\rangle$ that part of the complete matrix element which is proportional to $e^{-im\Phi}$ and $q=Mv\sin\Theta$ as usual.

For large Θ and Mv, the integrand of (59) oscillates rapidly in Z'. The back scattering is thus negligible when ξ_1 is small as is generally the case for atomic collisions.

V. NUCLEAR IDENTITY

For collisions involving identical nuclei, it is necessary to project, out of the solutions obtained above, the states of the appropriate symmetry in the nuclear coordinates. This involves interference terms between the direct scattering amplitude $f_k(\Theta)$ and the exchange scattering amplitude $\bar{f}_k(\pi-\Theta)$.

Our expansion is presumably valid only for small-angle scattering, although this may be generalizable. For example, the plane Fraunhofer "screen," which limits us to angles less than $\frac{1}{2}\pi$, could be replaced by spherical "screen," which would allow calculation of arbitrary scattering angles or two parallel screens to right and left of the target. However, atomic reactions are dominated by small-angle scattering. This implies that interference terms involving $f_k(\Theta)\bar{f}_k(\pi-\Theta)$ will be small, and nuclear identity is not expected to play an important role at any but the very low energies.

VI. CONCLUSIONS

In conclusion, we emphasize that the eikonal method gives an extremely simple prescription for converting a semiclassical calculation into a fully quantal calculation. The utility of the method rests on the smallness of the correction terms which, at moderate projectile energies, are indeed quite small. It avoids the difficult and ambiguous intermediate step of determining an effective potential. The eikonal method is not only complementary to the adiabatic method—which can also be developed systematically and fully quantally—but its range of validity penetrates deeply into the adiabatic realm.

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