(1940).
[4]M. J. Seaton, Phil. Trans. Roy. Soc. London A245, 469 (1953); M. J. Seaton, Proc. Roy. Soc. (London) A231, 37 (1955).
[5]K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. 157, 51 (1967).
[6]R. J. W. Henry, P. G. Burke, and A. L. Sinfailam, Phys. Rev. 178, 218 (1969).
[7]D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, Phil. Trans. Roy. Soc. London A243, 93 (1950).
[8]I. C. Percival, Proc. Phys. Soc. (London) A70, 241 (1957).
[9]A. D. Stauffer and M. R. C. McDowell, Proc. Phys. Soc. (London) A89, 289 (1966).
[10]A. E. S. Green, D. L. Sellin, and A. S. Zachor, Phys. Rev. 184, 1 (1969).
[11]J. E. Purcell, R. A. Berg, and A. E. S. Green, Phys. Rev. A 2, 107 (1970); 3, 509 (1971).
[12]P. S. Ganas and A. E. S. Green, Phys. Rev. A 4, 182 (1971).
[13]T. Sawada, J. E. Purcell, and A. E. S. Green, Phys. Rev. A 2, 193 (1971).
[14]R. A. Berg and A. E. S. Green, Adv. Quantum Chem. (to be published).
[15]P. A. Kazaks, P. S. Ganas, and A. E. S. Green, Phys. Rev. A 6, 2169 (1972).
[16]W. N. Shelton and E. S. Leherissey (report of work prior to publication, 1971).
[17]G. Sunshine, B. B. Aubrey, and B. Bederson, Phys. Rev. 154, 1 (1967).
[18]E. J. Stone and E. C. Zipf, Phys. Rev. A 4, 610 (1971).
[19]A. Messiah, *Quantum Mechanics* (Wiley, New York, 1965). The conventions for the angular-momentum couplings used throughout this work are those of this book.
[20]A. B. Prag, C. E. Fairchild, and L. C. Clarn, Phys. Rev. 137, A1358 (1965).
[21]F. A. Morse and F. Kaufman, J. Chem. Phys. 42, 1785 (1965).
[22]B. D. Savage and G. M. Lawrence, Astrophys. J. 146, 940 (1966).
[23]D. A. Parkes, L. F. Keyser, and F. Kaufman, Astrophys. J. 149, 217 (1967).
[24]G. Boldt and F. Labuhn, Z. Naturforsch. A22, 1613 (1967).
[25]J. E. Hesser, J. Chem. Phys. 48, 2518 (1968).
[26]G. M. Lawrence and M. George, Phys. Rev. 175, 40 (1968).
[27]C. Lin, D. A. Parkes, and F. Kaufman, J. Chem. Phys. 53, 3896 (1970).
[28]E. C. Zipf (private communication).
[29]K. Smith and L. A. Morgan, Phys. Rev. 165, 110 (1968).
[30]S. P. Rountree and R. J. W. Henry, Phys. Rev. Abstracts 3, 5 (1972).

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Impact-Parameter Theory Defined as a Constant-Collision-Velocity Semiclassical Limit of a Complete Quantum-Scattering Picture

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A semiclassical limit, defined in terms of large mass and energy at fixed arbitrary collision velocity, is shown to be a simple formal prescription for obtaining a quantum treatment of the impact-parameter method and the eikonal approximation. In particular, for atom-atom collisions, the resultant approximation is emphasized to be a proper strong-coupling equation for inelastic processes, as opposed to the adiabatic result of a large-mass limit at fixed energy.

I. INTRODUCTION

Semiclassical analysis and perturbation theory are two systematic means of obtaining approximate solutions in quantum mechanics to complex problems. This paper presents an argument for the recognition of a semiclassical limit distinct from the usual large-mass limit[1]; the new limit is called isovelocity for it is taken at large mass with fixed velocity rather than fixed energy. The usual semiclassical limit involves the construction of an asymptotic solution[2] of an ordinary differential equation,

$$\left(\alpha^2 \frac{d^2}{dr^2} + K^2(r)\right)\psi(r, \alpha) = 0 , \qquad K^2(r) = (2\mu/\hbar^2)[E - V(r)] , \tag{1}$$

as the dimensionless parameter α becomes small. α is sometimes associated with the physical constant $\hbar$, but an association with the mass μ, defined by replacing μ by μ/α^2 in the Schrödinger equation, is advantageous because it immediately shows that the asymptotic solutions are better for a proton than for a positron with the same energy in a given potential field. This paper will concern

scattering states, so the energy is a physical parameter, not a discrete eigenvalue of the Hamiltonian operator. The asymptotic solution of Eq. (1) greatly simplifies two-body elastic scattering since the differential cross section can be expressed as a series of spherical harmonics using the JWKB phase shifts from the radial Schrödinger equation,[3] which is of the ordinary type. The radial equation could have more than one transition point [where $K(r)=0$], but a uniform asymptotic solution is only known in simple form for one.[4] Uniform means[5]

$$\left(\alpha^2 \frac{d^2}{dr^2} + K^2(r)\right) \psi^{\mathrm{UNF}}(r, \alpha) = \alpha^2 R(r) , \tag{2}$$

where the residual $\alpha^2 R(r)$ is of the order of α^2 and bounded for all r. This implies $\psi - \psi^{\mathrm{UNF}} = O(\alpha)$ by a direct distorted wave correction.[6] The nonuniform JWKB solutions have a residual of the order of α^2, but it is unbounded at the transition (turning) point and not integrable on the real axis. The knowledge of a uniform solution properly determines all connection formulas for the one-dimensional problem.

A generalization of the usual large-mass limit defined through Eq. (1) is the $\alpha \to 0$ limit of

$$[\alpha^2 \nabla_R^2 + K^2(\vec{\mathrm{R}})]\, \psi(\vec{\mathrm{R}}, \alpha) = 0 , \tag{3}$$

where ∇_R^2 is the Laplacian in the coordinate space $\vec{\mathrm{R}}$, which might have any dimension. For two-body elastic scattering, where $\vec{\mathrm{R}}$ is the relative separation, the form of the asymptotic solution is well characterized[7-9]; in lowest order the solutions exhibit unbounded behavior on surfaces in $\vec{\mathrm{R}}$ space analogous to the JWKB singularities at the radial turning points. The theories of Miller[10] and Marcus[11] fall into the limit of Eq. (3) when more than two heavy particles are considered. Imposition of reactive scattering boundary conditions is then necessary and discussed in their works. For two-body scattering observed in a given experimental setup, the $\alpha \to 0$ limit ensures that the result will be described by classical mechanics.[3] For many heavy particles classical behavior would, at the least, also require all bounded motions to be prepared and detected on a large energy scale compared to the separation of quantized levels.

The purpose of the present paper is to establish the formal asymptotic limit that can be applied to scattering involving two heavy particles and that gives an approximation valid in the strong coupling region for inelastic processes. That this can be done seems interesting in itself. This strong coupling region occurs in atomic collisions when nuclear and electronic velocities are of the same order (excepting the avoided-crossing or near-degeneracy problem, where strong coupling persists at lower energy), and implies that when a parameter is introduced to define a unique, clearly stated limit, the heavy masses and energy should be scaled to be large together. This fulfills the conditions for the validity of the straight-line impact-parameter method,[12,13] but it does not require classical position and momentum localization of the heavy particles.[14] In the two-body problem, it also fulfills the conditions set up by Glauber[15] for the useful area of application of the eikonal approximation. It is not unexpected, therefore, that these approximations will develop in the isovelocity limit in a simple and straightforward way. As an additional clarification of purpose, it should be stated that high-energy theories, such as the Born and Glauber[15] approximations for inelastic processes, are not directly mass related and, moreover, are not strong coupling descriptions of the scattering event. What is discussed here is a proper placement of the impact-parameter method among approximations in scattering theory by finding the particular physical limit in which it becomes a good solution.

The remainder of the paper is structured as follows: Section II presents an outline of the large-mass limit at fixed energy in order to demonstrate that it is the expected adiabatic limit for atomic collisions connected with a three-dimensional asymptotic solution of the kind defined by Eq. (3) for nuclear motion. This is to be distinguished from the large-mass limit at fixed velocity developed in Secs. III and IV.

II. LARGE-MASS LIMIT AT FIXED ENERGY

The physical system consists of two heavy particles and other lighter particles which are bound to the heavier ones—an atom-atom collision in particular. For this problem one scales the nuclear masses m_A and m_B as m_A/α^2 and m_B/α^2 and obtains a solution to the Schrödinger equation whose residual error vanishes as $\alpha \to 0$.[16] This leads to a Born–Oppenheimer factorization of the electron and nuclear motion.[17-21] The full Schrödinger equation, including center-of-mass motion, is

$$\left(-\frac{\hbar^2}{2m_A} \nabla_{X_A}^2 - \frac{\hbar^2}{2m_B} \nabla_{X_B}^2 + H^{\mathrm{el}} - \mathcal{E}\right) \times \Psi(\vec{\mathrm{X}}_A, \vec{\mathrm{X}}_B, \{\vec{\mathrm{x}}_i\}) = 0 , \tag{4}$$

where H^{el} is the electronic Hamiltonian:

$$H^{\mathrm{el}} = -\frac{\hbar^2}{2m} \sum_i \nabla_{x_i}^2 - Z_A e^2 \sum_i \frac{1}{r_{Ai}} - Z_B e^2 \sum_i \frac{1}{r_{Bi}} + e^2 \sum_{i>j} \sum \frac{1}{r_{ij}} + Z_A Z_B e^2 \frac{1}{R} . \tag{5}$$

m_A and m_B are the nuclear masses, m is the electron mass, Z_A and Z_B are the nuclear charges, R is the nuclear separation, and r_{ij} is the various interparticle separations. m_A and m_B are now scaled with

the smallness parameter α^2 giving

$$\left[\alpha^2\left(-\frac{\hbar^2}{2m_A}\nabla_{X_A}{}^2-\frac{\hbar^2}{2m_B}\nabla_{X_B}{}^2\right)+H^{el}-\mathcal{E}\right]\times\Psi(\vec{X}_A,\vec{X}_B,\{\vec{x}_i\},\alpha)=0\ . \quad (6)$$

As $\alpha\to 0$, the wave function Ψ has an essential singularity in α; that is, Ψ is not expandable as a Taylor's series in α (like a perturbation series), if it is to represent bounded motion of the electrons. This does not disagree with the original Born–Oppenheimer method for nuclear bound states,[17] for there the expansion is in powers of a mass ratio after scaling the nuclear coordinates with the ratio (a "stretching," see Wasow, Ref. 2); the resulting expansion is valid for nuclear motion covering a range proportional to a power of α. By not introducing the coordinate scaling, the range of the nuclear motion is arbitrary and the solution is shown to be semiclassical. The essence of the construction of an approximate solution to Eq. (6) comes from the substitution

$$\Psi(\vec{X}_A,\vec{X}_B,\{\vec{x}_i\},\alpha)=A(\vec{X}_A,\vec{X}_B,\{\vec{x}_i\},\alpha)\times e^{iS(\vec{X}_A,\vec{X}_B,\{\vec{x}_i\})/\alpha}\ , \quad (7)$$

where A is assumed to have a Taylor's series in α analogous to the method for ordinary differential equations.[2] By requiring the coefficient of each power of α to vanish after substitution, one obtains a series of equations (possibly algebraic, differential, eigenvalue, etc.) that are solved successively to higher order in α in the simplest possible manner consistent with physical conditions. A formal solution of Eq. (6) is obtained as a series in α multiplying the essentially singular exponential, $e^{iS/\alpha}$. These expansions, called asymptotic, usually diverge[2] and may contain unacceptable singularities even at zero order in the A series; the singularities might be removed by a choice of function other than the exponential of the essential singular behavior in α.[4,5,8] In this paper no pretense of rigor in the sense of an asymptotic series is ever intended; the ordering of the expansions is clear, however, and they are interpreted in physical terms. From Eqs. (6) and (7) after substitution, the coefficients of α^0 and α^1 are[22]

$$\left(\frac{\hbar^2}{2m_A}\vec{\nabla}_{X_A}S\cdot\vec{\nabla}_{X_A}S+\frac{\hbar^2}{2m_B}\vec{\nabla}_{X_B}S\cdot\vec{\nabla}_{X_B}S-\mathcal{E}\right)A_0+H^{el}A_0=0\ , \quad (8)$$

$$\sum_{P=A,B}\left[-i\frac{\hbar^2}{2m_P}\left(2\vec{\nabla}_{X_P}S\cdot\vec{\nabla}_{X_P}A_0+A_0\nabla_{X_P}{}^2S\right)+\frac{\hbar^2}{2m_P}\vec{\nabla}_{X_P}S\cdot\vec{\nabla}_{X_P}SA_1\right]+(H^{el}-\mathcal{E})A_1=0\ , \quad (9)$$

where $A=A_0+\alpha A_1+\alpha^2A_2+\cdots$. The removal of barycentric motion is delayed to avoid the explicit appearance of nuclear mass[23] terms in H^{el} that do not enter the equations until second order in α. Define

$$\gamma^i_{jk}=\frac{m_i}{m_j+m_k}\ ,\quad \mu^i_j=\frac{m_im_j}{m_i+m_j}\ ,\quad M=m_A+m_B\ , \quad (10)$$

$$\vec{X}=\gamma^A_{AB}\vec{X}_A+\gamma^B_{AB}\vec{X}_B\ ,\quad \vec{R}=\vec{X}_A-\vec{X}_B\ ,\quad \vec{r}_i=\vec{x}_i-\vec{X}\ ,$$

so that,

$$\vec{\nabla}_{X_A}=\gamma^A_{AB}\vec{\nabla}_X+\vec{\nabla}_R-\gamma^A_{AB}\sum_i\vec{\nabla}_{r_i}\ ,$$

$$\vec{\nabla}_{X_B}=\gamma^B_{AB}\vec{\nabla}_X-\vec{\nabla}_R-\gamma^B_{AB}\sum_i\vec{\nabla}_{r_i}\ , \quad (11)$$

$$\vec{\nabla}_{x_i}=\vec{\nabla}_{r_i}\ .$$

$\vec{X}$ is the coordinate of the center of mass of the nuclei, denoted CN later. Since H^{el} is only a function of $\vec{\nabla}_{x_i}$ and distances between particles, it may be expressed

$$H^{el}(\vec{\nabla}_{x_i},\vec{x}_i,\vec{X}_A,\vec{X}_B)=\bar{H}^{el}(\vec{\nabla}_{r_i},\vec{r}_i,\vec{R})\ ,$$

$$S=S(\vec{X}_A,\vec{X}_B)=\bar{S}(\vec{X},\vec{R})\ . \quad (12)$$

Equation (8) becomes

$$\left(\frac{\hbar^2}{2M}\vec{\nabla}_X\bar{S}\cdot\vec{\nabla}_X\bar{S}+\frac{\hbar^2}{2\mu^A_B}\vec{\nabla}_R\bar{S}\cdot\vec{\nabla}_R\bar{S}-\mathcal{E}\right)A_0+\bar{H}^{el}A_0=0\ , \quad (13)$$

which is an eigenvalue equation in bound-state electron space $\{\vec{r}_i\}$, parametric on $\vec{R}$, which may be solved with any of the fixed-nuclei eigenfunctions:

$$\bar{H}^{el}\chi_m(\{\vec{r}_i\}|\vec{R})=W_m(R)\chi_m(\{\vec{r}_i\}|\vec{R})\ . \quad (14)$$

The vector dependence on $\vec{R}$ can be removed by a rotational transformation. A solution of Eq. (13) can be written

$$A_0=\chi_m(\{\vec{r}_i\}|\vec{R})f_m(\vec{X},\vec{R}) \quad (15)$$

by separation of variables, requiring

$$(\hbar^2/2M)\vec{\nabla}_X\bar{S}\cdot\vec{\nabla}_X\bar{S}+(\hbar^2/2\mu^A_B)\vec{\nabla}_R\bar{S}\cdot\vec{\nabla}_R\bar{S}=\mathcal{E}-W_m(R)\ . \quad (16)$$

Choosing $\bar{S}(\vec{X},\vec{R})=\vec{K}_{CN}\cdot\vec{X}+S(\vec{R})$ to satisfy linear motion of the center of mass of the nuclei and $f_m(\vec{X},\vec{R})=f_m(\vec{R})$ with $E=\mathcal{E}-(\hbar^2/2M)K^2_{CN}$, Eq. (16) reduces to

$$(\hbar^2/2\mu^A_B)\vec{\nabla}_RS_m\cdot\vec{\nabla}_RS_m=E-W_m(R)\ . \quad (17)$$

Equation (9), the first order in α coefficient, now

becomes

$$i\frac{\hbar^2}{M}\vec{K}_{CN}\cdot\sum_i\vec{\nabla}_{r_i}A_0 - i\frac{\hbar^2}{2\mu_B^A}(2\vec{\nabla}_R S_m\cdot\vec{\nabla}_R A_0 + A_0\vec{\nabla}_R^2 S_m) + [\bar{H}^{el} - W_m(R)]A_1 = 0 . \quad (18)$$

Introduction of Eq. (15) and the knowledge that χ_m vanishes as any particular electron coordinate becomes large, combined with a projection in electron space with χ_m on Eq. (18), gives the simple equation

$$2\vec{\nabla}_R f_m\cdot\vec{\nabla}_R S_m + f_m\nabla_R^2 S_m = 0 . \quad (19)$$

Equations (17) and (19) are sufficent to identify $f_m(\vec{R})e^{iS_m(\vec{R})/\alpha}$ as the asymptotic solution of the two-body Schrödinger equation[7,9]:

$$\left(-\alpha^2\frac{\hbar^2}{2\mu_B^A}\nabla_R^2 + W_m(R) - E\right)\psi(\vec{R},\alpha) = 0 . \quad (20)$$

This demonstrates that a zero-order Born–Oppenheimer approximation for scattering is just semiclassical nuclear motion on the fixed-nuclei electronic potential surface:

$$\Psi_m \simeq e^{i\vec{K}_{CN}\cdot\vec{X}/\alpha} f_m(\vec{R})e^{iS_m(\vec{R})/\alpha}\chi_m(\{\vec{r}_i\}|\vec{R}) . \quad (21)$$

The residual does not vanish anywhere independent of α, and Ψ_m may not be simply modified to satisfy scattering boundary conditions exactly.[24] An examination of the next-order part of the wave function A_1 shows that the expansion is not valid at first order in a region of electronic energy degeneracy. The resolvent of $\bar{H}^{el} - W_m(R)$ is used to solve Eq. (18) for A_1 (equivalent to basis expansion and projection):

$$A_1 = f_m\sum_{n\neq m}\chi_n(\{\vec{r}_i\}|\vec{R})C_n(\vec{R}) ,$$

$$C_n(\vec{R}) = \frac{1}{W_m(R) - W_n(R)}\left[i\frac{\hbar^2}{M}\langle\chi_n|\vec{K}_{CN}\cdot\sum_i\vec{\nabla}_{r_i}\chi_m\rangle - i\frac{\hbar^2}{\mu_B^A}\langle\chi_n|\vec{\nabla}_R S_m\cdot\vec{\nabla}_R\chi_m\rangle\right] . \quad (22)$$

The first term in brackets may be summed, and represents $i(m/M)\vec{K}_{CN}\cdot(\sum_i\vec{r}_i)f_m\chi_m$, a first-order correction appearing in A_1 owing to the use of the center of mass of the nuclei; this may be regrouped into the leading term, Eq. (21), and is ignored. An additional term in A_1, a coefficient of $f_m\chi_m$, would be determined from the next equation in the sequence beginning with (8) and (9). It contains the error in the semiclassical approximation $f_m e^{iS_m/\alpha}$ as a solution to Eq. (20), among other terms. Combining Eqs. (21) and (22) gives

$$\Psi_m \approx e^{i\vec{K}_{CN}\cdot\vec{X}/\alpha} f_m e^{iS_m/\alpha}\left(\chi_m - i\alpha\hbar\sum_{n\neq m}\chi_n\vec{V}_m\cdot\vec{D}_{nm}\right) ,$$

$$\vec{V}_m(\vec{R}) = (\hbar/\mu_B^A)\vec{\nabla}_R S_m , \quad (23)$$

$$\vec{D}_{nm}(\vec{R}) = \langle\chi_n|\vec{\nabla}_R\chi_m\rangle/[W_m(R) - W_n(R)] .$$

Taking the first-order term to be a measure of the *error*, it depends on a product of the nuclear velocity vector and an electronic quantity containing the eigenstates of Eq. (14). This was to be expected.[12,18] The order of the error is different, however, from that of the analysis of Gerber,[20] who carries through the original scaling[17] of nuclear coordinates and assumes that the nuclear energy is much less than the electronic energy. The mass parametrization used here does not require this.

Interesting studies of the large-mass limit have been initiated[25] in a finite basis electron space with the goal of determining transition amplitudes, but this shall not be pursued here. Neither is avoided crossing mentioned, for this depends on a specific property of the electronic eigenspectrum in conjunction with nuclear motion and has its own independent development in the literature.

III. LARGE-MASS LIMIT AT FIXED VELOCITY; THE TWO-BODY CASE

This section introduces the isovelocity parametrization, which is designed to give the limiting form of the Schrödinger wave function as mass and energy become large in such a way that the collision velocity, $v = (2E/\mu)^{1/2}$, remains constant. The masses in a given problem are not variables, but one could picture a series of scattering measurements on a three-body problem progressing from $e^+ + (e^+e^-)$, muonic species, $H^+ + H$, $D^+ + D$, to $T^+ + T$ carried out at either the same energy or collision velocity. If they are all at the same energy, the progression tends toward adiabatic behavior in the lighter particle; if they are all at the same velocity, only the description of the relative motion simplifies. This simplification in the two-body problem is the eikonal approximation which will be discussed now.

The coordinate $\vec{R}$ is used for relative separation, E is the relative collision energy, and μ is the reduced mass; the interaction must decay faster than $1/R$ at large R and be no more singular than $1/R$ at small R. The isovelocity asymptotic parametrization results from replacing μ by μ/ϵ and E by E/ϵ in the Schrödinger equation and the integral equation[3] defining the scattering state:

$$(\epsilon^2\nabla_R^2 + K^2 - \epsilon U)\psi(\vec{R},\epsilon) = 0 , \quad (24)$$

$$\psi(\vec{R},\epsilon) = e^{i\vec{K}\cdot\vec{R}/\epsilon} + \int d^3r'\frac{e^{iK|\vec{R}-\vec{R}'|/\epsilon}}{-4\pi\epsilon^2|\vec{R}-\vec{R}'|}\times\epsilon U(\vec{R}')\psi(\vec{R}',\epsilon) , \quad (25)$$

where

$$U = (2\mu/\hbar^2)V , \quad K^2 = (2\mu/\hbar^2)E ,$$

$$(\epsilon^2\nabla_R{}^2+K^2)\,\frac{e^{iK|\vec{R}-\vec{R}'|/\epsilon}}{-4\pi\epsilon^2|\vec{R}-\vec{R}'|}=\delta^3(\vec{R}-\vec{R}')\,, \qquad (26)$$

$$\int d^3R'\,\delta^3(\vec{R}-\vec{R}')\,f(\vec{R}')=f(\vec{R})\,.$$

Equation (24) indicates that $\psi(\vec{R},\epsilon)$ possesses an essential singularity in ϵ just as in the usual large-mass limit. The substitution

$$\psi(\vec{R},\epsilon)=A(\vec{R},\epsilon)\,e^{iS(\vec{R})/\epsilon} \qquad (27)$$

with the assumption that $A(\vec{R},\epsilon)$ is expandable as a Taylor's series in ϵ,

$$A(\vec{R},\epsilon)=A_0(\vec{R})+\epsilon A_1(\vec{R})+\cdots\,, \qquad (28)$$

leads to the following series of equations obtained by equating coefficients of powers of ϵ to zero:

$$\begin{aligned}&\vec{\nabla}_R S\cdot\vec{\nabla}_R S=K^2\,,\\ &i(2\vec{\nabla}_R A_0\cdot\vec{\nabla}_R S+A_0\nabla_R{}^2 S)-UA_0=0\,,\\ &\nabla_R{}^2 A_m+i(2\vec{\nabla}_R A_{m+1}\cdot\vec{\nabla}_R S+A_{m+1}\nabla_R{}^2 S)\\ &\qquad -UA_{m+1}=0\,,\quad m\geq 0\,.\end{aligned} \qquad (29)$$

An acceptable solution to the first equation, consistent with Eq. (25), is

$$\begin{aligned}&\vec{\nabla}_R S=\vec{K}=K\hat{e}_z\,,\quad S=\vec{K}\cdot\vec{R}=KZ\,,\\ &\nabla_R{}^2 S=0\,.\end{aligned} \qquad (30)$$

The remaining equations become

$$\begin{aligned}&2iK\,\frac{\partial}{\partial Z}\,A_0=UA_0\,,\\ &\nabla_R{}^2 A_m+2iK\,\frac{\partial}{\partial Z}\,A_{m+1}=UA_{m+1}\,,\quad m\geq 0\end{aligned} \qquad (31)$$

which may be generally solved:

$$\begin{aligned}&A_0(\vec{R})=P_0(X,Y)\exp\left(\frac{1}{2iK}\int_{-\infty}^{Z}U\,dz'\right)\,,\\ &A_{m+1}(\vec{R})=\exp\left(\frac{1}{2iK}\int_{-\infty}^{Z}U\,dz'\right)\left[P_{m+1}(X,Y)\right.\\ &\left.-\int_{-\infty}^{Z}dZ'\,\frac{1}{2iK}\,\exp\left(-\frac{1}{2iK}\int_{-\infty}^{Z'}U\,dz''\right)\nabla_{R'}{}^2 A_m\right]\,,\\ &m\geq 0\,.\end{aligned} \qquad (32)$$

The $P_m(X,Y)$ are arbitrary functions of the Cartesian components X and Y of $\vec{R}$; letting Z approach negative large values, one has

$$\begin{aligned}&A_0(\vec{R})\underset{Z\to-\infty}{=}P_0(X,Y)\,,\\ &A_m(\vec{R})\underset{Z\to-\infty}{=}P_m(X,Y)\,,\\ &\psi(\vec{R},\epsilon)\underset{Z\to-\infty}{=}e^{iKZ/\epsilon}(P_0+\epsilon P_1+\epsilon^2 P_2+\cdots)\,,\end{aligned} \qquad (33)$$

which, subject to the incoming boundary conditions in Eq. (25), implies $P_m(X,Y)=\delta_{0m}$. The wave function that remains is

$$\begin{aligned}\psi(\vec{R},\epsilon)=&e^{iKZ/\epsilon}\exp\left(\frac{1}{2ik}\int_{-\infty}^{Z}U\,dz'\right)\\ &\times\left[1-\epsilon\int_{-\infty}^{Z}dZ'\exp\left(-\frac{1}{2iK}\int_{-\infty}^{Z'}U\,dz''\right)\right.\\ &\left.\times\nabla_{R'}{}^2\exp\left(\frac{1}{2ik}\int_{-\infty}^{Z'}U\,dz''\right)+O(\epsilon^2)\right]\,.\end{aligned} \qquad (34)$$

The first-order term is unbounded on the forward axis ($X=Y=0$, $Z>0$) for a potential as singular as $1/R$ at the origin; it is dropped in any case, leaving

$$\psi^{\mathrm{EIK}}(\vec{R},\epsilon)=e^{iKZ/\epsilon}\exp\left(\frac{1}{2iK}\int_{-\infty}^{Z}U\,dz'\right)\,, \qquad (35)$$

which is the eikonal wave function discussed extensively by Glauber[15] and attributed to Molière,[26] who bases the construction on geometrical optics. A thorough and precise analysis concerning this approximation is given by Schiff,[27] who sums the Neumann–Born expansion of Eq. (25) after approximating the free-particle resolvent.

The difficulty inherent in ψ^{EIK} is that it does not have a scattered angular flux; the wave function is modified by the interaction only in the forward "shadow" of the potential. Consequently, ψ^{EIK} does not satisfy free-particle motion outside the interaction, as seen in the residual

$$\begin{aligned}&(\epsilon^2\nabla_R{}^2+K^2-\epsilon U)\,\psi^{\mathrm{EIK}}\\ &\qquad=\epsilon^2 e^{iKZ/\epsilon}\nabla_R{}^2\exp\left(\frac{1}{2iK}\int_{-\infty}^{Z}U\,dz'\right)\,,\end{aligned} \qquad (36)$$

which does not vanish independent of ϵ in the forward shadow. The residual is of the order of ϵ^2 but unbounded on the forward axis if U is singular at the origin. Suppose that U is not singular at $R=0$, then one may use the scattered amplitude determined by iterating Eq. (25) (see the Appendix). This expression is simplified by the arguments of Glauber[15] and leads to

$$\begin{aligned}&T(\epsilon\alpha,\epsilon)=(1/\epsilon)\,B(\alpha)+O(1)\,,\\ &B(\alpha)=-iK\int_0^{\infty}b\,db\,J_0(Kb\alpha)\\ &\qquad\times\left[\exp\left(\frac{1}{2iK}\int_{-\infty}^{\infty}dz'\,U\right)-1\right]\,,\\ &\hat{K}_f\cdot\hat{K}=\cos\theta\,,\quad\theta=\epsilon\alpha\,.\end{aligned} \qquad (37)$$

This displays the small-angle property of the eikonal amplitude very directly. The case of $U(\vec{R})$ singular at $R=0$ is yet to be treated; it is rather

obvious, for example, that a $1/R$ behavior at small R must give a negligible $O(\epsilon^2)$ contribution to the differential cross section at large angles. This section is concluded with an alternative derivation of the isovelocity limit in the partial-wave picture, which avoids the iteration of the integral equation.

The radial equations for scattering from a spherically symmetric potential[3]

$$\left(\frac{d^2}{dR^2}+K^2-\frac{l(l+1)}{R^2}-U(R)\right)R_l(R,K)=0\,,$$
$$R_l(R,K)\underset{R\to\infty}{=}(1/\sqrt{K})\sin(KR-\tfrac{1}{2}\pi l+\eta_l) \tag{38}$$

may be solved for the η_l to construct the differential scattering amplitude

$$T(\theta)=\frac{1}{2iK}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)(e^{2i\eta_l}-1)\,. \tag{39}$$

The isovelocity parametrization of Eq. (38) leads to the differential operator, $\epsilon^2d^2/dR^2+K^2-\epsilon^2l(l+1)/R^2-\epsilon U$ for a fixed l quantum number; however, the angular momentum is proportional to mass times velocity for a given separation and should be scaled as $1/\epsilon$. This is substantiated by the semiclassical correspondence of $l+\frac{1}{2}$ to Kb, where b is the impact parameter. By definition, the radial equations are to be solved in $\epsilon\to 0$ limit of

$$\left(\epsilon^2\frac{d^2}{dR^2}+K^2-\frac{L^2}{R^2}-\epsilon U\right)R_l(R,K,\epsilon)=0\,, \tag{40}$$

where $\epsilon^2l(l+1)$ was replaced by L^2, $L=\epsilon(l+\frac{1}{2})$, and the second-order term $\epsilon^2/4R^2$ was dropped.[28] The scaling choice $L=\epsilon l$ would have left a first-order quantity $\epsilon L/R^2$, which is of the same order as ϵU. The asymptotic-type solution of Eq. (40) is developed in two steps; the first is the usual connected JWKB or uniform solution in which one ignores the ϵ dependence in ϵU, the second is the further expansion of this solution in powers of ϵ. For R greater than the turning point at $T_L(\epsilon)$, one has

$$R_l(R,K,\epsilon)\simeq\frac{1}{[K_L(R,\epsilon)]^{1/2}}\times\sin\left(\frac{\pi}{4}+\frac{1}{\epsilon}\int_{T_L(\epsilon)}^{R}dx\,K_L(x,\epsilon)\right)\,,$$
$$K_L(R,\epsilon)=[K^2-L^2/R^2-\epsilon U(R)]^{1/2}\,, \tag{41}$$
$$K_L[T_L(\epsilon),\epsilon]=0\,,$$

and as R becomes large,

$$R_l(R,K,\epsilon)\underset{R\to\infty}{=}\frac{1}{\sqrt{K}}\sin\left(\frac{\pi}{4}+\frac{1}{\epsilon}\int_{T_L(\epsilon)}^{\infty}dx\,(K_L-K)+\frac{KR}{\epsilon}-\frac{KT_L(\epsilon)}{\epsilon}\right) \tag{42}$$

The phase integral appearing in Eq. (42) may be expanded in a power series in ϵ, which is apparent when the integration variable is changed to $s=x-T_L(\epsilon)$. One has

$$R_l(R,K,\epsilon)_{R\to\infty}=\frac{1}{\sqrt{K}}\sin\left(\frac{KR}{\epsilon}-\frac{\pi}{2}\frac{L}{\epsilon}+\frac{\pi}{4}-\int_{L/K}^{\infty}dx\,\frac{U(x)}{2K_L(x,0)}+O(\epsilon)\right)\,. \tag{43}$$

Returning to the amplitude expression, Eq. (39), the ϵ parametrization gives

$$T(\theta,\epsilon)=\frac{\epsilon}{2iK}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)(e^{2i\eta_l(\epsilon)}-1) \tag{44}$$

or, changing to sum variable $L=\epsilon(l+\frac{1}{2})$,

$$T(\theta,\epsilon)=\frac{1}{\epsilon iK}\int_0^{\infty}dL\,L\sum_{m=0}^{\infty}\delta(L-\tfrac{1}{2}\epsilon-m\epsilon)\times P_{L/\epsilon-1/2}(\cos\theta)(e^{2i\eta_{L/\epsilon-1/2}(\epsilon)}-1). \tag{45}$$

Equation (43) identifies

$$\eta_{L/\epsilon-1/2}(\epsilon)=\delta_L(\epsilon)\underset{\epsilon\to 0}{=}-\int_{L/K}^{\infty}dx\,\frac{U(x)}{(K^2-L^2/x^2)^{1/2}}+O(\epsilon)\,, \tag{46}$$

which is to be used in Eq. (45) with suitable limits for $P_{L/\epsilon-1/2}$. In the case of angles of order ϵ, one immediately derives Eq. (37), which demonstrates that the singularity of U at small R did not affect that result. For angles θ neither near 0 or π,

$$T(\theta,\epsilon)\underset{\epsilon\to 0}{=}\frac{1}{\epsilon iK}\int_0^{\infty}dL\,L\sum_{m=0}^{\infty}\delta(L-\tfrac{1}{2}\epsilon-m\epsilon)\times\left(\frac{2\epsilon}{\pi L\sin\theta}\right)^{1/2}\cos\left(\frac{L\theta}{\epsilon}-\frac{\pi}{4}\right)(e^{2i\delta_L(0)}-1)\,, \tag{47}$$

which indicates that, if $d\delta_L(0)/dL$ is singular as $L\to 0$, there exists a point of stationary phase in the L integral in the $\epsilon\to 0$ limit giving a large-angle cross section. However, the stationary-phase point occurs at an L proportional to a power of ϵ, which can ultimately be seen to conflict with the derivation of $\delta_L(0)$. In addition, the row of δ functions, $\delta(L-\frac{1}{2}\epsilon-m\epsilon)$, is not necessarily densely spaced compared to the variation in the rest of the integrand even in the region of stationary phase, making the stationary-phase approximation suspect in the $\epsilon\to 0$ limit. In general, only the original JWKB phase shifts seem valid for the range of l contributing to $T(\theta,\epsilon)$ at large θ.

IV. INELASTIC ATOM-ATOM SCATTERING

Using the full Schrödinger equation in the laboratory frame as expressed by Eqs. (4) and (5), one replaces m_A by m_A/ϵ, m_B by m_B/ϵ, and $\mathcal{E}$ by $\mathcal{E}/\epsilon$, and has

$$\left[\epsilon^2\left(-\frac{\hbar^2}{2m_A}\nabla_{X_A}{}^2-\frac{\hbar^2}{2m_B}\nabla_{X_B}{}^2\right)+\epsilon H^{el}(\vec{\nabla}_{x_i},\vec{x}_i,\vec{X}_A,\vec{X}_B)-\mathcal{E}\right]\Psi(\vec{X}_A,\vec{X}_B,\{\vec{x}_i\},\epsilon)=0\ . \quad (48)$$

The essential singularity in ϵ is again of the exponential type, so the substitution

$$\Psi=\mathcal{A}(X_A,X_B,\{\vec{x}_i\},\epsilon)e^{iS(\vec{X}_A,\vec{X}_B)/\epsilon}\ ,$$
$$\mathcal{A}=\mathcal{A}_0+\epsilon\mathcal{A}_1+\cdots \quad (49)$$

is used to define a formal series solution in ϵ. The two lowest-order equations are

$$\frac{\hbar^2}{2m_A}\vec{\nabla}_{X_A}S\cdot\vec{\nabla}_{X_A}S+\frac{\hbar^2}{2m_B}\vec{\nabla}_{X_B}S\cdot\vec{\nabla}_{X_B}S-\mathcal{E}=0\ , \quad (50)$$

$$-i\frac{\hbar^2}{2}\sum_{P=A,B}\frac{1}{m_P}(2\vec{\nabla}_{X_P}S\cdot\vec{\nabla}_{X_P}\mathcal{A}_0+\mathcal{A}_0\nabla_{X_P}^2S)+H^{el}\mathcal{A}_0=0\ . \quad (51)$$

Equation (50) is solved by[29]

$$S(\vec{X}_A,\vec{X}_B)=\vec{K}_{CN}\cdot\vec{X}+\vec{K}\cdot\vec{R}\ ,$$
$$\mathcal{E}=\frac{\hbar^2}{2M}K_{CN}^2+\frac{\hbar^2}{2\mu_B^A}K^2\ , \quad (52)$$

with the same definitions as Eq. (10). Since H^{el} is only a function of particle separations, Eq. (51) can be reduced to

$$i(\hbar^2/\mu_B^A)\vec{K}\cdot\vec{\nabla}_R A(\vec{R},\{\vec{r}_i\})=\overline{H}^{el}(\vec{\nabla}_{r_i},\vec{r}_i,\vec{R})A(\vec{R},\{\vec{r}_i\})\ , \quad (53)$$

where

$$\mathcal{A}_0=\exp\left(i\frac{m}{M}\vec{K}_{CN}\cdot\sum_i\vec{r}_i\right)\exp\left(i\frac{Nm}{2M}\vec{K}_{CN}\cdot\vec{X}\right)\times A(\vec{R},\{\vec{r}_i\})\ , \quad (54)$$

N = number of electrons .

Since the coordinate of the total center of mass is

$$\vec{X}_{COM}=(m_A\vec{X}_A+m_B\vec{X}_B+\epsilon m\sum_i\vec{x}_i)/(m_A+m_B+\epsilon Nm), \quad (55)$$

one can reconstruct the total solution up to $O(\epsilon)$ as

$$\Psi(\vec{X}_A,\vec{X}_B,\{\vec{x}_i\},\epsilon)=e^{i\vec{K}_{CN}\cdot\vec{X}/\epsilon}e^{i\vec{K}\cdot\vec{R}/\epsilon}\mathcal{A}_0$$
$$=\exp\{i\vec{K}_{CN}\cdot\vec{X}_{COM}[1+\epsilon\tfrac{1}{2}(Nm/M)]/\epsilon\}e^{i\vec{K}\cdot\vec{R}/\epsilon}A\ . \quad (56)$$

The obvious identification of the total center-of-mass wave vector, $\vec{K}_{COM}$, as $\vec{K}_{CN}[1+\epsilon\frac{1}{2}(Nm/M)]$ leaves an internal energy

$$E_I=\mathcal{E}-\frac{\hbar^2K_{COM}^2}{2(M+\epsilon Nm)}=\frac{\hbar^2K^2}{2\mu_B^A}+O(\epsilon^2)\ , \quad (57)$$

giving the asymptotic solution in the barycentric frame up to $O(\epsilon)$:

$$\psi(\vec{R},\{\vec{r}_i\})=e^{i\vec{K}\cdot\vec{R}/\epsilon}A(\vec{R},\{\vec{r}_i\})\ ,$$
$$i\frac{\hbar^2}{\mu_B^A}\vec{K}\cdot\vec{\nabla}_R A=\overline{H}^{el}A\ . \quad (58)$$

Equation (58) is precisely the parametric-time-dependent impact-parameter equation for rectilinear-heavy-particle trajectories[12] that describes the light particles as responding to the imposed motion of the nuclei. What is demonstrated here is that the equation is not purely classical in the treatment of the nuclei, but is akin to the eikonal methods as described by Byron,[30] and that the removal of barycentric motion leaves a unique equation. Equation (58) may be transformed to other coordinates, e.g., $\vec{r}_{iB}=\vec{r}_i+\alpha_{AB}^A\vec{R}$, $\vec{R}_B=\vec{R}$. This gives an equation of motion analogous in form to Eq. (58) in the new coordinates for a new solution which is related to A by a phase factor.

The construction of the scattering amplitude proceeds through a series of equations whose detail is not wholly relevant. A similar procedure has been described elsewhere.[30] The beginning is the extraction of a scattering T-matrix element from a wave function with many arrangement channels,[3]

$$T_{\beta f\alpha i}(\theta)=\langle X_{\beta f}|V_\beta\psi_{\alpha i}\rangle\ , \quad (59)$$

which is *assumed* to provide an accurate evaluation of amplitudes for small angles as was found to be the case in elastic scattering [Eq. (37) and preceding discussion]. Approximations are introduced for $X_{\beta f}$ and $\psi_{\alpha f}$ based on supposed exact solutions (channel and total) of Eq. (58); and the integral in Eq. (59) is rearranged to read

$$T_{\beta f\alpha i}(\theta,\epsilon)=\int d^3R\int d^3r_i\,e^{-i\vec{K}_f\cdot\vec{R}/\epsilon}e^{i\vec{K}_i\cdot\vec{R}/\epsilon}\times(-i/2\pi\epsilon)(\Phi_{\beta f}^*\vec{K}_i\cdot\vec{\nabla}_R A_{\alpha i}+A_{\alpha i}\vec{K}_f\cdot\vec{\nabla}_R\Phi_{\beta f}^*)\ , \quad (60)$$

where Φ will be defined immediately. If $\theta=\epsilon\alpha$, $\vec{K}_i$ and $\vec{K}_f$ differ by order ϵ; Eq. (60) is now written with a cylindrical coordinate integration volume in $\vec{R}$. The z axis is chosen along $\vec{K}_f+\vec{K}_i$ and the z integration is performed, since

$$\Phi_{\beta f}^*\vec{K}_i\cdot\vec{\nabla}_R A_{\alpha i}+A_{\alpha i}\vec{K}_f\cdot\vec{\nabla}_R\Phi_{\beta f}^*=K\frac{\partial}{\partial z}(\Phi_{\beta f}^*A_{\alpha i})+O(\epsilon)\ . \quad (61)$$

The result has the same structure as Eq. (37):

$$T_{\beta f\alpha i}(\epsilon\alpha,\epsilon)=(1/\epsilon)B_{\beta f\alpha i}(\alpha)+O(1)\ ,$$
$$B_{\beta f\alpha i}(\alpha)=-\frac{iK}{2\pi}\int_0^\infty b\,db\int_0^{2\pi}d\phi\,e^{-iKb\alpha\cos\phi}\times\left(\int d^3r_i\,\Phi_{\beta f}^*A_{\alpha i}\right)_{z=-\infty}^{z=\infty}. \quad (62)$$

$\Phi_{\alpha m}$ is a separated-atom electronic wave-function product, including plane wave factors[31–33] and nuclear parts, which is a solution of an arrangement-channel Hamiltonian defined as a particular group of electrons on nucleus A and the remainder on B. The explicit form is

$$\Phi_{\alpha m}(\vec{R},\{\vec{r}_i\}) = e^{i\vec{P}_m\cdot\vec{R}}\phi_m^A(\{\vec{r}_i-\gamma_{AB}^B\vec{R}\})\exp\left(i\vec{\lambda}_A\cdot\sum_i^{\text{on }A}\vec{r}_i\right)$$
$$\times\phi_m^B(\{\vec{r}_i+\gamma_{AB}^A\vec{R}\})\exp\left(i\vec{\lambda}_B\cdot\sum_i^{\text{on }B}\vec{r}_i\right),$$

$$\vec{\lambda}_A=(m/m_A)\vec{K}\,,\quad \vec{\lambda}_B=-(m/m_B)\vec{K}\,,$$

$$\vec{P}_m=-\frac{\mu_B^A}{\hbar^2K^2}(W_m^A+W_m^B)\vec{K}$$
$$-\frac{1}{2M}\left(\frac{m_B}{m_A}N_A m+\frac{m_A}{m_B}N_B m\right)\vec{K}\,,$$

where φ^A and φ^B are atomic wave functions (N_A electrons on A, distinguished from N_B electrons on B) with energies W^A and W^B.

The electron permutation operators P_{ij} commute with H^{el} and $\vec{\nabla}_R$, implying that electron permutation symmetry is maintained throughout the collision. This at first glance would seem to imply that fully antisymmetrized, fixed nuclei, molecular electronic eigenstates are a natural choice for a basis in the electron space needed to solve Eq. (58). They indeed are at slow collision velocity, but are complicated by the form of the channel states in Eq. (63), since one must untangle the exchange symmetry at large separation, insert the plane wave factors, and resymmetrize. This ensures that the proper boundary conditions are satisfied at large separation and that the different electron exchange symmetries (e.g., singlet, triplet) are solved separately. Simplification occurs with the use of an atomic basis (in which the $\Phi_{\alpha m}$ are that basis) and a solution of the impact-parameter equation (58) has been carried through for a two-electron problem including plane-wave factors.[34]

V. DISCUSSION

Section IV demonstrates that a meaningful approximation exists that does not decouple electronic motion at zero order, and is precisely the multichannel impact-parameter method for atom-atom collisions. The differential cross sections can be developed from scattering theory rather than "diffraction screen" arguments[26,35] and it is clear why the initial-final averaging of the relative collision vector[15] works in this limit for the scattering amplitude. The light-mass-particle motion is not required by the theory to be best described by an adiabatic (as in avoided-crossing analysis) or an atomic (as in high-energy theory) basis, but must be solved to determine the lowest-order part of the whole scattering problem. It is felt to be important that this *coupling* occurs at zero order in the equations derived from the isovelocity limit. Although a many-particle system is too complex to compare to a single differential equation, the implications are that all terms which arise beyond zero order in an asymptotic-type approximation may not be helpful for the construction of a better solution. This occurs in atom-atom scattering if one uses only the large-mass-limit JWKB solutions to investigate excitation.[36,37] In addition to this, the isovelocity limit clarifies the higher-order effect of the mass-polarization-type terms that appear in the barycentric electronic Hamiltonian, and incorporates full in-out decoupling into the coupled equations for nuclear motion.

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APPENDIX

If ψ is defined by

$$\psi=\chi+\int G\,U\psi\,,\quad (E-H)\psi=0\,, \tag{A1}$$

and has an approximation $\psi^{(1)}$ satisfying

$$(E-H)\psi^{(1)}=R^{(1)}\,,$$
$$\psi^{(1)}=\chi+\int GU\psi^{(1)}+\int GR^{(1)}\,, \tag{A2}$$

then a construction of $\psi^{(2)}$ by iterating the integral equation

$$\psi^{(2)}=\chi+\int GU\psi^{(1)}\,, \tag{A3}$$

can be shown to lead to a residual

$$(E-H)\psi^{(2)}=U\int GR^{(1)}=R^{(2)}\,. \tag{A4}$$

Thus if $U\int GR^{(1)}$ is bounded and of the same order in a smallness parameter as $R^{(1)}$, $\psi^{(2)}$ has a residual of the same order as $\psi^{(1)}$ and satisfies free-particle motion outside U.

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[1]M. E. Riley, Bull. Am. Phys. Soc. 16, 1356 (1971).

[2]W. Wasow, *Asymptotic Expansions for Ordinary Differential Equations* (Interscience, New York, 1965); also, J. Heading, *Phase Integral Methods* (Wiley, New York, 1962).

[3]R. G. Newton, *Scattering Theory of Waves and Particles*

(McGraw-Hill, New York, 1966).

[4]The Miller–Good method has the potential to uniformize many transition points; see (a) S. C. Miller, Jr. and R. H. Good, Jr., Phys. Rev. 91, 174 (1953); (b) S. C. Miller, Jr., Phys. Rev. 94, 1345 (1954); (c) P. Pechukas, J. Chem. Phys. 54, 3864 (1971); (d) P. Hsieh and Y. Sibuya, J. Math. Anal. Appl. 16, 84 (1966).

[5]R. E. Langer, Phys. Rev. 51, 669 (1937).

[6]P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), pp. 1096–1097.

[7]A. Messiah, *Quantum Mechanics* (Wiley, New York 1961), Vol. I; L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1948).

[8]The following papers discuss various aspects of the semiclassical problem, $(\alpha^2\nabla^2+K^2)\psi=0$: (a) J. B. Keller, Ann. Phys. (N.Y.) 4, 180 (1958); (b) J. B. Keller and S.I. Rubinow, Ann. Phys. (N.Y.) 9, 24 (1960); (c) L. Brillouin, Arc. Rational Mech. Anal. 5, 76 (1960); (d) D. Secrest and J. Hirschfelder, Proc. Natl. Acad. Sci. 47, 227 (1960); (e) D. Ludwig, Commun. Pure Appl. Math. 19, 215 (1966).

[9]The stationary phase evaluation of Feynman path integrals leads to an asymptotic-type solution: P. Pechukas, Phys. Rev. 181, 166 (1969). In general, the two-body solution may be derived from the partial-wave expanded scattering state using JWKB radial solutions and large-l approximations to the Legendre functions, by performing the l sum in stationary phase [M. E. Riley and T. A. Green (unpublished)]. This as in the Pechukas approach, avoids the establishment of new connection formulas for a multidimensional wave function.

[10]W. H. Miller, J. Chem. Phys. 53, 1949 (1970); J. Chem. Phys. 53, 3578 (1970); also, B. C. Eu, J. Chem. Phys. 57, 2531 (1972).

[11]R. A. Marcus, Chem. Phys. Letts. 7, 525 (1970).

[12]N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford, Fair Lawn, N. J., 1949).

[13]B. L. Moiseiwitsch, Proc. Phys. Soc. (London) 87, 887 (1966).

[14]J. Delos, W. Thorson, and S. Knudson, Phys. Rev. A 6, 709 (1972).

[15]R. J. Glauber, *High Energy Collision Theory, Lectures in Theoretical Physics*, edited by W. Brittin and L. Durham (Interscience, New York, 1958), Vol. I.

[16]Except on various surfaces in $\vec{R}$ space, as in the elastic scattering case.

[17]M. Born and R. Oppenheimer, Ann. Phys. (Paris) 84, 457 (1927).

[18]M. Born, Nachr. Akad. Wiss. Gottingen, Math. Physik. Klasse IIa (1951).

[19]M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., New York, 1962).

[20]R. Gerber, Proc. Roy. Soc. (London) A309, 221 (1969).

[21]That suitably modified fixed-nuclei electronic eigenstates can serve as a good basis in slow collisions is well known (see Refs. 12, 18, and 24); what is demonstrated here is that the large-mass limit alone implies both adiabatic and semiclassical properties of the whole system.

[22]It is not necessary for S to be a function of the $\vec{x}_i$ coordinates, so they are dropped immediately.

[23]A. Dalgarno and R. McCarroll, Proc. Roy. Soc. (London) A237, 383 (1956).

[24]W. R. Thorson, J. Chem. Phys. 42, 3878 (1965).

[25]G. V. Dubrovskii, Zh. Eksp. Teor. Fiz. 58, 1075 (1970) [Sov. Phys. JETP 31, 577 (1970); B. C. Eu, J. Chem. Phys. 52, 1882 (1970); 52, 3903 (1970); 55, 5600 (1971); 56, 2507 (1971).

[26]G. Molière, Z. Naturforsch. 2A, 133 (1947).

[27]L. I. Schiff, Phys. Rev. 103, 443 (1956).

[28]The use of $(l+\frac{1}{2})^2$ in place of $l(l+1)$ is required for the regularity of a uniform approximation at $R=0$; see Ref. 5.

[29]If one assumes that the zero-order part of the solution contains elastic scattering deflections, obtained in our formalism by inserting an effective interaction $U(R)$ into Eq. (50) and subtracting it from H^{el} in Eq. (51), a different picture develops for the heavy particle motion. It is felt by the author that this circumstance is easier treated in the partial wave picture [(to be published), also see Ref. 14], than in the full three-dimensional scattering state. These theories lie in the important intermediate energy range between the pure limits distinguished by Secs. II and IV. See D. R. Bates and A. R. Holt, Proc. Roy. Soc. (London) A292, 168 (1966), and J. C. Y. Chen and K. M. Watson, Phys. Rev. 174, 152 (1968); Phys. Rev. 188, 236 (1969) for the non-partial-wave approach.

[30]F. W. Byron, Jr., *Proceedings of VI ICPEAC, Cambridge, Mass.*, 1969, published in Phys. Rev. A 4, 1907 (1971).

[31]D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) A245, 175 (1958).

[32]M. E. Riley and T. A. Green, Phys. Rev. A 4, 619 (1971).

[33]P. Pechukas, Phys. Rev. 181, 174 (1969).

[34]T. A. Green, H. E. Stanley, and Y-C. Chiang, Helv. Phys. Acta 38, 109 (1965).

[35]L. Wilets and S. J. Wallace, Phys. Rev. 169, 84 (1968).

[36]D. R. Bates and D. S. F. Crothers, Proc. Roy. Soc. (London) A315, 465 (1970); also, M. E. Riley, J. Chem. Phys. 55, 2606 (1971).

[37]Work is in preparation for publication on the proton-hydrogen atom scattering problem in the partial wave picture which is based on the work of S. K. Knudson and W. R. Thorson, Can. J. Phys. 48, 313 (1970). Here it will be specifically demonstrated that a partial wave isovelocity limit affords the inclusion of elastic scattering corrections under much the same restrictions as stated in Ref. 14.