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Unified treatment of collisions

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Eigenfunctions of a collision complex branch into different channels when propagating from a condensed-complex to a fragmented-complex limit. The branching ratios depend on separate processes localized where propagation becomes nonadiabatic. The cumulative effect of branching is represented by Jost matrices, which consist of the coefficients of the asymptotic expansion of a base set of eigenfunctions and serve to construct scattering matrices and cross sections. The formulation presented here blends theoretical elements of different origin and includes resonant and bound states of the complex.

I. INTRODUCTION

Over the last decade diverse collision processes have been found to follow a common pattern. Stages of smooth development along alternative channels are separated by critical subprocesses—such as interchannel transitions at avoided crossings—which are of the same kind regardless of whether the reactants are atoms, molecules, or electrons. This similarity of diverse phenomena appears to warrant outlining a single analytical framework that encompasses them all. The discrete spectra observed in photoabsorption and Raman scattering will fit into the same frame—though the primary photon interactions are still treated as external agents—as well as the resonances arising from quasibound states in closed channels.

The unifying theme to be developed is that it suffices to consider the evolution of any system under study from the limit where it condenses into a minimal volume of physical space to a limit where it is fragmented. (The evolution of molecular states between united- and separate-atom limits provides a model.) This evolution generally involves repeated branching of a state into separate channels. Combination of branching ratios will determine the outcome of observable processes. The main future activities will presumably aim at determining branching ratios for specific stages in the evolution of specific systems, within the context of a theoretical frame such as the one to be outlined here.

This paper will combine preexisting elements, stressing the import of each but referring to original literature for details. It should provide the skeleton of a general theory within which one may place current developments but which remains to be complemented in two main respects. On the one hand, the analytical formulation will have to be detailed and fitted to the specifics of each application. More importantly, several critical aspects of the theory are only perceived dimly at this time. Such areas will be indicated as targets for further study. We deal here only with collisions in which the reactants coalesce temporarily into a complex, thus excluding the familiar collisions of fast charged particles which act most frequently at large impact parameters.

Clues to our development emerge from the familiar treatment of elastic scattering of a particle by a central potential $V(r)$ through partial-wave analysis of the wave function

$$\psi(\vec{r})=\sum_l (2l+1)i^l e^{i\delta_l} f_l(r) P_l(\cos\theta)\,, \tag{1}$$

$$\xrightarrow[r\to\infty]{} \frac{1}{2ikr}\sum_l (2l+1)i^l e^{i\delta_l} \times\left(e^{i(kr-l\pi/2+\delta_l)} - e^{-i(kr-l\pi/2+\delta_l)}\right) P_l(\cos\theta)\,. \tag{2}$$

Two points are stressed here:

(a) The radial wave functions $f_l(r)$ are to be calculated *separately* for each l value, by integrating the radial Schrödinger equation with potential $V(r)+(\hbar^2/2m)l(l+1)/r^2$ from $r=0$ *outward* until the solution attains its asymptotic form $\sin(kr-l\frac{1}{2}\pi+\delta_l)/kr$. (Negative eigenvalues of the same Schrödinger equation represent bound-state levels of the particle.) The radial function $f_l(r)$ represents a real standing-wave *invariant* under time reversal and under space rotations; it may be viewed as the superposition of ingoing and outgoing complex components.

(b) On the other hand, the complete wave function pertains to a specific physical situation, namely, incidence along the z axis, which is identified by the *noninvariant* complex coefficients of the expansion (1). These coefficients may seem capricious but in fact combine with the coefficient of the incoming wave part of the asymptotic expansion to yield

$$\sum_l (2l+1) i^l e^{i\delta_l} e^{-i(kr - l\pi/2 + \delta_l)} P_l(\cos\theta) = 2e^{-ikr}\delta(1+\cos\theta) \,, \quad (3)$$

thus singling out the direction of the source of incident particles as $\theta = \pi$.

Both features (a) and (b) will be retained here in suitably generalized form. We must represent, of course, not merely one particle and a potential well centered at the origin, but a "collision complex," that is, a system of particles which has a condensation limit and a fragmentation limit. The first step required for our generalization is to replace the radial distance by an index of the system's dimension, which performs under broader conditions the same role, namely, of measuring the progress of the complex's expansion from condensation to fragmentation.

II. THE RADIAL VARIABLE

The main lead for selecting a radial variable emerges from discussing the condensation limit in which two or more particles, equal or different, are concentrated within a volume of radius r far smaller than the volume they would occupy in their stationary state of lowest energy. (Matter is thus condensed in a white dwarf star.) In this limit the expectation value of the kinetic energy predominates over that of the electric potential energy; typically each particle's centrifugal energy is of order $\hbar^2 \vec{l}^{\,2}/2mr^2$.

Further insight is provided by the simplest nontrivial example of two electrons at positions $(\vec{r}_1, \vec{r}_2)$ with respect to a fixed point nucleus.[1] (Equivalent examples are afforded by the nucleons of tritium[2] or by three atoms in collisions.[3]) Here the kinetic-energy operator

$$-\frac{\hbar^2}{2m}(\vec{\nabla}_1^2 + \vec{\nabla}_2^2) = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r_1^2} - \frac{\vec{l}_1^{\,2}}{r_1^2} + \frac{\partial^2}{\partial r_2^2} - \frac{\vec{l}_2^{\,2}}{r_2^2}\right] \quad (4)$$

is conveniently transcribed to stress that *both* electrons are close to the nucleus in the condensation limit. To this end one introduces a variable no smaller than either r_1 or r_2. Setting

$$R^2 = r_1^2 + r_2^2 \,, \quad \tan\alpha = r_2/r_1 \quad (5)$$

reduces Eq. (4) to its "hyperspherical" form[4]

$$-\frac{\hbar^2}{2m}(R^{5/2}\sin\alpha\,\cos\alpha)^{-1} \times \left[\frac{\partial^2}{\partial R^2} - \frac{1}{R^2}\left[-\frac{\partial^2}{\partial\alpha^2} + \frac{\vec{l}_1^{\,2}}{\cos^2\alpha} + \frac{\vec{l}_2^{\,2}}{\sin^2\alpha} - \frac{1}{4}\right]\right] \times (R^{5/2}\sin\alpha\,\cos\alpha) \,. \quad (6)$$

The "hyperradius" R represents here the size of the system. The angular variable α represents the relative distance of the two electrons from the nucleus; the derivative $\partial/\partial\alpha$ contributes to the kinetic energy much as $\partial/\partial\theta_1$, $\partial/\partial\phi_1$, $\partial/\partial\theta_2$, and $\partial/\partial\phi_2$ do in the orbital momentum operators $\vec{l}_1^{\,2}$ and $\vec{l}_2^{\,2}$. Indeed the entire operator that multiplies $1/R^2$ in (6) is treated as a generalized orbital momentum or "grand angular momentum" $\vec{\Lambda}^2$. [This operator is the analog of the orbital momentum, i.e., the Casimir operator for the group of rotations in the six-dimensional space $(\vec{r}_1, \vec{r}_2)$.] Renormalization of the wave function by the factor $R^{5/2}\sin\alpha\cos\alpha$ reduces (6) finally to

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2mR^2}\vec{\Lambda}^2 \equiv \tfrac{1}{2}\hbar^2\left[-\frac{\partial^2}{(\partial\sqrt{I}\,)^2} + \frac{\vec{\Lambda}^2}{I}\right], \quad (7)$$

where $I = mR^2$ is the moment of inertia of the electron pair.

The last form of (7) suggests that the moment of inertia I of the electron pair, or rather its square root $\sqrt{I}$, constitutes a basic non-negative parameter whose variation from 0 to ∞ traces the evolution from the condensation limit to the fragmentation limit where one or both electrons have escaped from the nuclear field. What is significant for us is that this parameter serves equally for *any system* of N particles when defined as the moment of inertia of the whole system with respect to its center of mass,

$$I=\sum_{i=1}^{N} m_i r_i^2 = mR^2 \ . \tag{8}$$

Linear transformations of the N-particle positions $\vec{r}_i$ with respect to their center of mass that *leave I invariant* form an orthogonal group $O(3N-3)$ whose Casimir operator is indicated by $\vec{\Lambda}^2$. With thus understanding we shall represent the kinetic energy of any complex of interest in the form (7). The factoring of I into m and R will be preserved as a matter of convenience; here we shall regard m as representing the total mass $\sum_i m_i$ while R is an effective radius of inertia. [Equation (5) departs from this convention by a factor of 2.]

Note that the centrifugal energy $\hbar^2\vec{\Lambda}^2/2mR^2$ includes *two* types of contributions: (a) the familiar ones reflecting the dependence of the wave function on angular coordinates of the particles (θ_i,ϕ_i), and (b) contributions reflecting its dependence on the *ratios* of radial distances r_i/r_j, exemplified by the $\partial^2/\partial\alpha^2$ term of (6).

This general representation of the kinetic energy of a system of particles has been studied extensively by a Russian school of nuclear theorists.[5] A key feature is that *all particles* are treated *symmetrically*, including electrons and nuclei of a molecule. The eigenvalues of $\vec{\Lambda}^2$ are quadratic functions of an integer quantum number λ, e.g., $(\lambda+2)^2-\frac{1}{4}>0$ in the example of O(6), depending only on the number N of particles. They are highly degenerate and their eigenfunctions, $\Phi_{\lambda\lambda'\lambda''\ldots}(\Omega)$ may be classified by the quantum numbers $\{\lambda',\lambda'',\ldots\}$ of alternative subgroups of $O(3N-3)$. In the example of two electrons and a nucleus, one may set $\lambda=l_1+l_2+2n_{rc}$, where l_1 and l_2 are the usual orbital numbers and the radial correlation quantum number n_{rc} represents the number of nodes along α; the quantum number set $\{\lambda,\lambda',\lambda'',\ldots\}$ becomes here $\{l_1,l_2,n_{rc}\}$ (Refs. 2 and 4). It is essential here that all the coordinates indicated globally by Ω run over a *finite range,* in contrast to the single coordinate R which runs from 0 to ∞. For this reason the spectrum of eigenvalues of $\vec{\Lambda}^2$ is *discrete*.

Reference 5 deals extensively with the transformations of the coordinates $\{\Omega\}$ at constant $I=mR^2$. It stresses that each mode of fragmentation at $R\rightarrow\infty$ implies the vanishing of a particular coordinate. (In the example of two atomic electrons, the escape of electron number 1 implies $\alpha\rightarrow 0$.) Applications of this key concept to specific examples remain scarce, possibly because nuclear workers have dealt with ground-state properties rather than with fragmentation. (Incidentally, the approach of Ref. 5 would apply to particle physics as well if a system's transformation at constant I were extended to allow variations of N.)

Reference 5 also describes the construction of complete sets of eigenfunctions of $\vec{\Lambda}^2$ $\{\Phi_{\lambda\lambda'\lambda''\ldots}(\Omega)\}$, taking into account the identity of any subset of particles of the system. This identity enables one to deal with just one sector of the space of variables Ω—e.g., with the region $r_2\le r_1$, i.e., $\alpha\le 45°$, in the example of two electrons—with spin-dependent conditions at the sector's boundary. Actual construction of a complete set will permit expansion of any energy eigenfunction into "channel functions" Φ

$$\Psi_E=\sum_{\lambda\lambda'\lambda''\ldots} F_{E\lambda\lambda'\lambda''\ldots}(R)\Phi_{\lambda\lambda'\lambda''\ldots}(\Omega) \ . \tag{9}$$

A *single* term of this expansion constitutes by itself an approximate eigenfunction in the *condensation limit* of small R where $\vec{\Lambda}^2/2mR^2$ far exceeds the potential energy $V(R,\Omega)$ of the system. A fuller expansion becomes necessary instead at larger R because $\vec{\Lambda}^2$ and $V(R,\Omega)$ generally do not commute, in contrast to the example of a single particle in a central potential. The set of quantum numbers $\{\lambda,\lambda',\lambda'',\ldots\}$ serves nevertheless to classify the complete set of eigenfunctions Ψ_E whose expansion (9) reduces to a single term in the limit $R\rightarrow 0$. This classification of eigenfunctions in the condensation limit provides a starting point for mapping the evolution of each eigenstate toward fragmentation at $R\rightarrow\infty$ through the variation of expansion coefficients $F(R)$.

Reference 5 thus provides a novel approach to the classification of the states of any aggregate of nuclei and electrons in its condensation limit. This limit, it should be recalled, corresponds to a density far higher than that of ordinary matter. Its investigation, and the investigation of the transition to ordinary density, are among the tasks envisaged here.

III. THE ADIABATIC BASE AND ITS VARIANTS

The analysis of an eigenfunction through the variations of its expansion coefficients proves particularly instructive insofar as a small subset of such coefficients remains nonnegligible. The expansion (9) is itself unsuitable from this point of view because an infinity of its terms would be required to represent the fragmentation limit of Ψ_E, where one of the variables Ω vanishes as noted above. More suitable expansions embody advance information on the evolution of eigenfunctions Ψ_E into the construction of their base set of channel functions $\Phi(\Omega)$.

Considerable success along this path has been obtained by using adiabatic bases or variants thereof.[4,6] The procedure may start from the condensation limit where the eigenfunctions $\Phi_{\lambda\lambda'\lambda''\ldots}(\Omega)$ of the operator $\vec{\Lambda}^2$ provide a suitable base for constructing a set of Ψ_E represented *locally* in the product form $F_{\lambda\lambda'\lambda''\ldots}(R)\Phi_{\lambda\lambda'\lambda''\ldots}(R)$. As R increases, the potential energy becomes appreciable and we must deal with the full Hamiltonian

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}+\frac{\hbar^2\vec{\Lambda}^2}{2mR^2}+V(R,\Omega)\ . \qquad (10)$$

Recall at this point that the potential energies of atomic particles are Coulombic and scale accordingly in inverse ratio to our parameter R,

$$V(R,\Omega)=\frac{C(\Omega)}{R}\ . \qquad (11)$$

[Mass differences among the particles are incorporated in the function $C(\Omega)$.] Equations (10) and (11) show explicitly that the contributions of V and $\vec{\Lambda}^2$ to H vary in a ratio $(1/R)/(1/R^2)=R$ as $R\to 0$, i.e., that the influence of V upon the eigenfunctions Ψ_E is of first order in R. Evaluation of this influence at small R by degenerate perturbation theory requires that the quantum numbers λ', λ'', . . . be so selected as to diagonalize the submatrix of V within each manifold of degenerate eigenstates of $\vec{\Lambda}^2$. Each element of the diagonalized submatrix adds then to the relevant eigenvalue of $\hbar^2\vec{\Lambda}^2/2mR^2$ a contribution of relative order R which depends on $\{\lambda', \lambda'', \ldots\}$. (Reference 4 found this contribution to be adequate over a surprisingly large range of R.) Extension of this perturbation expansion to higher order in V and R would have a limited range and requires generally the inclusion of powers of $\ln R$ (Ref. 1).

Adiabatic expansions utilize instead a base set $\Phi_\mu(R;\Omega)$ adjusted to the comparative strength of V and $\vec{\Lambda}^2$ *at each value of* R and defined by the eigenvalue problem

$$\frac{1}{R^2}\left[\frac{\hbar^2}{2m}\vec{\Lambda}^2+RC(\Omega)\right]\Phi_\mu(R;\Omega)=U_\mu(R)\Phi_\mu(R;\Omega)\ . \qquad (12)$$

This equation is viewed as the Schrödinger equation at fixed R, i.e., shorn of its derivatives with respect to R. The eigenfunctions Φ_μ depend on R as a parameter while all the Ω are treated as independent variables. Boundary or periodicity conditions on the Ω cause the spectrum of eigenvalues $U_\mu(R)$ to be *discrete at all* R. The lowest eigenvalues are generally well separated over most of the range of R. The study of the spectrum of $U_\mu(R)$ constitutes an important step to the dynamics of any given system.

Completeness of the set $\{\Phi_\mu(R;\Omega)\}$ enables us to expand any eigenfunction of the Hamiltonian (10) as in Eq. (8),

$$\Psi_E(R;\Omega)=\sum_\mu F_{E\mu}(R)\Phi_\mu(R;\Omega)\ . \qquad (13)$$

This expansion reduces the Schrödinger equation to the coupled system of radial equations[7]

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}+U_\mu(R)-E\right]F_{E\mu}(R)=\sum_{\mu'}W_{\mu\mu'}(R)F_{E\mu'}(R)\ . \qquad (14)$$

The coupling coefficients $W_{\mu\mu'}(R)$ originate from the dependence of the functions $\Phi_{\mu'}$ on R; only independent scattering in each separate channel would result if all $W_{\mu\mu'}$ were to vanish. The usefulness of Eq. (14) hinges on most of the coupling factors $W_{\mu\mu'}$ being very small over most of the range of R, a condition that often obtains especially for low-energy channels. In this event the study of collisions can deal separately with the influence of single $W_{\mu\mu'}$—or small sets thereof—and with the ranges of R where they are significant, as we had anticipated at the outset. That is, channel coupling is understood here to be *locally strong,* in contrast to more restrictive applications of adiabatic expansions. Pairs of channels labeled by different values of a constant of the motion, such as the total angular momentum of a complex, remain of course wholly uncoupled.

Phenomena arising from strong but localized channel couplings will be described in Sec. IV and their origin will be indicated. The rest of this section deals instead with other aspects of the adiabatic expansion.

The adiabatic expansion has been introduced here in the context of the coordinates (R,Ω) which encompass all particles of a complex. However, the procedure is flexible and has in fact been applied previously to certain subsets of these variables. In the most familiar application, to diatomic molecules, the nuclear and electronic coordinates are separated at the outset and (R,Ω) represent the internuclear distance and the electron coordinates, respectively. [The value of R given by (8) differs from this internuclear distance only to $O(m/M)$.] This application utilizes the adiabatic expansion under the restriction the Born-Oppenheimer approximation, namely, that the nuclear motion is much slower than the electronic one. We stress here that many different circumstances may minimize the values of the $W_{\mu\mu'}(R)$ over most of the range of R. An important circumstance stems from the simple ratio of the kinetic (i.e., centrifugal) and potential (i.e., Coulombic) terms in the large parentheses of (12); the smooth variation of this ratio generally causes the Φ_μ to depend on R slowly. The analytical structure of the coupling coefficients $W_{\mu\mu'}(R)$ simplifies when the system of second-order equations (14) is replaced by a system of twice as many first-order equations.[7]

The wave-function expansion (13) may be modified according to circumstances by adjusting the eigenvalue problem (12). Typically, the symmetry of the potential $C(\Omega)$ and of the eigenfunctions Φ_μ may be increased by removing from $C(\Omega)$ small interaction terms which are then reintroduced in the coefficients $W_{\mu\mu'}$ of Eq. (14). The greater invariance then allows pairs of potential curves $(U_\mu, U_{\mu'})$ to cross "diabatically" and may facilitate the subsequent analysis. This flexibility is very wide, within the confines of preserving the completeness of the base set $\{\Phi_\mu(R;\Omega)\}$. The definition of the generalized radial variable R is itself open to adjustment.

Centering attention on wave functions such as (13), expanded into products of radial standing waves and of eigenfunctions $\Phi_\mu(\Omega)$ with a discrete spectrum, has important physical implications. Solving at the outset the eigenvalue equation (12), possibly by variational techniques, enhances the stability of the calculation and ensures symmetry under time reversal. It also leads to an analysis of dynamics of the complex shorn of any reference to the specific boundary conditions of any single collision experiment. The approach thus departs radically from the analysis of collisions by following events along a trajectory, in a manner that will be-

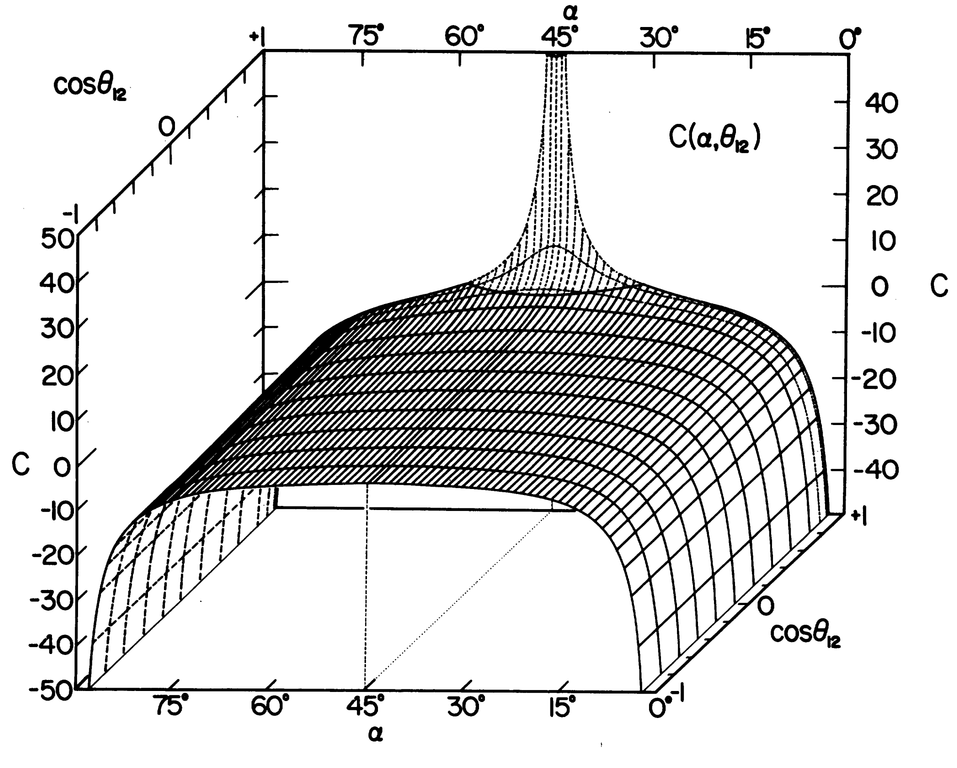

FIG. 1. Potential function $C(\Omega) \equiv C(\alpha,\theta_{12})$ for a pair of electrons in the field of H^+ (Ref. 4); $\cos\theta_{12} = \hat{r}_1 \cdot \hat{r}_2$.

come apparent in Sec. V. Conducting the dynamical analysis in a stationary frame independent of initial conditions hinders the use of direct intuition, an effect shared by all forms of Fourier analysis. More precisely it requires a greater effort for translating independent information into the formalism of eigenfunction expansions. Yet it disentangles key aspects of phenomena from incidental ones.

Evolution of the base functions

The functions $\Phi_\mu(R;\Omega)$ constructed in Ref. 4, for the simple example of an electron pair, display properties that stem only from the topology of Eq. (12) and have accordingly general significance. In the condensation limit, where the $\vec{\Lambda}^2$ term is dominant, the functions Φ_μ reduce to hyperspherical harmonics which oscillate with comparable amplitude throughout the range of all variables Ω (except for influence of centrifugal potentials around a few points). In the fragmentation limit, the dominant potential term $C(\Omega)$ generally restricts the modes of fragmentation accessible at any given energy $U_\mu(R\rightarrow\infty)$. The restriction results from the dependence of C on the variables Ω. Maxima of $C(\Omega)$ represent barriers that confine nonzero values of the wave functions $\Phi_\mu(R\rightarrow\infty;\Omega)$ to separate valleys (Fig. 1). Typically each valley corresponds to a particular mode of fragmentation; reactive collisions are represented by propagation of a wave function $\Psi(R,\Omega)$ from one valley to another. The potential-energy surfaces of quantum chemistry result from averages of $C(\Omega)/R$ over the electron coordinates.

Figure 2 shows sample plots of eigenvalues $U_\mu(R)$ from Ref. 4. The rise of all curves as $R\rightarrow 0$ reflects the positive character of the eigenvalues of $\vec{\Lambda}^2$ for multidimensional systems. As $R\rightarrow\infty$, instead, each eigenvalue $U_\mu(R)$ approaches an eigenvalue of the separate fragments, including kinetic energy of relative motion in the event of multiple fragmentation. As in the example of molecular potentials, the eigenvalue $U_\mu(R)$ passes through a minimum for "bonding" states of the complex. States with antibonding character yield instead curves $U_\mu(R)$ that rise faster with decreasing R than for bonding states. This circumstance leads generally to numerous level crossings, which are "avoided" in an adiabatic base by switching the character of relevant states (Sec. IV A).

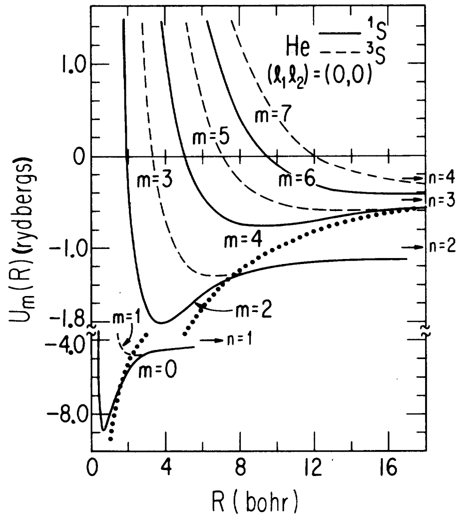

FIG. 2. Potential curves $U_m(R)$ for He. Dotted line representing $C(\alpha=45°, \theta_{12}=180°)/R$ marks boundary between condensation and fragmentation (Ref. 4).

As $R\rightarrow\infty$, the nonnegligible values of a function $\Phi_\mu(R;\Omega)$ become restricted not merely to a potential valley but eventually to an infinitesimal strip of coordinate space at its bottom. This strip is generally characterized by a zero value of one coordinate, as noted in Sec. II. [However, degeneracy of eigenvalues $\{U_\mu(\infty)=U_{\mu'}(\infty)\}$ allows the corresponding eigenfunctions to be distributed in different valleys tunneling through the intervening barrier.] Constructing the eigenfunctions Φ_μ conveniently as $R\rightarrow\infty$ is facilitated by transforming the coordinate set Ω to an appropriate form that will be denoted by Ω_∞. The transformation is trivial in the simple example of an electron pair[4] but it generally requires special analysis, e.g., when a molecule fragments into atoms with nonzero spins. Applying the approach of Ref. 5 to particular examples of this transformation should prove instructive, e.g., by providing a unique prescription of the translational factors for molecular dissociation.

The coordinate transformation $\Omega\rightarrow\Omega_\infty$ has an important bearing on the expression (11) of the potential energy $C(\Omega)/R$. This expression seems to vanish as $R\rightarrow\infty$, but it actually does so only in the limit of complete fragmentation in which none of the coordinates Ω vanishes. Otherwise C/R remains finite as $R\rightarrow\infty$ and simultaneously one of the Ω vanishes. In the example of an electron pair in a Coulomb field the potential energy of electron number 2, $-e^2/r_2=-e^2/R\sin\alpha$ remains finite when $r_1\rightarrow\infty$, $R\rightarrow\infty$, and $\alpha\rightarrow 0$. In the event of partial fragmentation, one or more of the coordinates Ω_∞ combines with R in a manner that yields a finite limit as $R\rightarrow\infty$ and serves for the physics of each fragment in the same role as R did for the complex.

Last, but far from least, we note that the propagation of an eigenfunction $\Phi_\mu(R;\Omega)$ from $R=0$ to ∞ meets a critical stage when it passes from the condensation region, where motion in Ω is unhindered, to the fragmentation region where it is restricted by potential barriers. This occurs along a line $\Omega=\Omega_{\max}$, where $C(\Omega)$ has a local maximum at the critical value of $R=R_{c\mu}$ for which the potential energy $C(\Omega_{\max})/R$ rises above the eigenvalue $U_\mu(R)$. (In the example of an electron pair the line $\Omega=\Omega_{\max}$ is represented by $\alpha=45°$, $\theta_{12}=180°$ in Fig. 1, and the critical values $R=R_{c\mu}$ lie along the dotted line in Fig. 2.) According to (12), this reversal of the sign of $U_\mu-C(\Omega_{\max})/R$ implies a sign reversal of $\vec{\Lambda}^2\Phi_\mu(R;\Omega)/\Phi_\mu(R;\Omega)$, i.e., a transition of $\Phi_\mu(R;\Omega)$ from oscillatory behavior to tunneling across the "ridge" line $\Omega=\Omega_{\max}$ (Fig. 3). Here then, the rising potential prevents the μth component of the wave function (13) from propagating further along the potential barrier. At all $R>R_c$ this component will generally concentrate in a valley on one side of the barrier. Drastic effects of this evolution will be described in Sec. IV C.

IV. NONADIABATIC EFFECTS

This section describes certain phenomena that induce transitions between adiabatic channels by raising the values of $W_{\mu\mu'}(R)$ coefficients in Eq. (14) in limited ranges of R for one or a few pairs of channels (μ,μ'). Relevant information has been developing rapidly but remains fragmentary. Additional phenomena with similar effects might well emerge in the future.

A. Isolated avoided crossings

The most familiar model of transitions between adiabatic channels is that of Landau-Zener-Stückelberg (LZS).[8] It deals with a pair of adiabatic channels whose energy functions $U_\mu(R)$ and $U_\nu(R)$ would vary linearly with R intersecting at a radial distance R_c were it not for a weak interaction δV. This interaction looms large in the narrow interval $R\sim R_c$ where $\delta V \gtrsim |U_\mu(R)-U_\nu(R)|$. The emergence of δV then causes $U_\mu(R)$ and $U_\nu(R)$ to swerve sharply whereby the intersection is replaced by an "avoided crossing." The pair of eigenfunctions $\{\Phi_\mu(R;\Omega),\Phi_\nu(R;\Omega)\}$ also evolves rapidly nearly R_c as represented by an orthogonal transformation

$$\begin{vmatrix}\Phi_\mu(R;\Omega)\\ \Phi_\nu(R;\Omega)\end{vmatrix} = \begin{vmatrix}\cos\beta(R) & \sin\beta(R)\\ -\sin\beta(R) & \cos\beta(R)\end{vmatrix} \begin{vmatrix}\Phi_\mu(R';\Omega)\\ \Phi_\nu(R';\Omega)\end{vmatrix}_{R'<<R_c} . \tag{15}$$

In the LZS model the transformation angle β rises rapidly from 0 to $\frac{1}{2}\pi$ as R traverses the region $\sim R_c$; the net effect of (15) is to interchange Φ_μ and Φ_ν in the sense that $\Phi_\mu(R>>R_c;\Omega)=\Phi_\nu(R<<R_c;\Omega)$ and vice versa. The energy $U_\mu(R)$ is also found to lie at $R>>R_c$ on the straight line extrapolation of $U_\nu(R<<R_c)$ and vice versa.

This model applies typically when the Hamiltonian is quasiseparable—e.g., in an independent particle approximation—to within the perturbation δV. For example, many energy levels of molecular electrons that are low in the united-atom limit rise toward the separate-atom limit while antibonding levels fall instead, thus intersecting each other. The localized breakdown of quasiseparability at $R\sim R_c$ then has very striking manifestations.[9] In the framework of Eq. (14) the model implies a Lorentzian dependence of $W_{\mu\mu'}(R)$ on R,[10] which seldom obtains accurately throughout its extended

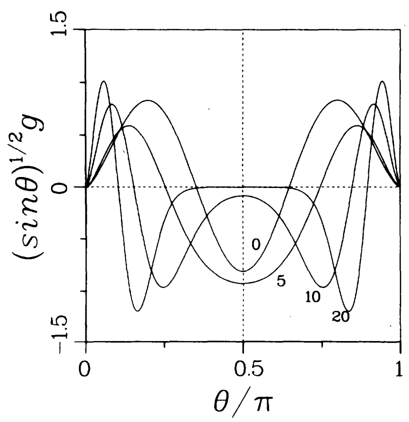

FIG. 3. Eigenfunctions of

$$[\Lambda_1^2-r^2U_{l1}(r)]g_{l1}(r;\theta)=0$$

for

$$\Lambda_1^2=-\partial^2/\partial\theta^2-\cot\theta\,\partial/\partial\theta+1/\sin^2\theta+\alpha^2r^4 .$$

$l=3$, $\alpha r^2=0,5,10,20$ (Ref. 19).

tails.

If our complex starts in channel μ at small R, that is, if its wave function (13) has a single nonzero term at $R << R_c$, the probability of finding it in channel ν at $R >> R_c$ is given in the LZS model by

$$P_{\nu\mu} = |F_{E\nu}(R >> R_c)|^2$$
$$= \exp\left[-2\pi(\delta V)_c^2 \Big/ \hbar v \left|\frac{d(U_\mu - U_\nu)}{dR}\right|_{R=R_c}\right] . \tag{16}$$

Here v indicates the velocity through the crossing

$$v_\mu = \{ 2[E - U_\mu(R_c)]/m \}^{1/2} . \tag{17}$$

The probability $P_{\nu\mu}$ reaches unity at high speeds. In this "diabatic" limit a wave function represented by $F_{E\mu}(R)\Phi_\mu(R;\Omega)$ at $R << R_c$ turns into $F_{E\nu}(R)\Phi_\nu(R;\Omega)$ at $R >> R_c$ but remains in fact substantially unchanged. Indeed $\Phi_\nu(R >> R_c;\Omega)$ coincides with $\Phi_\mu(R << R_c;\Omega)$ according to (15) with $\beta = \frac{1}{2}\pi$ as we have seen, and $F_{E\nu}(R >> R_c)$ is generated by Eq. (14) as an extrapolation of $F_{E\mu}(R << R_c)$. The adiabatic limit corresponds instead to low speeds at which $P_{\nu\mu}$ vanishes and the complementary probability of the complex staying in channel μ reaches unity. However, the state actually evolves in this case, since $\Phi_\mu(R >> R_c;\Omega)$ becomes the same as $\Phi_\nu(R << R_c;\Omega)$.

Classes of avoided crossings also occur frequently in which the angle $\beta(R)$ in the transformation (15) rises by an amount lower than $\frac{1}{2}\pi$ as R traverses the region of R_c. Typically this occurs when a channel eigenfunction Φ_μ evolves from being an eigenstate of certain variables (e.g., of LS coupling) into an eigenstate of other variables (e.g., of *jj* coupling). Nikitin has introduced a mathematical model for this class which is analogous to that of Landau-Zener-Stückelberg but is designed to apply more generally.[11] Actual calculations of $P_{\nu\mu}$ have been performed recently by numerical integration of a pair of coupled Eqs. (14) through the range $R \sim R_c$.[12] Experience should show how to estimate $P_{\nu\mu}$ under broad conditions from data on $W_{\nu\mu}(R)$ and on $\{ U_\mu(R), U_\nu(R) \}$. Small clusters of avoided crossings have been treated numerically as well.[13]

B. Frame transformations under diabatic conditions

The diabatic limit has been characterized above as the propagation of a wave function $\Psi_E(R,\Omega)$ through an avoided crossing, at high values of the speed (17), which leaves Ψ_E substantially unchanged even though its adiabatic expansion (13) changes drastically. We consider here the example of diabatic behavior in which a subset of p nearly degenerate adiabatic channel functions $\Phi_\mu(R;\Omega)$ evolve gradually over a range $R_1 < R < R_2$ into a new set $\Phi_i(R;\Omega)$. The details of the evolution, the avoided crossings occurring between R_1 and R_2, and even the one-to-one correspondence between the labels μ and i are irrelevant once diabatic behavior is assumed. What matters is that each Φ_μ at R_1 be represented as a specific superposition of Φ_i at R_2,

$$\Phi_\mu(R_1;\Omega) = \sum_i \Phi_i(R_2;\Omega) O_{i\mu} , \tag{18}$$

where $O_{i\mu}$ is an orthogonal transformation of order p reciprocal to (15). Diabatic propagation from R_1 to R_2 of a wave function initially concentrated in the single channel μ is then represented by writing

$$F_\mu(R_1)\Phi_\mu(R_1;\Omega) \underset{R \geq R_2}{\rightarrow} \sum_i \Phi_i(R;\Omega) F_i^{(\mu)}(R) O_{i\mu} , \tag{19}$$

where $F_i^{(\mu)}(R_2)$ is propagated from $F_\mu(R_1)$ by solving Eq. (14) in an *independent-channel* approximation, i.e., with $W_{\mu\mu'} = 0$. The label i has been added to the $F_i^{(\mu)}(R)$ in Eq. (19) only to allow for different propagation at $R > R_2$.

This treatment applies particularly to the evolution of adiabatic channel functions from one to another fine-structure pattern— e.g., from (LS) to (*jj*) coupling in atoms[14] or from one "Hund case" to another in molecules.[15] Diabaticity requires here, of course, small values of the coefficients $W_{\mu\mu'}(R)$ in Eq. (14) and near-degeneracy of the subset of p channel energies $U_\mu(R)$. It hinges more specifically on disregarding the small differences among the channel propagation *velocities* $v_\mu = \{ 2[E - U_\mu(R)]/m \}^{1/2}$ throughout the range of evolution, $R_1 < R < R_2$. The velocities v_μ (or v_i) in our subset of p channels must thus be nearly equal and yet high enough to ensure diabaticity in the range of evolution. This diabaticity criterion is no longer relevant beyond the region of avoided crossing at $R > R_2$. Here the propagation velocities v_i in the various new channels may taper off, exhibiting significant differences even though the channel energies $U_i(R)$ converge to the same limit. These features of channel velocities underlie the extensive spectroscopic applications of the quantum-defect theory.[16]

C. Diffraction on potential ridges

We have noted at the end of Sec. III how a ridge line, $\Omega=\Omega_{\max}$, of the potential-energy function $C(\Omega)$ acts as a watershed in diverting the outward propagation of wave-function components $F_\mu(R)\Phi_\mu(R;\Omega)$ away from the barrier top into potential valleys. Inertia, on the other hand, acts to conserve the direction of wave propagation for atomic processes as well as for water waves climbing up a sand bar. These contrasting influences result in departures from adiabatic propagation, which are a *major source of energy transfers* among the degrees of freedom of a collision complex. The prominent role of potential ridges in excitation appears to have been discovered by Wannier for a pair of electrons in a Coulomb field.[17] It is also observed for the radial motion of a single atomic electron in directions orthogonal to a magnetic field[18,19] and is being elucidated through the study of further examples.[12,13] Note how ridges necessarily occur in the potential surface of any complex consisting of nuclei and electrons where the coincidence of equal charges leads to a spike and the coincidence of oppositely charged particles to a sink.

Qualitative evidence on ridge effects emerges from plots of adiabatic eigenvalues $U_\mu(R)$, such as Fig. 2. The dotted line in that figure represents the value of $C(\Omega_{\max})/R$, where $\Omega_{\max}\equiv(\alpha=45°, \theta_{12}=180°)$ in Fig. 1. Successive pairs of black lines exhibit avoided crossings just as they traverse the dotted ridge line. (The dashed lines in Fig. 2 pertain to triplet states whose wave functions have a node on the ridge and are thus hardly affected by it.) A more complete picture is shown in Fig. 4 whose scales are adjusted to display many avoided crossings in a limited space. Consider, e.g., the propagation of a wave function $\Psi_E(R,\Omega)=\Sigma_\mu F_{E\mu}(R)\Phi_\mu(R;\Omega)$ whose $F_{E\mu}(R)$ vanish at $R\sim 0$ except in the lowest channel. As R reaches the ridge a part of the initial amplitude is transferred to the next higher channel at the first avoided crossing, according to Sec. IV A. This process repeats again and again, transferring amplitude to higher and higher channels at the successive avoided crossings. Note how each of these amplitude transfers implies a transfer of energy from the motion along R to the motion along coordinates Ω; indeed, the substitution $U_\mu\rightarrow U_{\mu+1}>U_\mu$ raises the eigenvalue of Eq. (12) and simultaneously reduces the energy $E-U_\mu(R)$ available for radial motion in Eq. (14).

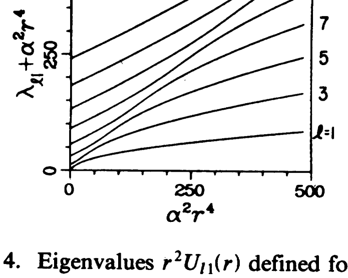

FIG. 4. Eigenvalues $r^2U_{l1}(r)$ defined for Fig. 3.

A remarkable effect of channel coupling at a ridge has emerged in a recent analysis of photoabsorption by the Be valence shell.[12] This process excites the valence electron pair from its initial configuration $2s^2$ into the lowest ${}^1P°$ channel with wave function $\Psi_E(R,\Omega)=F_{E1}(R)\Phi_1(R;\Omega)$. The adiabatic function $\Phi_1(R;\Omega)$ is approximately symmetric under reflection on the ridge line $\Omega=\Omega_{\max}$ throughout the condensation region $R<R_{c1}$, but it draws into the deeper potential valley on one side of the ridge as R increases through the critical range $R\sim R_{c1}$, where $U_1(R)$ falls below $C(\Omega_{\max})/R$. The avoided crossing in this range has been found to transfer about half the amplitude of $\Psi_E(R,\Omega)$ into the second channel, $F_{E2}(R)\Phi_2(\Omega;R)$, whose adiabatic function $\Phi_2(R;\Omega)$ draws into the potential valley on the side opposite to $\Phi_1(R;\Omega)$ at $R>R_{c2}$. Propagation of $\Psi_E(R;\Omega)$ through the range $R\sim R_c$ thus preserves the initial approximate symmetry of Ψ_E with respect to the ridge, compensating for the fact that Φ_1 and Φ_2 become grossly asymmetric. This analysis accounts for a previously identified but unexplained pattern of spectral data.

The simple Eq. (16) appears hardly suited to treating a whole sequence of avoided crossings such as that shown in Fig. 4. Preliminary studies have led to the construction of local solutions $\Psi_E(R,\Omega)$ that propagate along the ridge, with $\Omega\sim\Omega_{\max}$.[17,19] However, these solutions remain to be connected to the general expansion (13). Providing an adequate treatment of ridge effects is the main unfinished portion of the present treatment.

Note finally the contrasting emphasis between the discussion of propagation *along* the ridge, here and at the end of Sec. III, and the usual treatment of reactive collisions following a trajectory *across* the ridge. We deal in fact with complementary aspects of the same process. Their connection will become explicit in Sec. V.

D. Multiple fragmentation

A simple example of complete fragmentation is afforded by the double photoionization of He. The final state $\Psi_E(R,\Omega)$ of the electron pair has energy $E > 0$ and its expansion (13) consists, at large R, entirely of adiabatic components with energies $U_\mu > 0$ above the ridge. Accordingly the eigenfunctions $\Phi_\mu(R;\Omega)$ of these components extend over the entire range of Ω instead of being confined in a potential valley; specifically the coordinate α defined in Eq. (5) ranges from 0 to 90°, i.e., from one to the other valley bottom of Fig. 1. As $R \rightarrow \infty$, the dependence of $\Psi_E(R,\Omega)$ on α still represents the probability distribution of relative radial distances of the two electrons r_1 and r_2; by implication it also represents the probability distribution of the relative escape velocities of the two electrons.

The substance of this description applies to multiple fragmentation in general. If fragment number 1 detaches alone along a potential valley bottom with coordinates Ω_1 and fragment number 2 along coordinates Ω_2, joint detachment of the two fragments is represented by a wave function $\Psi_E(R \rightarrow \infty,\Omega)$ which has nonzero values along a continuous range of Ω extending from Ω_1 to Ω_2. Also, the energy E must exceed the height of the potential barrier that separates Ω_1 from Ω_2. The description extends also to the joint detachment of a higher number of fragments.

Since collision complexes are usually formed in low-energy adiabatic channels, the avenue to multiple fragmentation is expected to proceed from channel to channel, along a ladder of avoided crossings such as the one shown in Fig. 4. Each step of the ladder affords the complex an opportunity to proceed toward $R \rightarrow \infty$ along an adiabatic channel in which a fragment departs with fairly high speed, leaving the residue with insufficient energy for further fragmentation. Multiple fragmentation is favored when the whole complex expands instead with speed sufficient to traverse each avoided crossing *diabatically*, i.e., with high probability of passing to a higher channel. This is the content of Wannier's analysis of ionization of atoms by electron collision at energies near threshold.[17] In this process the incident electron and the target atom A form an excited negative-ion complex A^{-*}; ionization results if A^{-*} fragments into $A^{+}+e+e$ rather than into $A^{*}+e$. In Wannier's semiclassical treatment, ionization is reached by the narrow bundle of trajectories that remain close to a potential ridge over a long distance without dropping off into a valley.

V. EXPANSION AT LARGE R: JOST MATRICES

We have dealt in Secs. II–IV only with the propagation of a wave function from the condensation limit of a complex to its fragmentation limit. A collision involves also the reciprocal process of condensation from an initially fragmented state. We shall see how the processes are combined by considering the asymptotic expansion of energy eigenfunctions $\Psi_E(R,\Omega)$.

A complete set of orthogonal degenerate eigenfunctions $\Psi_\alpha(R;\Omega)$ in the form (13) with a given energy E can be identified through its behavior at $R \rightarrow 0$, for example, by setting

$$\lim_{R\rightarrow 0} R^{-c_\alpha} F_{\alpha\mu}(R) = \delta_{\alpha\mu} \,. \tag{20}$$

Here c_α is a positive root of the indicial equation for (14), determined by $U_\mu(R=0)$; multiple roots c_α are classified further by $(dU_\mu/dR)_{R\rightarrow 0}$ (Sec. III).

In the opposite limit, $R \rightarrow \infty$, the expansion (13) of each Ψ_α consists generally of several nonnegligible terms resulting from breakdowns of adiabaticity such as described in Sec. IV. We represent this expansion in a form analogous to that of $f_l(r)$ in Eq. (2), namely,

$$\Psi_\alpha(R;\Omega) \underset{R\rightarrow\infty}{\longrightarrow} \sum_i \phi_i(\Omega_\infty)(e^{ik_iR}R^{\zeta_i}J_{i\alpha}^{+} + e^{-ik_iR}R^{-\zeta_i}J_{i\alpha}^{-})[1+O(R^{-1})] \,. \tag{21}$$

Here the function $\phi_i(\Omega_\infty)$ represents one channel of fragmentation and may or may not coincide exactly with the $R \rightarrow \infty$ limit of one adiabatic function $\Phi_\mu(R;\Omega)$. (The index i is frequently used to label fragmentation channels.) The subscript of Ω_∞ in Eq. (21) reminds one that a transformation of Ω coordinates is generally required as $R \rightarrow \infty$ (Sec. III). Familiar examples of fragmentation are ionization, in which one fragment consists of an ejected electron, and molecular dissociation. The wave number k_i in Eq. (21) corresponds to the kinetic energy of fragment separation $E - U_i(R \rightarrow \infty)$. When this energy is negative the fragments remain bound, often very loosely, and k_i takes the imaginary form $i\kappa_i$, as will be discussed in Sec. VI. The exponent ζ_i is the root of an indicial-type equation at $R\rightarrow\infty$[20]; it generally vanishes in the absence of a Coulomb force between the fragments. The expansion coefficients $J^{\pm}_{i\alpha}$ are called "Jost functions," with reference to their analytic dependence on the energy E,[21,7] and constitute two matrices whose rows and columns are labeled by i and α, thus correlating eigenfunction properties at $R\rightarrow\infty$ and $R\rightarrow 0$. Notice that the standing-wave character of the wave function (21) implies $J^{-}_{i\alpha}=J^{+*}_{i\alpha}$ for all i channels whose k_i is real.

The formulation of the expansion (13) in terms of Jost matrices facilitates the superposition of standard Ψ_α to represent states specified by experimental boundary conditions. The most familiar of such states—a generalization of (1)—has an incoming wave in a single channel j and outgoing wave components in other channels,

$$\begin{aligned}\Psi_j^{+}&=\sum_\alpha \Psi_\alpha\left[\frac{1}{J^{-}}\right]_{\alpha j}\\&\underset{R\rightarrow\infty}{\rightarrow}\sum_i \phi_i(\Omega_\infty)\left[e^{-ik_iR}R^{-\zeta_i}\delta_{ij}+e^{ik_iR}R^{\zeta_i}\sum_\alpha J^{+}_{i\alpha}\left[\frac{1}{J^{-}}\right]_{\alpha j}\right].\end{aligned}\tag{22}$$

The $^+$ index identifies this wave function as satisfying an "outgoing wave" boundary condition.[21] An "incoming wave" condition characterizes instead the wave function resulting from (22) by time reversal,

$$\begin{aligned}\Psi_j^{-}&=\sum_\alpha \Psi_\alpha\left[\frac{1}{J^{+}}\right]_{\alpha j}\\&\underset{R\rightarrow\infty}{\rightarrow}\sum_i \phi_i(\Omega_\infty)\left[e^{ik_iR}R^{\zeta_i}\delta_{ij}+e^{-ik_iR}R^{-\zeta_i}\sum_\alpha J^{-}_{i\alpha}\left[\frac{1}{J^{+}}\right]_{\alpha j}\right].\end{aligned}\tag{23}$$

In Eq. (22) the matrix product

$$\sum_\alpha J^{+}_{i\alpha}\left[\frac{1}{J^{-}}\right]_{\alpha j}=\left[J^{+}\frac{1}{J^{-}}\right]_{ij}=S_{ij}\tag{24}$$

clearly represents a scattering matrix, whose reciprocal appears instead in Eq. (23). Collision cross sections are expressed routinely in terms of the scattering matrix S_{ij}.

Calculation of the coefficients $(J^{\pm})_{i\alpha}$ of the expansion (21) for a complete set of Ψ_α is thus seen to provide *all the information* that is *necessary* for the evaluation of collision cross sections at a given energy. Notice how the calculation itself does *not concern collisions* explicitly but rather the propagation of the standing-wave stationary eigenfunctions Ψ_α from the condensation to the fragmentation limit. In the course of this propagation each Ψ_α—initially concentrated in a single channel α—generally spreads over several fragmentation channels ϕ_i. The structure of Eq. (24) displays the scattering parameter S_{ij} as resulting from the amplitude $(1/J^{-})_{\alpha j}$ of incoming wave propagation from $R=\infty$ in channel j to $R=0$ in channel α and the amplitude $J^{+}_{i\alpha}$ of outward propagation from $R=0$ in α to $R=\infty$ in i; these amplitudes are multiplied and the result is summed over all pathways α.

The probability of photoabsorption by an atomic system with a ground-state wave function Ψ_0 through a dipole process represented by D is proportional to

$$\sum_\alpha |D_\alpha|^2=\sum_\alpha |(\Psi_\alpha|D|\Psi_0)|^2\tag{25}$$

Here the integration in each matrix element is confined to the limited volume over which $\Psi_\alpha\neq 0$. The probability of a fragment's ejection in the various channels j,

$$\left|\sum_\alpha\left[\frac{1}{J^{+}}\right]^{*}_{\alpha j}(\Psi_\alpha|D|\Psi_0)\right|^2,\tag{26}$$

depends thus in the main on the Jost coefficients $J^{+}_{i\alpha}$, that is, on a *single* set of the component factors of the scattering matrix (24). This formal remark reflects the fact that the effect of photoabsorption propagates outward from the initially condensed volume of the system whereas collisions involve first a condensation and then a fragmentation. Accordingly one often characterizes photoabsorption as a *half-scattering* process.

VI. OPEN CHANNELS AND CLOSED CHANNELS: RESONANCES

The occurrence of closed channels, for which the wave number k_i in Eq. (21) is imaginary, has conspicuous effects on the spectrum of a collision complex. Pairs of Jost matrix elements $J_{i\alpha}^{+}$ and $J_{i\alpha}^{-}$ are real and unequal for closed channels, in contrast to open channels where they are complex conjugate. The exponentials in (21) are real, too, and more importantly the factor $\exp(-ik_iR) = \exp(\kappa_i R)$ diverges as $R\rightarrow\infty$. This divergent factor appears in the closed-channel terms of the expansion (21) of any solution Ψ_α of the Schrödinger equation. Accordingly, a single Ψ_α no longer constitutes a bounded eigenfunction. Bounded eigenfunctions are then constructed as particular superpositions of Ψ_α,

$$\Psi_b = \sum_\alpha \Psi_\alpha A_\alpha \ , \tag{27}$$

for which the coefficient of each diverging exponential vanishes,

$$\sum_\alpha J_{i\alpha}^{-} A_\alpha = 0 \ , \quad \text{for} \, \mathrm{Im} k_i > 0 \ . \tag{28}$$

For values of the energy E lower than all the separation energies $U_i(R\rightarrow\infty)$ all channels are closed and fragmentation of the complex cannot proceed to its limit. The complex remains thus bound in stable eigenstates. Considering that $\mathrm{Im} k_i > 0$ for every channel i, in the present case we see that the matrix $J_{i\alpha}^{-}$ is square. Accordingly the energy eigenvalues are determined by the compatibility condition of the system (28),

$$\det | J_{i\alpha}^{-} | = 0 \ . \tag{29}$$

This equation may be viewed as an extension of the original Jost analysis[21] which dealt with a single channel and therefore with a scattering matrix consisting of a single element J^{+}/J^{-}. Jost pointed out how J^{-} can be continued analytically from positive to negative values of the fragment kinetic energy $E - U(R\rightarrow\infty)$. Bound-state levels occur then at the zeros of J^{-}, which are poles of the scattering matrix. Jost dealt only with the short-range interactions between the fragments. Introduction of the factors $R^{\pm\zeta_i}$ in Eq. (21) amounts to representing the Jost matrices in a base of eigenfunctions of a long-range potential. It permits us to circumvent Jost's restriction at the price of introducing a singularity of $J_{i\alpha}^{-}$ at $E = U_i(R\rightarrow\infty)$; thus it requires us to extrapolate $J_{i\alpha}^{-}$ carefully around its singularity.[22]

In the study of collision processes at a given energy E the channels i can usually be subdivided into three classes: (1) open channels, with $E > U_i(R\rightarrow\infty)$, to be labeled by $i = 1, 2, \ldots, N_0$, (2) "weakly closed" channels, with $U_i(R\rightarrow\infty) > E \gtrsim [U_i(R)]_{\min}$, whose radial function $F_{E_i}(R)$ vanishes at $R\rightarrow\infty$ but is nonnegligible at lower R values where the complex is bound, and (3) "strongly closed" channels, with $U_i(R) >> E$ at all R, whose $F_{E_i}(R)$ is altogether negligible. This last class includes an infinity of channels with minimal influence on the open channels. This influence can be taken into account indirectly through optical potentials or even disregarded altogether by truncating the sum over μ' in Eq. (14). In the presence of open channels Eq. (28) does not restrict the energy E, of course, nor does it suffice to determine the coefficients A_α. In fact, N_0 additional parameters are required to determine the A_α; they are normally drawn from boundary conditions imposed on the N_0 open channels.

Recall in this connection how the fitting of typical boundary conditions by Eqs. (22) and (23) hinges on the completeness of the base set $\{\Psi_\alpha\}$ ensured by their boundary property (20) at $R\rightarrow 0$. To attain analogous flexibility in the presence of closed channels we introduce a complete set of N_0 open channels, $\{\Psi_\rho\}$, selected as eigenvectors of the scattering matrix, i.e., by a boundary property at $R\rightarrow\infty$. (This procedure originates from quantum defect applications[14].)

Consider then superpositions $\Psi_\rho = \sum_\alpha \Psi_\alpha A_\alpha^{(\rho)}$ with the understanding that the coefficients $A_\alpha^{(\rho)}$ satisfy Eq. (28) for all closed channels. The asymptotic expansion (21) of Ψ_ρ has the form

$$\Psi_\rho = \sum_\alpha \Psi_\alpha A_\alpha^{(\rho)} \rightarrow \sum_{i=1}^{N_0} \phi_i(\Omega_\infty) \left[e^{ik_iR} R^{\zeta_i} \sum_\alpha J_{i\alpha}^{+} A_\alpha^{(\rho)} + e^{-ik_iR} R^{-\zeta_i} \sum_\alpha J_{i\alpha}^{-} A_\alpha^{(\rho)} \right] [1 + O(R)]$$
$$+ \sum_{i > N_0} \phi_i(\Omega_\infty) e^{-\kappa_i R} R^{\zeta_i} \sum_\alpha J_{i\alpha}^{+} A_\alpha^{(\rho)} \ . \tag{30}$$

To characterize the Ψ_ρ as scattering eigenvectors we require their coefficients $\sum_\alpha J_{i\alpha}^{\pm} A_\alpha^{(\rho)}$ with $i \leq N_0$ to have the same phase δ_ρ in all channels,

$$\sum_\alpha J_{i\alpha}^{\pm} A_\alpha^{(\rho)} = T_{i\rho} e^{\pm i\delta_\rho} \qquad (i,\rho) \leq N_0 \ . \tag{31}$$

The square matrix of coefficients

$$T_{i\rho}=e^{i\delta_\rho}\sum_\alpha J^-_{i\alpha}A^{(\rho)}_\alpha \tag{32}$$

is thus to be made real by setting

$$\sum_\alpha \mathrm{Im}(e^{i\delta_\rho}J^-_{i\alpha})A^{(\rho)}_\alpha=0\ . \tag{33}$$

Notice now that these N_0 equations combine with the Eqs. (28) to form a real homogeneous system adequate to determine the superposition coefficients $A^{(\rho)}_\alpha$ to within normalization. The compatibility condition of this system is viewed as a generalization of (29)

$$\det|\mathcal{J}^-_{i\alpha}|=0\ , \tag{34a}$$

$$\mathcal{J}^-_{i\alpha}=\begin{cases}\mathrm{Im}(e^{i\delta_\rho}J^-_{i\alpha})\ ,\ i\le N_0\\ J^-_{i\alpha}\ ,\ i>N_0\end{cases}\ . \tag{34b}$$

As Eq. (29) determines the discrete energy eigenvalues of the complex when all channels are closed, so does Eq. (34a) determine the discrete eigenphase shifts of its scattering states Ψ_ρ. That Eq. (34a) has N_0 roots δ_ρ is manifested by casting it as an N_0th degree algebraic equation in $\tan\delta_\rho$. Once the δ_ρ and the $A^{(\rho)}_\alpha$ are obtained from Eqs. (28), (33), and (34), Eq. (32) gives the matrix of coefficients $T_{i\rho}$ as

$$\begin{aligned}T_{i\rho}&=\sum_\alpha \mathrm{Re}(e^{i\delta_\rho}J^-_{i\alpha})A^{(\rho)}_\alpha\\ &=\frac{\partial}{\partial\delta_\rho}\sum_\alpha \mathrm{Im}(e^{i\delta_\rho}J^-_{i\alpha})A^{(\rho)}_\alpha\ .\end{aligned} \tag{35}$$

The last expression of Eq. (35) displays its connections to Eq. (33). The coefficients $A^{(\rho)}_\alpha$ and $T_{i\rho}$ may be normalized by setting $\sum_i T^2_{i\rho}=1$. Wave functions satisfying out- or ingoing wave boundary conditions in the open channels may finally be constructed from Eq. (30) in analogy to Eqs. (22) and (23).

The closed channels of the complex are included explicitly in the last term of the wave function (30) but are otherwise largely eliminated from explicit consideration. They contribute to Eq. (34a) and to the eigenvectors $A^{(\rho)}_\alpha$ through the values of large minors of the real matrix $J^-_{i\alpha}$, $i>N_0$. Approximations to their treatment may be introduced directly into the evaluation of these minors.

Resonances, often very sharp, in the energy dependence of δ_ρ and $T_{i\rho}$ are the major manifestation of closed channels of the "weakly closed" class with modest values of $U_i(R)-E$. Qualitatively they are attributed to the occurrence of quasibound discrete levels in such weakly-closed channels. Mathematically one notices that Jost matrix elements (34c) of these channels depend on the phase accumulation of radial functions $F_i(R)$ at large R (Ref. 22) and are thus sensitive sinusoidal functions of the energy E. The vanishing of a minor of the matrix $J^-_{i\alpha}$ $(i>N_0)$, or even of a single element $J^-_{i\alpha}$ in the case of weak channel coupling, may have a magnified effect upon an eigenvalue δ_ρ of Eq. (34a) and upon the coefficients $T_{i\rho}$. Strictly speaking, the spectral position and width of each resonance is identified by the position and width of a sharp peak of an eigenvalue of the time-delay matrix[23]

$$-i\hbar\sum_l (S^{-1})_{il}\frac{d}{dE}S_{lj}\quad (i,j)\le N_0 \tag{36}$$

where $S_{ij}=\sum_\rho T_{i\rho}e^{2i\delta_\rho}(T^{-1})_{\rho j}$ is the scattering matrix of the open channels.

VII. CONCLUSIONS

The determination of the coefficients $J^\pm_{i\alpha}$ (Jost matrix elements) of the asymptotic expansion (21) is viewed in this paper as the primary objective of collision theory. The path to this goal involves the study of those critical processes (Sec. IV) that are particularly relevant to any specific application. Among these studies, that of diffraction by potential ridges is still in a primitive stage; additional critical processes may well be identified in the future. Substantial sharpening of the analysis presented here is also required throughout the various stages of evolution of a collision complex from its condensation limit to fragmentation, particularly for the approach to fragmentation. Most of these problems have been familiar in various forms; our objective was to fit them into a single framework.

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