Semiclassical perturbation theory of electron-molecule collisions

W. H. Miller
Department of Chemistry, University of California, Berkeley, California 94720

F. T. Smith
SRI International, Menlo Park, California 94025
(Received 25 July 1977)

The theory of the classical or semiclassical $S$ matrix is combined with the use of perturbation dynamics to derive an approximately unitary expression for the scattering matrix for a very general class of potential interactions. The $S$ matrix takes the form of a sum over products of Bessel functions whose orders are related to the changes in quantum numbers occurring in the transition, and whose arguments depend on the dynamical variables of the problem, including the unperturbed quantum numbers. In the general case, these arguments can be expressed as simple integrals over the unperturbed trajectory, and for well-behaved potentials they can be explicitly evaluated in terms of the modified Bessel functions $K_0$ and $K_1$. The connection between the semiclassical perturbation scattering theory and other approximations, such as the Born and eikonal approximations, is demonstrated. The general theory is illustrated by applications to electron- (or ion-) polar-molecule scattering, including quadrupole as well as dipole interactions and including coupling to vibrations in both harmonic and anharmonic approximations. The more complicated interactions involve longer products of Bessel functions in the sum-and-product representation, but these are easily and systematically evaluated, and they reduce smoothly to the appropriate simpler expressions when the coupling coefficients of the higher-order terms become small. More complicated potentials, including interactions between polyatomic molecules, can be handled by a simple systematic extension of the same principles. For electron-molecule scattering, these expressions can be used in their present form since the sums are dominated by Bessel functions of comparatively low order which can be evaluated directly; extensions to molecule-molecule scattering and ion-molecule scattering are equally valid formally, but their practical application will often require the use of asymptotic approximations to the Bessel functions.

I. INTRODUCTION

One of the most important aspects of the classical $S$-matrix theory introduced in 1970 is that it showed how dynamically exact classical mechanics can be combined with quantum mechanics in a consistent way for describing complex (i.e., inelastic and reactive) collision processes. Exact classical mechanics for an inelastic collision, however, means numerically computed classical trajectories, and although these are readily obtainable nowadays, simpler models for the dynamics are often of sufficient accuracy and provide more insight into the mechanism of the process. They are also easier to apply and may even lead to simple analytic expressions for the cross sections of interest.

This paper explores the form taken by classical $S$-matrix theory when the collision dynamics is treated by perturbation theory. In this limit the theory becomes essentially equivalent to the perturbative models from other approaches by Cross, Beigman, Vainshtein, and Sobel’man, Levine and Johnson, and Percival and Richards. A recent review by Clark, Dickinson, and Richards gives an extensive summary of the approach of Percival and Richards and applications that have been made by them and their co-workers. An important difference between our work and that of Percival and Richards for the case of rotational excitation is that we have taken correct account of total angular momentum conservation by applying the theory in a total angular momentum representation. Thus, our $S$-matrix elements are labeled by the (conserved) total angular momentum quantum number and the full complement of other quantum numbers and energy variables, while they have worked within an impact parameter representation that makes no reference to total angular momentum. This makes it possible, for example, to calculate differential scattering cross sections, momentum transfer cross sections, etc., simply by substituting our $S$-matrix elements into the appropriate quantum-mechanical expressions.

Section II shows how semiclassical perturbation scattering theory is obtained in a very simple way from the more general classical $S$-matrix theory, and its relation to some other theoretical models that have a very similar structure is discussed in Sec. III. In particular, we demonstrate the similarity between the semiclassical expressions and various exponentiated forms, including the distorted-wave Born approximation; since the general semiclassical theory leads naturally to an exponential form, it provides some justification for some of these ad hoc exponential models.
The initial applications we have in mind are to rotational and vibrational excitation of molecules by electrons, and Sec. IV gives some specifics of how the theory proceeds for these applications. It is of considerable practical importance that one obtains closed-form expressions for the S-matrix elements for these inelastic processes. In general, these expressions take the form of sums over multiple products of Bessel functions. They are suited to the rapid evaluation of cross sections, and they have convenient and transparent convergence properties that make it possible easily to assess quantitatively the effects of additional interaction terms that are usually assumed small and dismissed with a qualitative argument. We show, as a specific example, how vibrational and rotational interactions can be incorporated together, and how the expressions converge smoothly to the pure rotational form at low energies. It is easy to treat the consequences of other interactions such as higher multipole terms and anharmonic vibrational effects by the same procedure.

Our S-matrix expressions show that the perturbation results are justified in two limits that are in principle independent, though the domains of convergence they define may sometimes overlap. There is a domain of low-energy convergence, related to the fact that inelastic transitions become impossible when the available energy is less than the next excitation threshold. There is also a high-energy convergence, reflecting the need for some matching between the collision time and the characteristic response time of the internal mode whose excitation is being examined. The dimensionless parameters characterizing these convergence properties depend strongly on the re-

\[
S_{n_p n_f} = (2\pi)^2 \int_0^\infty \frac{d^2 q}{q^4} \left( \frac{\partial^2 \Phi(q_i, n_i)}{\partial q_i^2} \right)^{1/2} \exp \left( i \cdot \Phi(q_i, n_i) + \frac{\theta}{q_i} \right) n_f(q_i, n_i) \left( n_f(q_i, n_i) - n_f \right) \]  

(2.3)

(units being used so that \(\hbar = 1\)), where \(n_f(q_i, n_i)\) and \(\phi_f(q_i, n_i)\) are the final values of the action and angle variables, respectively, as determined by classical trajectory with initial values \(n_i\) and \(\theta_i\) for these variables \(q_i\) and \(\phi_i\) are, more precisely, the differences of the angle variables from their unperturbed values; see Ref. 8 for more details); \(n_f\) and \(n_i\) are integers specifying the initial and final quantum states of the internal degree of freedom. The action integral \(\Phi(q_i, n_i)\) is defined in Ref. 8; for present purposes it is only necessary to note that its derivative with respect to \(q_i\) is given by

\[
\frac{\partial \Phi(q_i, n_i)}{\partial q_i} = -\frac{\theta_i(q_i, n_i)}{q_i} \frac{\partial n_f(q_i, n_i)}{\partial q_i} \]  

(2.2)

II. GENERAL THEORY: PERTURBATIVE LIMIT OF THE CLASSICAL S MATRIX

It is simplest first to consider a system with only one internal degree of freedom, for which the classical Hamiltonian is

\[
H(P, R, n, q) = P^2/2m + \epsilon(n) + V(R, n, q),
\]  

(2.1)

\(R\) and \(P\) are the coordinate and momentum for relative translation of the two collision partners, \(n\) and \(q\) are the action-angle variables for the internal degree of freedom, and \(\epsilon(n)\) is the WKB eigenvalue function for the internal degree of freedom. The collinear collision of an atom with a diatomic molecule is an example of this type of system. The reader should see Ref. 8 for a more detailed discussion of this model and application of the general classical S-matrix approach to it.

The initial-value representation for the classical S matrix is given by

\[
V(R, q, n) = V_0(R) + \Delta V(R, q, n),
\]  

(2.4)

and the zeroth-order trajectory is determined using the interaction \(V_0(R)\). With this zeroth-order Hamiltonian,

\[
H_0(P, R, n, q) = P^2/2m + V_0(R) + \epsilon(n),
\]  

(2.5)

the translational and internal motions are uncoupled, and it is easy to see that the zeroth-order approximation to the trajectory is

\[
R(t) = R_0(t),
\]  

(2.6a)

\[
n(t) = n_0,
\]  

(2.6b)
\[ q(t) = \bar{q}_i + \omega t, \quad (2.6c) \]

where
\[ \omega = \epsilon' (n_i), \quad (2.6d) \]

and where \( R_i(t) \) is the translational trajectory determined by \( V_0(R) \). \( n_f(\bar{q}_i, n_i) \) is then given to first order in the perturbation by

\[
\begin{align*}
  n_f(\bar{q}_i, n_i) &= n_i + \int_{-\infty}^{\infty} dt \, \frac{\delta H}{\delta q} \\
  &= n_i - \int_{-\infty}^{\infty} dt \, \frac{\delta V_i(R_i(t), \bar{q}_i + \omega t, n_i)}{\delta q} \\
  &= n_i - \frac{\partial A(\bar{q}_i, n_i)}{\partial q} \quad (2.7)
\end{align*}
\]

where
\[ A(\bar{q}_i, n_i) = \int_{-\infty}^{\infty} dt \, V_i(R_i(t), \bar{q}_i + \omega t, n_i) \quad (2.8) \]

It is necessary to determine \( q_f(\bar{q}_i, n_i) \) only to zeroth order:
\[ \bar{q}_i(\bar{q}_i, n_i) = \bar{q}_i. \quad (2.9) \]

Using Eq. (2.3) with Eqs. (2.7) and (2.9) gives
\[ \frac{\partial \Phi(\bar{q}_i, n_i)}{\partial \bar{q}_i} = \frac{\partial A(\bar{q}_i, n_i)}{\partial \bar{q}_i} \quad (2.10a) \]

or
\[ \Phi(\bar{q}_i, n_i) = \Phi_0 + \int d\bar{q}_i \, \bar{q}_i \quad (2.10b) \]

where \( \Phi_0 \) is the phase if \( \Delta V = 0 \). Integrating Eq. (2.10) by parts gives the action function as
\[ \Phi(\bar{q}_i, n_i) = \Phi_0 - A(\bar{q}_i, n_i) + \int d\bar{q}_i \, \frac{\partial A(\bar{q}_i, n_i)}{\partial \bar{q}_i} \quad (2.11) \]

Substituting the perturbation approximations for \( q_f(\bar{q}_i, n_i, n_f(\bar{q}_i, n_i), n_f(\bar{q}_i, n_i)) \), and \( \Phi(\bar{q}_i, n_i) \)—Eqs. (2.9), (2.7), and (2.11)—into the initial value representation, Eq. (2.2), gives
\[ \delta_{n_f} = \epsilon^{2\delta} (2\pi)^{-1} \int_0^{2\pi} d\bar{q}_i e^{-i\delta_{n_f} n_i} e^{iA(\bar{q}_i, n_i)} \quad (2.12) \]

The unperturbed phase \( \Phi_0 \) is twice the phase shift for the potential \( V_0(R) \),
\[ \Phi_0 = 2\delta, \quad (2.13) \]

where
\[ \delta = \frac{\pi}{4} + \lim_{R \to \infty} \left( -kR + \int_0^R dR' \left\{ 2m[E_i - V_0(R')] \right\}^{1/2} \right) \quad (2.14) \]

\( E_i = k^2/2m \) being the translational energy. As it stands, the \( S \) matrix in Eq. (2.12) is not symmetric (as the exact \( S \) matrix is), and it can be symmetrized in one of several ways. The usual procedure is to use for the unperturbed parameters the average of initial and final values, making
\[ 2\delta = \delta_i + \delta_f, \]
\[ n_i = \frac{1}{2} (n_i + n_f) \equiv n, \quad E_i = \frac{1}{2}(E_i + E_{f,i}), \quad (2.15) \]

where \( \{ \delta_i \}, i = 1, 2 \) is given by Eq. (2.14) with \( E_{f,i} = E - \epsilon(n_i) \). This symmetrized version of the perturbation approximation for the classical \( S \) matrix is thus given by
\[ S_{\pi, n} = e^{i\delta_{\pi}^{(1)} n} (2\pi)^{-1} \int_0^{2\pi} d\bar{q}_i e^{-i\delta_{\pi}^{(1)} n} e^{iA(\bar{q}_i, n)} \quad (2.16a) \]

with
\[ A(\bar{q}_i, n) = \int_{-\infty}^{\infty} dt \, \Delta V(R_i(t), \bar{q}_i + \omega t, n). \quad (2.16b) \]

This perturbative result has been obtained by a number of other workers using a variety of formalisms, most notably by Cross,\(^a\) by Beigman, Vainshtein, and Sobel'man,\(^b\) by Levine and Johnson,\(^c\) and by Percival and Richards.\(^d\)

In this section of the paper, and in Sec. III, we use a detailed notation suitable for deriving the general formulas for the semiclassical perturbation \( S \) matrix, Eqs. (2.16a) and (2.16b), and other approximations. In Sec. IV we adopt a simplified notation, based on Eq. (2.15) and the following further substitutions:
\[ \bar{q}_i - q, \quad n_f - n_i = \Delta n, \quad (2.17) \]

and on an alternative notation for the \( S \)-matrix elements that segregates unperturbed (average) values of quantum numbers from the changes in them,
\[ S_{\pi, n} = S_{\Delta n}. \quad (2.18) \]

(See the Appendix for further discussion.) In this notation, Eqs. (2.16a) and (2.16b) become
\[ S_{\Delta n} = e^{i\delta_{\pi}^{(1)} (2\pi)^{-1}} \int_0^{2\pi} d\bar{q}_i e^{-i\Delta n} e^{-iA(\bar{q}_i, n)} \quad (2.16a') \]

\[ A(q, n) = \int_{-\infty}^{\infty} dt \, \Delta V(R_i(t), q + \omega t, n). \quad (2.16b') \]

This notation is easily generalized to apply to systems with multiple quantum numbers; in Sec. IV we shall generally label these with the con-
venational symbols \((J, j, l\) for angular momenta, \(v\) for vibration), thereby liberating the protean letter "\(n\)" for other uses.

### III. COMPARISON WITH OTHER PERTURBATIVE MODELS

It is illuminating to compare the perturbative limit of classical \(S\)–matrix theory, Eq. (2.16), with some other similar models.

Consider first the semiclassical version of the **distorted-wave Born approximation** (DWBA) for the \(S\) matrix:

\[
S_{\text{DWBA}}^{\phi} = e^{i(\delta_f + \delta_f)} \left( \delta_{\phi, \phi} - \frac{i}{\hbar} \int_0^\infty d\tau \int_0^{2\pi} dq f(R,R') \phi(q) \right) V_{\phi}(R'),
\]

(3.1)

where the semiclassical internal wave functions \(\phi(q)\) are

\[
\phi(q) = (2\pi)^{-1/2} e^{i\epsilon q},
\]

(3.2)

and the translational wave functions \(f(R)\) are given by their WKB approximation,

\[
f_i(R) = \sin \left( \frac{\pi}{4} + \int R_i \frac{d}{dR} k_i(R) \right) \left[ k_i(R) \right]^{1/2}
\]

(3.3)

with

\[
k_i(R) = \left\{ 2 \mu \left[ E - \epsilon(n_i) - V_0(R) \right] / \hbar^2 \right\}^{1/2}
\]

(3.4)

With the following rather standard set of approximations,

\[
S_{\text{DWBA}}^{\phi} = e^{i(\delta_f + \delta_f)} \left( \delta_{\phi, \phi} - \frac{i}{\hbar} \int_0^\infty d\tau \int_0^{2\pi} dq e^{-i\epsilon n_i} \epsilon \Delta V(R_0(t),q,\bar{n}),
\]

(3.5)

Changing the integration variables \(q\) to \(\bar{q}\),

\[
q = \bar{q} + \omega t,
\]

(3.6)

then gives (setting \(\hbar = 1\))

\[
S_{\text{DWBA}}^{\phi} = e^{i(\delta_f + \delta_f)} \left( \delta_{\phi, \phi} - i(2\pi)^{-1} \int_0^{2\pi} dq \int_0^\infty dt \Delta V(R_0(t),\bar{q}, \omega t, \bar{n}) \right).
\]

(3.7)

Since

\[
\delta_{\phi, \phi} = (2\pi)^{-1} \int_0^{2\pi} dq \int_0^\infty dt \Delta V(R_0(t),\bar{q}, \omega t, \bar{n})
\]

(3.8)

the result may be written as

\[
S_{\text{DWBA}}^{\phi} = e^{i(\delta_f + \delta_f)} \left( \delta_{\phi, \phi} - \frac{1}{\hbar} \int_0^\infty d\tau \int_0^{2\pi} dq f(R,R') \phi(q) \right) V_{\phi}(R'),
\]

(3.9)

where

\[
\epsilon(R) = \left[ k_i(R) k_f(R) \right]^{1/2}
\]

(3.10)

and with

\[
\int_0^\infty d\tau \int_0^{2\pi} dq f(R,R') \phi(q)
\]

it is not hard to show that Eq. (3.1) becomes

\[
S_{\text{DWBA}}^{\phi} = e^{i(\delta_f + \delta_f)(2\pi)^{-1}} \sum_{n_1} e^{-i\epsilon n_1} \Delta V(R_0(t),q,\bar{n})
\]

(3.11)

If one now exponentiates the integrand in Eq. (3.12),

\[
1 - iA(\bar{q},\bar{n}) = e^{-iA(\bar{q},\bar{n})}
\]

(3.12)

one sees that the perturbative classical \(S\)–matrix result, Eq. (2.16), is obtained. The procedure of the DWBA, joined with a particular type of exponentiation, thus leads back to the perturbation limit of classical \(S\)–matrix theory.

The exponentiation indicated in Eq. (3.13), which gives the perturbative classical \(S\)–matrix expression, is different from the usual ad hoc exponential approximation.\(^{10}\) The usual approach is

\[
S_{\text{Exp. Approx.}}^{\phi} = e^{i(\delta_f + \delta_f)}(\epsilon^{-1})^{\phi, \phi} A(\bar{q},\bar{n})
\]

(3.13)

where \(A\) is the matrix.
i.e., the usual approach exponentiates the matrix of $A$, while Eq. (3.13) is the exponentiation of the integrand of the matrix element.

Another kind of exponential approximation can be obtained as follows. Returning to the DWBA expression in Eq. (3.6), one sees that it can also be written as

$$S_{np}^{\text{DWBA}} = e^{i\left(\theta_1 + \theta_2\right)} \left(1 - \frac{i}{\hbar} \int_0^{2\pi} dq \, e^{-i\left(\pi f_{n'1}\right)q} \int_{-\infty}^{\infty} dt \, e^{i\left(\pi f_{n'1}\right)\omega t} \Delta V(R_0(t), q, \vec{n})\right)$$

If one here exponentiates in the following indicated way,

$$1 - \frac{i}{\hbar} \int_0^{2\pi} dq \, \exp\left[i(n_f - n_i)\omega t\right] \Delta V(R_0(t), q, \vec{n}) - \exp\left(-\frac{i}{\hbar} \int_0^{2\pi} dq \, \exp\left[i(n_f - n_i)\omega t\right] \Delta V(R_0(t), q, \vec{n})\right),$$

then one obtains a result which may be thought of as an extension of the eikonal approximation to inelastic scattering:

$$S_{np}^{\text{eikonal}} = \exp\left[i\left(\delta_1 + \delta_2\right)\right] \left(2\pi\right)^{-1}$$

$$\times \int_0^{2\pi} dq \, \exp\left[-i(n_f - n_i)q\right]$$

$$\times \exp\left(-\frac{i}{\hbar} \int_0^{2\pi} dq \, \exp\left[i(n_f - n_i)\omega t\right] \Delta V(R_0(t), q, \vec{n})\right).$$

Although similar to the perturbative classical S-matrix expression, Eq. (2.16), Eq. (3.18) is clearly different.

Finally, the sudden approximation is obtained from Eq. (2.16), or Eq. (3.18) by setting $\omega = 0$, i.e., the eikonal approximation and the perturbation limit of classical S-matrix theory become identical in the sudden limit.

The perturbative limit of classical S-matrix theory, the exponentiated distorted-wave Born approximation, and the semiclassical eikonal approximation all have a family relationship arising from the use of some quantity related to a classical action integral. The semiclassical perturbative S matrix, being obtained from the general classical S-matrix formalism, rather than by an ad hoc exponentiation, is in general conceptually preferable. The semiclassical expressions are known generally to represent an asymptotic approximation to the true solution of a quantum-mechanical problem. As such, they may oscillate about the true solution as various parameters are changed. A systematic quantitative study of their accuracy in comparison with numerical quantum calculations and with other analytical models will be illuminating; in companion papers we report such a comparison for the problem of electron collisions with polar diatomic molecules.

IV. UNIFORM CLASSICAL S-MATRIX ELEMENTS FOR SPECIFIC SYSTEMS

One extremely convenient feature of using the initial-value representation for the classical S matrix is that it effectively produces the uniform classical S-matrix elements directly, particularly so for the perturbative situation considered here.

For inelastic but nonreactive processes, it is often legitimate to treat the dynamics with a perturbation approximation. If we make maximal use of rotational coordinates, sinusoidal functions, and Fourier expansions in the description of the unperturbed motion and the perturbation, the S matrix turns out to be expressible in general as a sum over products of Bessel functions, with very useful convergence properties. We shall illustrate the procedure first with some simple examples, and then discuss the general form of the expressions.

A. Ion-dipole collisions

We have considered the case of rotational excitation of a dipole by a charged particle previously. The perturbation potential is

$$V_4 = (e\mu / R^3) \cos \gamma,$$

where $\gamma$ is the instantaneous angle between the orientation of the dipole and the line from it to the other particle,

$$\cos \gamma = -\cos \theta_1 \cos \phi_1 + \cos \phi_1 N \sin \theta_1 \sin \phi_1,$$

and $N = (J^2 + l^2 - J^2)/2l$ is the cosine of the angles between the planes of the rotational translational motions. Cross sections for various processes are given in terms of the S-matrix...
elements $S_{J_lJ_{r_1}J_{r_2}}(J)$, where $J$ is the total angular momentum of the system, and $j$ and $l$ are the rotational angular momentum of the dipole and the orbital momentum of relative translation, respectively. Equation (2.16a) of Sec. II must thus be generalized to the case of two internal degrees of freedom, and for this case the unperturbed potential $V_0(R)$ is zero.

Equation (2.16a') then gives

$$S_{\Delta J\Delta l} = S_{J_lJ_{r_1}J_{r_2}l_jl_1}(J)$$

$$= (2\pi)^{\frac{3}{2}} \int_0^{2\pi} dq_l \int_0^{2\pi} dq_{r_1} e^{i\Delta l q_l} e^{i\Delta q_{r_1}} e^{i\Delta l J_{r_1}} e^{i\Delta l J_{r_2}} e^{i\Delta l J},$$

(4.3)

where

$$\Delta l = l_2 - l_1, \quad \Delta j = j_2 - j_1.$$ For the ion-dipole interaction we have shown earlier\textsuperscript{11} that

$$A(q_1, q_2) = \left(2\pi\mu m \omega / l \right) \left(\left[K_1(\omega) - NK_0(\omega)\right] \cos q_1 \cos q_1 + \left[K_0(\omega) - NK_1(\omega)\right] \sin q_1 \sin q_1, \right.$$  

(4.4)

where $\omega = Bj / E_t$, $K_0$ and $K_1$ are the usual modified Bessel functions, $l = \frac{3}{2}(l_1 + l_2)$, $j = \frac{3}{2}(j_1 + j_2)$, $\mu$ is the dipole moment, $m$ is the reduced mass for translation, and $e$ is the electronic charge of the ion. Since

$$\cos q_1, \cos q_2 = \frac{1}{2} \cos(q_1 + q_2) + \frac{1}{2} \cos(q_1 - q_2),$$

$$\sin q_1, \sin q_2 = -\frac{1}{2} \cos(q_1 + q_2) + \frac{1}{2} \cos(q_1 - q_2),$$

(4.5)

Eq. (4.3) takes the form

$$S_{\Delta J\Delta l} = (2\pi)^{\frac{3}{2}} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_2 e^{i\Delta l q_1} e^{i\Delta l q_2}$$

$$\times e^{i\Delta l q_1} \cos(q_1 - q_2) e^{i\Delta l q_2} \cos(q_2 - q_2),$$

(4.6)

where

$$Z_1 = \left(\frac{\mu m}{l}\right)(1 + N)\omega [K_1(\omega) - K_0(\omega)],$$

(4.7)

$$Z_2 = \left(\frac{\mu m}{l}\right)(1 - N)\omega [K_1(\omega) + K_0(\omega)].$$

Changing integration variables from $q_1$ and $q_2$ to $Q_1$ and $Q_2$,

$$Q_1 = q_1 + q_2, \quad Q_2 = q_1 - q_2,$$

(4.8)

gives

$$S_{\Delta J\Delta l} = (2\pi)^{\frac{3}{2}} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_2 e^{i\Delta l q_1} Q_1 e^{-i\Delta l Q_2}$$

$$\times e^{i\Delta l q_1} \cos(q_1 - q_2) e^{i\Delta l q_2} \cos(q_2 - q_2),$$

(4.9)

where

$$\kappa_1 = \frac{3}{2} (\Delta j + \Delta l), \quad \kappa_2 = \frac{3}{2} (\Delta l - \Delta j);$$

(4.10)

the integrals in Eq. (4.9) factor and are recognized as integral representations of the regular Bessel function, so that

$$S_{\Delta J\Delta l} = \delta_{\kappa_1}(Z_1) \delta_{\kappa_2}(Z_2)$$

(4.11)

with $\kappa_i$ and $Z_i, i = 1, 2$, given by Eqs. (4.10) and (4.7), and

$$\delta_{\kappa}(Z) = i^{-\kappa} J_\kappa(Z).$$

(4.12)

Equation (4.11) is our result obtained earlier,\textsuperscript{12} modified by inclusion of the phase factor $i^{\kappa_2}$ to insure symmetry and approximate unitarity of the $S$ matrix (unitarity is approached rapidly as $j$ and $l$ increase). It is also obtained if the "primitive" expression for the classical $S$ matrix is used, rather than the initial-value representation, with subsequent "uniformization" via the Bessel function scheme.\textsuperscript{13} Use of the initial-value representation thus provides a simple, direct route to the desired uniform semiclassical expression.

The quantities $j_1, j_2, J_{r_1}, J_{r_2}$, and $l$ as we have introduced them are classical angular momenta, and we have assumed units such that $\hbar = 1$. For comparison with full quantal calculations (or with experiment), we use the usual equivalence

$$j_{ct} = (j_{ce} + \frac{1}{2})\hbar, \quad l_{ct} = (l_{ce} + \frac{1}{2})\hbar,$$

which is strictly valid in the asymptotic limit of large quantum numbers and approximately true even for small ones. We now recapitulate the salient results using the dimensionless parameters

$$\beta_2 = m \mu e / \hbar^2, \quad \alpha = \hbar^2 / 2IE_t = B/E_t,$$

(4.13)

and assuming hereafter that $j$'s and $l$'s are quantal variables in the semiclassical limit. Then Eq. (4.10) is unchanged and we have

$$N = \frac{(j + \frac{1}{2})^2 + (l + \frac{1}{2})^2 - (j + \frac{1}{2})^2}{2(j + \frac{1}{2})(l + \frac{1}{2})},$$

(4.14)

$$\omega_d = \alpha(j + \frac{1}{2})(l + \frac{1}{2}),$$

(4.15)

$$Z_1 = \frac{\beta_2}{l + \frac{1}{2}} (1 + N)\omega_d [K_1(\omega_d) - K_0(\omega_d)],$$

(4.16)

$$Z_2 = \frac{\beta_2}{l + \frac{1}{2}} (1 - N)\omega_d [K_1(\omega_d) + K_0(\omega_d)].$$

$\omega_d$ can be recognized as the ratio of the angular velocity of the colliding pair at closest approach to that of the rotor, and the functions of $\omega_d$ appearing in $Z_1, Z_2$ are of the nature of resonance integrals.

The semiclassical $S$ matrix for ion-dipole scattering is completely defined by Eqs. (4.10) to (4.13). The interaction strength parameter $\beta_2$ can be used as the basis for a power-series expansion of the $S$ or $T$ matrices and the cross sections. From the expansion formulas for the Bessel functions it is seen that the lowest power of $\beta_2$ in $S_{\Delta J\Delta l}$ is $\beta_2^n$, where
\[ \nu = |\kappa_1| + |\kappa_2| \quad (4.17) \]

Terms with \( \nu = 1 \) correspond to the first Born approximation. The \( \nu = 1 \) and \( \nu = 0 \) terms are confined to the following combinations of \( \Delta l, \Delta j \):

\[ \nu = 1 \quad \nu = 0 \]
\[ \Delta j = +1 \quad +1 \quad -1 \quad -1 \quad 0 \]
\[ \Delta l = +1 \quad +1 \quad -1 \quad -1 \quad 0 \]

Because pure dipole scattering does not produce a phase shift for \( \nu = 0 \), elastic scattering does not enter until the \( \nu = 2 \) terms; correspondingly, it is absent in the first Born approximation. Terms with \( \nu = 2 \) (\( \Delta j = 0, \pm 2 \)), \( \nu = 3 \) (\( \Delta j = \pm 1, \pm 3 \)), and higher are easily evaluated.

### B. Ion-quadrupole collisions

The interaction potential for this case is

\[ V_4(R, \cos \gamma) = (eQ/2R^3)(3 \cos^2 \gamma - 1) = (eQ/2R^3)(3 \cos^2 \gamma + 1), \quad (4.18) \]

where \( Q \) is the quadrupole moment and \( \gamma \) is again given by Eq. (4.2). The function \( A(q_1, q_2) \) can be expressed through the use of the auxiliary variables

\[ Q_1 = 2q_1, \quad Q_2 = 2q_2, \quad Q_3 = (q_1 + q_2) = Q_1 + Q_2, \]
\[ Q_4 = (q_1 - q_2) = -Q_1 + Q_2. \quad (4.19) \]

Because of the symmetry of the potential, the characteristic frequency for the quadrupole interaction is twice that for the dipole case,

\[ \omega_q = 2\omega_d, \quad (4.20) \]

and the interaction strength is reflected in the dimensionless parameter

\[ \beta_4 = \frac{em^2Q}{R^3} \left( \frac{2E}{m} \right)^{1/3}. \quad (4.21) \]

These parameters appear in some resonance integrals:

\[ Z_0 = \beta_4^2 \left( \frac{3N^2 - 1}{8} \right), \]
\[ Z_1 = \beta_4^2 \left( \frac{1 - N^2}{8} \right), \]
\[ Z_2 = \beta_4^2 \left( \frac{3(1 - N^2)}{8} \right) \omega_d K_1(\omega_d), \quad (4.22) \]
\[ Z_3 = \beta_4^2 \left( \frac{1 + N^2}{16} \right) [\omega_d(1 - 2\omega_d)K_1(\omega_d) + 2\omega_d^2K_2(\omega_d)], \]
\[ Z_4 = \beta_4^2 \left( \frac{1 - N^2}{16} \right) [\omega_d(1 + 2\omega_d)K_1(\omega_d) + 2\omega_d^2K_2(\omega_d)]. \]

The function \( A(q_1, q_2) \) is then found to be

\[ R^{-1} A(q_1, q_2) = Z_0 + \sum_{i=1}^{4} Z_i \cos \theta_i. \quad (4.23) \]

The S-matrix elements of Eqs. (2.16) and (4.3) are then

\[ S_{\Delta l, \Delta j} = (2\pi)^{-1} \int_0^{2\pi} \int_0^{2\pi} dQ_1 dQ_2 \]
\[ \times \exp \left( -i \left( \frac{3}{2} \Delta l Q_1 + \frac{3}{2} \Delta j Q_2 \right) \right) \]
\[ \times \exp ( -i\lambda ) \quad (4.24) \]

Introducing the identities

\[ 1 = \int_0^{2\pi} dQ_3 \delta(Q_3 - Q_1 - Q_2), \]
\[ \delta(Q_3 - Q_1 - Q_2) = \frac{1}{2\pi} \sum_{k_3, k_4} \sum_{i=1}^{4} \delta_{\nu_i(Z_i)}, \quad (4.25) \]

and following with similar identities involving \( \delta(Q_3 + Q_1 - Q_2) \) and \( k_3, k_4 \), and interchanging the order of summation and integration, we can integrate Eq. (4.24) as a sum of Bessel function products:

\[ S_{\Delta l, \Delta j} = e^{i\lambda} \sum_{k_3, k_4} \sum_{i=1}^{4} \delta_{\nu_i(Z_i)}, \quad (4.26) \]

where

\[ \nu_1 = \frac{1}{2} \Delta l + k_3 + k_4, \]
\[ \nu_2 = \frac{1}{2} \Delta j - k_3 + k_4, \]
\[ \nu_3 = -k_3, \]
\[ \nu_4 = -k_4. \quad (4.27) \]

The symmetry of the potential allows only transitions with even values of \( \Delta l \) and \( \Delta j \), and the indices \( \nu_i \) are all integers. The index

\[ \nu = \sum_{i=1}^{4} |\nu_i| \quad (4.28) \]

identifies the leading power of \( \beta_4 \) in a power series expansion. For \( \nu = 0 \) and \( \nu = 1 \), the indices \( \Delta j, \Delta l, k_3, k_4 \) appear in the following combinations:

\[ \nu = 0 \quad \nu = 1 \]
\[ \Delta j = 0 \quad 0 \quad 2 \quad 0 \quad -2 \quad 0 \quad 2 \quad 2 \quad -2 \]
\[ \Delta l = 0 \quad 0 \quad 2 \quad 0 \quad -2 \quad -2 \quad 0 \quad 2 \quad -2 \]
\[ k_3 = 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 1 \quad 1 \]
\[ k_4 = 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 1 \quad -1 \quad 0 \quad 0 \]

The nonvanishing \( Z_0 \) phase-shift term in Eq. (4.26) produces elastic scattering in the quadrupole case unlike the dipole; expanding the exponential one gets the first-Born elastic contribution. The \( \nu = 1 \) terms give the inelastic selection rules for small \( \beta_4 \) : \( \Delta j = +2, -2(\Delta l = 0, \pm 2) \).
C. Vibrational inelasticity in ion-dipole collisions

We treat vibrational inelasticity in ion-dipole collisions as an example of the general case. Vibrationally inelastic transitions may be included in the charge-dipole model in a straightforward manner. The interaction potential is

\[ V(R, r, \cos \gamma) = e \mu(r) \cos \gamma / R^2, \]

(4.28a)

where \( \mu(r) \) is the dipole moment as a function of the vibrational coordinate \( r \). The perturbation limit of the classical S matrix is given by the obvious extension of Eq. (4.3):

\[ S_{\Delta v \Delta \omega} = (2\pi)^{\frac{3}{2}} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} dq_x dq_y dq_z \int_0^{\infty} dr \int_0^{\infty} \cos \gamma(t) \rho(\mathbf{r}) e^{-i\Delta \omega t} e^{-i\Delta \omega \mathbf{r} \cdot \mathbf{q}} e^{-i\Delta \omega \mathbf{r} \cdot \mathbf{q}} e^{-i\Delta \omega \mathbf{r} \cdot \mathbf{q}}, \]

(4.29)

where \( v, q_v \) are connected with the action-angle variables for the vibrational degree of freedom \( \Delta v = v_f - v_i \) and

\[ A(q_v, q_f, q_i) = \hbar^{-1} \int_0^{\infty} dt V(R(t), r(t), \cos \gamma(t)). \]

(4.30)

\( R(t) \) and \( \cos \gamma(t) \) are the same functions of \( t \) as for the rigid-rotor case. \( r(t) \), the unperturbed motion of the vibration coordinate, is given in the simplest approximation—a harmonic oscillator—by

\[ r(t) = r_{eq} + \left( \frac{\hbar(2v+1)}{2\pi \nu_0 v_p} \right)^{1/2} \cos(q_v + 2\pi \nu_v t), \]

(4.31)

where \( r_{eq} \) is the equilibrium vibrational coordinate, \( 2\pi \nu_0 \) is the vibrational frequency, \( m_0 \) is the reduced mass of the oscillator, and \( v \) is taken to be the average of the initial and final vibration quantum numbers, \( v = \frac{1}{2}(v_1 + v_2) \). For highly excited vibrational states this harmonic approximation may not be adequate, but it can be readily extended: the right-hand side of Eq. (4.31) becomes

\[ A_v(q_v, q_f, q_i) = \frac{e \mu_v(r_{eq})}{\hbar} \left( \frac{\hbar(2v+1)}{2\pi \nu_0 v_p} \right)^{1/2} \int_0^{\infty} dt \frac{\cos(q_v + 2\pi \nu_v t)}{(\hbar^2 + 2m_0^2 \nu_v^2)^{1/2}} \]

\[ \times \left[ -b \cos q_{\gamma_1} + (2E_i/m_i)^{1/2} \sin q_{\gamma_1} \right] \cos[q_v + 2B(j + \frac{1}{2}) \hbar^{-1} t] \]

\[ + N[b \sin q_{\gamma_1} + (2E_i/m_i)^{1/2} \cos q_{\gamma_1}] \sin[q_v + 2B(j + \frac{1}{2}) \hbar^{-1} t] \].

(4.35)

Evaluating this integral gives

\[ A_v(q_v, q_f, q_i) = \frac{m_0 e \mu_v(r_{eq})}{2\hbar^2 (l + \frac{1}{2})} \left( \frac{\hbar(2v+1)}{2\pi \nu_0 v_p} \right)^{1/2} \]

\[ \times \left\{ (1+N)\omega_s[K_0(\omega_s) - K_1(\omega_s)] \cos(q_v + q_f + q_i) \right. \]

\[ + (N-1)\omega_s [K_1(\omega_s) - K_0(\omega_s)] \cos(q_v + q_f - q_i) \]

\[ + (N-1)\omega_s [K_1(\omega_s) - K_0(\omega_s)] \cos(q_v - q_f + q_i) \]

\[ + (N+1)\omega_s [-K_1(\omega_s) - K_0(\omega_s)] \cos(-q_v + q_f + q_i) \right\}, \]

(4.36)

where \( K_0 \) and \( K_1 \) are, as before, modified Bessel functions, and

\[ \omega_s = \omega_\omega \pm \omega_d, \]

(4.37)

\[ \omega_\omega \] as in Eq. (4.15). The function \( A_v \) (and \( A_\omega \)) can be simplified by defining

\[ \omega_\omega = (l + \frac{1}{2}) \hbar \nu_v / 2E_i \]

(4.38)
\[ \beta_\nu = \frac{m_e \mu_e}{2k^2} \left( \frac{\hbar}{\pi m_e \nu_0} \right)^{1/2}, \]  

\[ I_\nu(x) = x [K_\nu(x) + K_{\nu+1}(x)], \]  

and taking

\[ Z_1 = \frac{\beta_\nu}{l + \frac{1}{2}} (1 + N) I_\nu(\omega_1), \]

\[ Z_2 = \frac{\beta_\nu}{l + \frac{1}{2}} (1 - N) I_\nu(\omega_2), \]

\[ Z_3 = \frac{\beta_\nu}{l + \frac{1}{2}} (1 + N) I_\nu(\omega_3), \]

\[ Z_4 = \frac{\beta_\nu}{l + \frac{1}{2}} (1 - N) I_\nu(\omega_4), \]

\[ Z_5 = \frac{\beta_\nu}{l + \frac{1}{2}} (1 - N) I_\nu(\omega_5), \]

\[ Z_6 = \frac{\beta_\nu}{l + \frac{1}{2}} (1 + N) I_\nu(\omega_6). \]

Then we have

\[ A_\nu = \sum_{i=1}^{6} Z_i \cos Q_i, \]

\[ A = A_\nu + A_\nu = \sum_{i=1}^{6} Z_i \cos Q_i. \]

Now the S-matrix elements can again be expressed in the integral form of Eqs. (2.16) and (4.3). Introducing identities like Eq. (4.25), we can perform the integrations. The result is

\[ S_{\Delta \nu_1, \Delta \nu_2}^{\nu_1, \nu_2} = \sum_{k_1, k_2, k_3} \prod_{i=1}^{6} \beta_{\nu_i}(A_1), \]

where

\[ \nu_1 = \frac{1}{2}(\Delta j + \Delta \ell) - \Delta \nu - k_4 - k_5 - k_6, \]

\[ \nu_2 = \frac{1}{2}(\Delta j - \Delta \ell) + k_4 - k_5, \]

\[ \nu_3 = \Delta \nu + k_4 + k_5 - k_6, \]

\[ \nu_4 = -k_4, \quad \nu_5 = -k_5, \quad \nu_6 = -k_6. \]

Again, we can use the index

\[ \nu = \sum_{i=1}^{6} \nu_i, \]

of an expansion in \( \beta_\nu \) and \( \beta_\nu \) to examine the small-\( \beta \) selection rules for this interaction. From (4.45) we find

\[ \Delta \nu = \nu_3 + \nu_4 + \nu_5 - \nu_6, \]

\[ \Delta j = \nu_1 + \nu_2 + \nu_3 + \nu_4 - \nu_5 + \nu_6, \]

\[ \Delta \ell = \nu_1 - \nu_2 + \nu_3 - \nu_4 + \nu_5 + \nu_6. \]

We can tabulate the available combinations for \( \nu = 0, 1 \):

\[
\begin{array}{cccccccc}
\nu & 0 & 1 \\
\nu_1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
\nu_2 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\nu_3 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\
\nu_4 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
\nu_5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\nu_6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

To conserve parity, changes of one unit in \( j \) are accompanied by changes in \( \ell \). More significant is the selection rule (for \( \nu = 1 \): first order in \( \beta \)) requiring a change in \( j \) and \( \ell \) to accompany any change in \( \nu \). This is, of course, a specific consequence of the potential we have assumed, which couples the vibrational motion with rotation through the ion-dipole term with a varying dipole moment. For this potential, we expect the same result to appear in the first Born approximation.

At first sight, the multiple-sum-and-product form of the S matrix, as in Eq. (4.44), may seem intrinsically complex. Fortunately, it has very satisfactory convergence properties, and it is easy to show that (4.44) collapses smoothly to the simple form of (4.11) both at low energies \( E \) and when \( \beta_\nu \) is much smaller than \( \beta_\ell \). To demonstrate the behavior in these limits it is helpful to inspect the form of the functions \( I_\nu(x) \), Eq. (4.40), that appear in all the arguments \( Z_i \) of the Bessel functions, Eq. (4.41). The functions \( I_\nu \) are everywhere positive, never exceed an upper bound slightly greater than unity, and decline exponentially toward zero at large arguments. When the translational energy \( E \) falls significantly below the vibrational spacing, \( \omega_\nu \), and consequently \( \omega_\nu \) become large, the \( I_\nu \) functions in \( Z_3 \) to \( Z_6 \) become small exponentially, and so do \( Z_3 \) to \( Z_6 \) them-
selves. On the other hand, if $\beta_i \ll 1$ (and $< \beta_j$), and the vibrational quantum number $v$ is not excessively large, $Z_0$ to $Z_0$ will be small at all energies (the factor $1 + N$ always falls between 0 and 2). Whenever the arguments $Z_i$ are very small, the functions $\delta_i(Z_i)$ approach zero except for $\delta_i(Z_i)$, which approaches unity, i.e., $\delta_i(Z_i) \to \delta(v_i)$ ($i = 3, \ldots, 6$), and consequently Eq. (4.44) to Eq. (4.11). Furthermore, when some of the $Z_i$'s are small but not negligible, the corrections to (4.11) can be evaluated by a power series expansion of the appropriate $\beta$'s combined with a direct Bessel function evaluation of the others.

D. General formula

It is now sufficiently obvious that we are dealing with a general procedure that can be applied in a great variety of atomic, molecular, ionic, and electronic collisions. The principal limitations are (a) that the transition is produced by a perturbation, which should not be too large, and (b) that the transition does not involve a chemical reaction or the transfer of an electron, ion, atom, or other particle. With these conditions, when the unperturbed collision problem and the perturbation potential are described by the use of angular (periodic) functions (including multipole expansions or expansions of anharmonic terms in Fourier series), except for one radial degree of freedom, the $S$ matrix can be expressed as a sum of products of Bessel functions whose orders $\nu_i$ depend linearly on the changes in the quantum numbers $\Delta n_i$ and whose arguments $Z_i$ are integrals over the unperturbed trajectory expressible in terms of the unperturbed quantum numbers $n_i$.

Suppose there are $n$ periodic degrees of freedom with unperturbed (average) quantum numbers $n_i$ and changes $\Delta n_i$, each associated with a coordinate $x_i = x_i(t) + q_i$, and a perturbation $\Delta V(E, n_i, x_i)$. The perturbation $S$ matrix can be expressed with the help of the phase function

$$\Phi = -\sum_{i=1}^{n} \Delta n_i q_i - A,$$  
(4.48)

where

$$A = \frac{1}{\hbar} \int \Delta V dt = Z_0 + \sum_{i=1}^{m} Z_i (E, n_i) \cos Q_i, \quad (m \geq n)$$  
(4.49)

with

$$Q_i = q_i \quad (i \leq n)$$  
(4.50)

(by sometimes it is useful to make a linear transformation on the $q_i$'s first), and

$$Q_j = \sum_{i=1}^{n} \lambda_{ij} Q_i \quad (n < j \leq m).$$  
(4.51)

If we again use the convention

$$S_{n+\Delta n} \cdot S_{m+\Delta m} \cdot \frac{1}{\Delta n \Delta m} = S_{\Delta n},$$  
(4.52)

and similarly for multiple indices, the $S$ matrix can be expressed as

$$S_{\Delta n_1, \ldots, \Delta n_m} = (2\pi)^n \int_{0}^{2\pi} \cdots \int_{0}^{2\pi} dq_1 \cdots dq_m e^{i\Phi}$$  

$$= e^{i\Phi} \sum_{k_{n+1} = 0}^{k_m} \prod_{j=1}^{m} \beta_j (Z_j),$$  
(4.53)

where

$$\nu_i = \Delta n_i + \sum_{j=i+1}^{m} k_j \lambda_{ij} \quad (i \leq n),$$  
(4.54)

$$\nu_j = -k_j \quad (n < j \leq m).$$

The proof can be carried out by changing variables from $q_i$'s to $Q_i$'s and inserting identities like Eq. (4.25) in the multiple integral.

The general formula has several useful properties. The $S$ matrix it describes is symmetric because all the indices $\nu_i$ are integers, and it follows from the properties of the Bessel function that $\beta_j (Z) = \beta_j (Z)$. In the Appendix we show that

$$\sum_{k_{m+1} = 0}^{m} \beta_{m+1} (Z) \beta_{m} (Z) = \delta (n - m),$$  
(4.55)

where $\beta_j (Z) = \beta_j (Z)$.

By successive applications of this identity, it can be shown that our approximate $S$ matrix is approximately unitary—it would be strictly unitary if all the $Z_i$'s were constant (as functions of the average quantum numbers $n_i$) and if all the $\nu_i$'s (or their differences $\Delta n_i$) were allowed to run from $-\infty$ to $\infty$. The derivation from these two conditions are only severe when one or more of the quantum numbers is very small, and the semi-classical $S$ matrix approaches unitarity rapidly when the quantum numbers are large.

It is easy to apply these general formulas to extend the results we have given earlier. For instance, rotational excitation with a combined potential having dipole and quadrupole terms requires six $Q$'s, combining Eqs. (4.8) and (4.19), and the $S$ matrix is a fourfold sum over a sixfold product of $S$'s. Similarly, an anharmonic vibrational term can be added to the rotating oscillator. If the classical motion of the anharmonic oscillator is described by a Fourier expansion, additional $Q$'s and $Z$'s can be defined extending Eqs. (4.41) and (4.42), and additional $S$'s will appear in the product $S$ matrix. When the effect
of the new terms added to the potential is small, this will appear through the behavior of the new \( Z_i \)'s that are arguments of the added \( \beta_i \) functions: when we have \( Z_i < 1 \), it follows that \( \beta_i(Z_i) \sim O(\nu_i) \). As we have seen in the vibrational-rotation case above, the S matrix then collapses smoothly to a simpler form with fewer terms under these conditions, just as we should expect intuitively.

In general, the behavior of the arguments \( Z_i \) of the Bessel functions controls the rapidity of convergence both of the infinite sums in the \( S \) matrix of Eq. (4.53) and of the sums over \( S \) that define differential and total cross sections. Especially important are the conditions under which \( Z_i \rightarrow 0 \).

In the cases we have seen, and many others, the \( Z_i \)'s can be factored into several components:

\[
Z_i = \left( \beta_i/(l + \frac{1}{2}) \right) f_i I_i(\omega_i),
\]

(4.56)

where \( \beta_i \) is a dimensionless parameter measuring the interaction strength, \( f_i \) is a function of some of the unperturbed quantum numbers such as \( v, j, l, \) \( j' \) [typical factors in \( f_i \) are \( 1 \pm N, (v + \frac{1}{2})^{1/2} \)], and \( I_i \)'s are collision integrals involving the modified Bessel functions \( K_\nu \) and \( K_\nu \) with an argument \( \omega_i \) that often represents a ratio of angular velocities; in particular, the \( I_i \)'s \( \sim 0 \) exponentially as \( \omega_i \rightarrow -\infty \). If the unperturbed collisional motion is in a simple straight line, \( \omega_i \) can be factored in turn:

\[
\omega_i = g_i (l + \frac{1}{2})/E_i = (2g_i/k)(b/v_i),
\]

(4.57)

where \( E_i \) is the translational energy, \( v_i \) the translational velocity, \( b \) the impact parameter, and \( g_i \) depends on internal quantum numbers and parameters of the colliding partners. Thus, \( \omega_i \) increases with \( l \) and with \( 1/E_i \). As a result, the factor \( I_i(\omega_i) \) in \( Z_i \) approaches zero as \( E_i \) decreases and as \( l \) increases. This decrease in \( Z_i \) at large \( l \) is reinforced by the direct factor \((l + \frac{1}{2})^{-1}\) in \( Z_i \).

\( \beta_i \) itself contains the reduced mass \( m_i \) as a direct factor. For electron collisions, \( \beta_i \) and the other terms in \( Z_i \) seldom much exceed unity, and therefore the Bessel functions are to be evaluated only in regions where their arguments are small or moderate in size. If follows also that we need to consider only small to moderate values of the indices \( \nu_i \), because the Bessel functions decline exponentially toward zero for \( \nu_i \gg Z_i \).

In the case of heavy-particle collisions, \( m_i \) is very large (in atomic units), and correspondingly large values of \( \nu_i \) and \( Z_i \) are often attainable.

Consequently, the Bessel functions need to be evaluated in a very different region of \( Z_i \), and also to \( \nu_i \), and different approximating schemes must be used. For this reason, we concentrate our attention initially on electron collisions.

For heavy particles, it is useful to express some of the criteria in terms of classical quantities such as the impact parameter \( b \) and the collision velocity \( v_i \), rather than \( l \). Thus we note that

\[
\frac{\beta_i}{l + \frac{1}{2}} = \frac{\hbar \beta_i}{m_i} \frac{m_i}{\hbar(l + \frac{1}{2})} = \frac{\hbar \beta_i}{m_i} \frac{1}{bv_i}.
\]

(4.58)

Through this factor, \( Z_i \) depends inversely on \( bv_i \). Through \( \omega_i \), on the other hand, \( Z_i \) ultimately decreases as \( b/v_i \) increases. The \( \beta_i(l + \frac{1}{2}) \) term thus causes \( Z_i \) to decrease at high energy, and the \( I_i(\omega_i) \) term causes \( Z_i \) to decrease also in the opposite limit of low energy. The low-energy behavior reflects the fact that a threshold amount of energy must be available before a given transition is feasible. The high-energy behavior is probably connected with the mismatch between the collision time and the response function of the mode being excited or deexcited.

E. Anharmonic oscillator

Using the general expressions we have just derived, it is simple to extend the expressions we have derived earlier for the harmonic oscillator to include anharmonic terms, rotation-vibration interaction, higher multipoles in the angular dependence, and other intermolecular forces. The case of the anharmonic oscillator serves to illustrate the effect of the increased complexity that such an additional potential term introduces, and the way in which the more complete expression converges to the simpler prototype when the magnitude of the new potential term becomes negligibly small. We do not give details of the derivation, but we present the results as a further example of the use of the general formulas. The inclusion of a simple anharmonic component in the motion requires inclusion of \( Z_{10} \) to \( Z_{10} \) like \( Z_{20} \) to \( Z_{20} \) but with new frequencies

\[
\omega_{2s} = 2\omega_s \pm \omega_d
\]

(4.59)

and a new factor \( \beta_4 \) incorporating anharmonic parameters from the vibrational potential and the dipole moment function \( \mu(r - r_0) \). Four new \( \nu_i \)'s are added, and the first three \( \nu_i \)'s are replaced by

\[
\nu_1 = \nu_1 - 2k_1 + 4k_{10},
\]

\[
\nu_2 = \nu_2 + 2k_2 - 2k_8,
\]

\[
\nu_3 = \nu_3 + 2k_7 + 2k_8 + 2k_9 - 2k_10,
\]

\[
\nu_{7, \ldots, 10} = -k_{1\ldots10}.
\]

(4.60)

Four new \( Q \)'s are also needed:

\[
Q_7 = 2Q_3, \quad Q_8 = -2Q_1 + 2Q_2 + 2Q_3,
\]

\[
Q_9 = -2Q_1 - 2Q_2 + 2Q_3, \quad Q_{10} = 4Q_1 - 2Q_3.
\]

(4.61)
These anharmonic terms appear as additional Bessel functions \( \beta_\nu(Z, \ldots, \beta_{10}(Z)) \) and additional summations in the formula for the \( S \) matrix. There are no convergence difficulties. As long as the anharmonic effects are small, \( Z, \ldots, Z_{10} \approx 0 \), the additional \( \beta \) functions \( \beta_\nu(0) = 0 \), and the whole \( S \) matrix collapses to the pure harmonic oscillator form. The corrections needed for high vibrational levels can be evaluated directly from the fuller expression.

From the relations

\[
\begin{align*}
\Delta v &= \nu_4^2 + \nu_3 - \nu_2 - \nu_3 + 2\nu_4 + 2\nu_3 - 2\nu_4 - 2\nu_3 + 2\nu_4 + 2\nu_3 - 2\nu_4 - 2\nu_3 + 2\nu_4 + 2\nu_3, \\
\Delta j &= \nu_4^2 + \nu_3^2 + \nu_2^2 - \nu_3 - \nu_3 + 2\nu_4 + 2\nu_3 - 2\nu_3 + 2\nu_3 - 2\nu_3 + 2\nu_3 - 2\nu_3 + 2\nu_3, \\
\Delta l &= \nu_4^2 - \nu_3^2 + \nu_2^2 + \nu_3 + \nu_3 + 2\nu_4 + 2\nu_3 - 2\nu_3 - 2\nu_3 + 2\nu_3 + 2\nu_3 - 2\nu_3 + 2\nu_3 - 2\nu_3 + 2\nu_3 - 2\nu_3 + 2\nu_3.
\end{align*}
\]

(4.62)

by tabulating all the possibilities for the index \( \nu = \sum |\nu_i| = 1 \) we find the first-order perturbation selection rules for transitions given by the following table:

\[
\begin{array}{cccccccc}
\Delta v & 0 & 0 & \pm 1 & \pm 1 & \pm 1 & \pm 2 & \pm 2 & \pm 2 \\
\Delta j & 1 & 1 & 1 & 1 & -1 & -1 & 2 & 2 & -2 \\
\Delta l & 1 & -1 & 1 & -1 & 1 & -1 & 2 & -2 & 2
\end{array}
\]

As is to be expected, the anharmonic terms in first order can introduce changes of \( \Delta v = \pm 2 \), but these are associated with angular momentum changes of \( \pm 2 \) in \( \Delta j \) and \( \Delta l \). This connection is again a special consequence of the potential we have assumed. Since the anharmonicity is usually small, the first-order terms in \( \beta_\nu \) will ordinarily compete with second- and higher-order terms in \( \beta_\nu \), so these first-order selection rules are not likely to be observable in practice to any significant extent. However, the full Bessel function expressions will be very useful in assessing the relative magnitude of the anharmonic effects in the cross sections for various inelastic transitions. We therefore examine the relevant equations leading to the coefficients needed in the explicit evaluations.\(^{14}\)

Consider the general potential \( V(\nu) \) and the effective potential

\[
U_j(\nu) = V(\nu) + \frac{(j + \frac{1}{2})^2 \hbar^2}{2m_\nu \nu^2}.
\]

(4.63)

The relation between \( r \) and the time \( t \) for the unperturbed oscillator is

\[
(\frac{1}{\nu}) = \int_0^r dr \left( \frac{2}{m_\nu} [E - U_j(\nu)] \right)^{-1/2}.
\]

(4.64)

For the oscillator in a potential well, the period is

\[
\tau = \frac{1}{\nu} = \int_0^r dr \left( \frac{2}{m_\nu} [E - U_j(\nu)] \right)^{-1/2}.
\]

(4.65)

The relation between energy and vibrational quantum number is given by

\[
\langle v + \frac{1}{2} \rangle = \int_0^r dr \left[ 2m_\nu [E - U_j(\nu)] \right]^{-1/2}.
\]

(4.66)

We can invert to get \( E(\nu, v) \), \( \nu(j, v) \), and \( r(j, v; t) \). Since \( r \) is periodic in \( t \) with the period \( \tau(j, v) \), it can be expanded in a Fourier series:

\[
r - r_0 = A_\nu \sum_{n=1}^{\infty} \left[ A_n \cos 2\pi nu \nu'(t - t_0) + B_n \sin 2\pi nu \nu'(t - t_0) \right],
\]

(4.67)

where the coefficients are

\[A_\nu = \frac{2}{\tau} \int_0^\tau \cos \left[ r(t) - r_0 \right] \cos 2\pi nvt d\tau,
\]

\[B_\nu = \frac{2}{\tau} \int_0^\tau \sin \left[ r(t) - r_0 \right] \sin 2\pi nvt d\tau.
\]

Comparing with Eq. (4.31), it can be shown that the angle variable conjugate to \( v \) is

\[\varphi_\nu = -2\pi nu \nu'(t_0).
\]

(4.69)

When the action integral \( A_\nu \) analogous to Eq. (4.36) is constructed, its Fourier expansion will contain all harmonics of \( \varphi_\nu \) leading to the introduction of additional \( Q_i \)'s such as \( n_\nu + q_i \pm q_i \). Furthermore, this Fourier expansion will contain, in general, sine as well as cosine terms just as in Eq. (4.67). We need examine only one such pair. Consider

\[A_i = Z_A \cos Q_i + Z_B \sin Q_i = Z_i \cos Q_i - \alpha_i, \]

(4.70)

\[Z_i = (Z_A^2 + Z_B^2)^{1/2}, \quad \tan \alpha_i = Z_B / Z_A \cdot
\]

In constructing the \( S \) matrix this will lead to the integral

\[\frac{1}{2\pi} \int_0^{2\pi} e^{-i \nu \nu' \cos(Q_i - \alpha_i)} e^{-i \nu' j} \nu \nu' j dQ_i
\]

\[= \frac{1}{2\pi} e^{-i \nu \nu' \cos(Q_i - \alpha_i)} \int_0^{2\pi} e^{-i \nu \nu' \cos Q_i} e^{-i \nu' j} dQ_i
\]

\[= e^{-i(\nu \nu' \cos \alpha_i / 2) j} j(Z_j), \]

(4.71)

The additional phase \( e^{i \alpha_i} \) enters because of the \( \sin \alpha_i \) terms in the Fourier expansion of \( A \).

The Fourier expansion is a general technique which can be applied to molecules of considerable complexity. Through this examination of the anharmonic oscillator, we have shown that the Fourier expansion leads to the same sum-and-product of Bessel functions for the \( S \)-matrix expression, modified only by an additional phase factor.
V. CONCLUSIONS

We have given general expressions and several illustrative examples showing how the sum-and-product Bessel function representation can be derived in a systematic way for a very wide class of collision problems involving electrons, ions, atoms, and molecules. Exactly the same techniques can be applied to interactions with more complicated couplings of angular momenta including higher multipoles and other more complicated potentials, and higher anharmonic terms in vibrational coordinates. The principal limitation is the requirement that there be no change in chemical structure, such as dissociation or ionization of molecule or exchange of an atom, electron, or other structural unit.

Ordinarily, when the potentials are analytically well behaved over the entire range of the dynamical variables, it appears to be a very general feature of this approach that the arguments of the Bessel functions, the functions \( Z_i \) of our expressions, can be explicitly evaluated through the use of various combinations of the modified Bessel functions \( K_\nu \) and \( K_\nu \) whose arguments depend only on the dynamical variables such as collision energy and on the unperturbed quantum numbers. When the interactions involve less well behaved potentials, such as step functions, or functions expressed as a numerical tabulation, the arguments \( Z_i \) must be evaluated by numerical integration over the unperturbed trajectories. At the expense of an acceptable increase in numerical manipulations, the procedure can then be adapted to these less well behaved interactions, and the S matrix will still take the form of a sum and product of Bessel functions.

The multiple Bessel function form of our S matrix is most directly suited to evaluation when one of the collisions partners is an electron, because the coupling coefficients \( \beta_i \) are small enough so that the expressions will converge with the use of Bessel functions of comparatively low order. For heavy-particle collisions, the same expressions are formally valid but the actual evaluation of cross sections will require greater use of further devices such as the introduction of asymptotic expansions for the Bessel functions. In such cases, our procedure will lead to forms similar to those obtained by Percival, Richards, Clark, and Dickinson.\(^6,7\)

The expressions we have obtained have a number of desirable properties. They correctly preserve the symmetry of the S matrix, and to a good approximation its unitarity (except when some of the quantum numbers are extremely small). They include the Born approximation as a special limiting case in the region where it is valid, essentially a region of quantum tunneling where one-quantum transitions predominate and transition probabilities are not very large. They behave in a quantitatively correct way through the important transition region from quantum tunneling to classically allowed motion, and they describe the quantum oscillations (interference effects) that are often characteristic in the classically allowed region. When proper averaging over the oscillations is carried out, the purely classical result should be obtained. Thus they build a correct bridge between the Born and classical types of motion and describe both of them with a comparatively simple and flexible functional form adapted to a great variety of problems.

With these advantages go certain limitations. These reflect the limitations of any perturbation theory in that they cannot correctly describe the motion in regions where the interaction is very strong and the limitations of the semiclassical theory, which does not fully represent all the details of a complete quantum-mechanical description, particularly when angular momentum quantum numbers are very small. It is significant to note that this breakdown of the semiclassical theory is likely to be much more severe for angular momentum quantum numbers than it is for vibrational quantum numbers. The reason for this is that the assumed equivalence \( j^\mu \to (j + \frac{1}{2}) \hbar \) between classical variables and quantum numbers is imprecise for small angular momenta when \( j \) is small, but the corresponding one for vibrations \( v^\mu \to (v + \frac{1}{2}) \hbar \) is correct even for \( v = 0 \).

ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research under Contract No. F44620-75-C-0073 and the Air Force Geophysics Laboratory under Contract No. F19628-75-C-0050.

APPENDIX

A. Unitary Bessel functions

We define the following for integer order \( \nu \) through the standard Bessel functions \( J_\nu(z) \):

\[
\delta_\nu(z) = \frac{1}{2}i^\nu J_\nu(z),
\]

and we use the notation \( \delta_{\nu}^*(z) = \delta_{\nu}^*(z) \) because of the connection of \( \delta_\nu \) with the S matrix, such as \( \delta_{2\nu-1}(z) = S_{2\nu-1} \). A number of symmetry properties follow:

\[
\delta_{-\nu}(z) = \delta_{\nu}(z),
\]

\[
\delta_{-\nu}^*(z) = \delta_{\nu}^*(z),
\]

\[
\delta_{0}(z) = (-)^\nu \delta_{\nu}(z).
\]
The Neumann addition theorem becomes
\begin{align}
\beta_n(u-v) &= \sum_{\ell=0}^{\infty} \beta_{\nu+\ell}(u) \beta^*_{\nu}(v) \\
&= \sum_{\ell=0}^{\infty} \beta_{\nu+\ell}(u) \beta_{\nu}^*(v) \\
&= \sum_{\ell=0}^{\infty} \beta_{\nu+\ell}(u) \beta_{\nu}(v) \\
&= \sum_{\ell=0}^{\infty} \beta_{\nu+\ell}(u) \beta_{\nu}^*(v). \tag{A5}
\end{align}

The unitarity of the $\beta$ functions (at constant argument) is a special case of Eq. (A5):
\begin{align}
\sum_{\nu=0}^{\infty} \beta_{\nu}(u) \beta_{\nu}^*(u) &= \sum_{\nu=0}^{\infty} \beta_{\nu}(u) \beta_{\nu}^*(u) \\
&= \delta(u). \tag{A7}
\end{align}

Thus, if $S_{n_1,n_2}=S_{n_2,n_1}(Z)$, and $Z$ is assumed to be a constant independent of $n_1$ and $n_2$, the unitarity and symmetry of $S$ follow from Eqs. (A7) and (A2), respectively. The recurrence relations of greatest importance are
\begin{align}
\beta_n(Z) &= \frac{1}{2} \left[ \beta_{n-1}(Z) + \beta_{n+1}(Z) \right], \tag{A8} \\
\nu \beta_n(Z) &= \frac{1}{2} i \nu \left[ \beta_{n-1}(Z) - \beta_{n+1}(Z) \right]. \tag{A9}
\end{align}

B. Perturbation notation for the S matrix

It is convenient to label the $S$ matrix separately with the unperturbed variables (quantum numbers) and with the changes induced by the collision, and sometimes only with the latter. We use the definitions
\begin{align}
(n_1, n_2) \rightarrow n = \frac{1}{2}(n_1 + n_2), & \quad \Delta n = n_2 - n_1, \\
(m_1, m_2) \rightarrow m = \frac{1}{2}(m_1 + m_2), & \quad \Delta m = m_2 - m_1, \text{ etc.} \tag{A10}
\end{align}

Then we write
\begin{align}
S_{n_1,n_2} &= S_{\Delta n, \Delta m}, S_{n_1,m_1; n_2,m_2} = S_{\Delta n, \Delta m} = S_{\Delta n, \Delta m}, \text{ etc.} \tag{A11}
\end{align}

When matrix products are formed, it is important to note that the upper as well as the lower indices in these expressions will vary with the dummy index of the summation. Consider, for example, the product involved in a test of unitarity:
\begin{align}
U_{n_1,n_2} &= U_{\Delta n}^{\Delta m} = \sum_{\Delta n'=0}^{\Delta n} S_{n_1,n_2}^{\Delta m} S_{\Delta m, \Delta n'}^{\Delta n} \tag{A12}
\end{align}

where $n, \Delta n$ are as in Eq. (A10), and
\begin{align}
\Delta n' &= n_3 - n_1, \quad \Delta n'' = n_2 - n_3 = \Delta n - \Delta n'. \tag{A13}
\end{align}

C. Reduction of matrix products

Matrix products such as Eq. (A12) can be evaluated by substituting a Bessel form for the $S$ matrix. With the further definitions
\begin{align}
n' = \frac{1}{2}(n_1 + n_3) = n - \frac{1}{2} \Delta n'', \quad n'' = \frac{1}{2}(n_3 + n_2) = n + \frac{1}{2} \Delta n', \tag{A14}
\end{align}

we can write
\begin{align}
U_{\Delta n}^{\Delta m} = \sum_{\Delta n' = -\frac{1}{2} \Delta n}^{\frac{1}{2} \Delta n} \beta_{\Delta n'}(Z(n')) \beta_{\Delta m'}^*(Z(n'')), \tag{A15}
\end{align}

and rearrange the sum into two terms:
\begin{align}
U_{\Delta n}^{\Delta m} = (U_{\Delta n}^{\Delta m})^0 - \Delta U_{\Delta n}^{\Delta m}, \tag{A16}
\end{align}

where
\begin{align}
(U_{\Delta n}^{\Delta m})^0 &= \sum_{\Delta n' = -\frac{1}{2} \Delta n}^{\frac{1}{2} \Delta n} \beta_{\Delta n'}(Z(n')) \beta_{\Delta m'}^*(Z(n'')), \tag{A17}
\end{align}

and
\begin{align}
\Delta U_{\Delta n}^{\Delta m} &= \sum_{\Delta n' = -\frac{1}{2} \Delta n}^{\frac{1}{2} \Delta n} \delta_{\Delta n'}(Z(n')) \delta_{\Delta m'}(Z(n'')), \tag{A18}
\end{align}

with $n^0$ an integer such that
\begin{align}
-\frac{1}{2} \Delta n - 1 < n^0 < n - \frac{1}{2} \Delta n. \tag{A19}
\end{align}

Finally, we can expand the $\beta$'s about $Z \equiv Z(n)$. Utilizing the identities (A2) to (A9), we find the first-order correction terms in (A17) vanish, and the expression up to second order reduces to
\begin{align}
(U_{\Delta n}^{\Delta m})^0 &= \delta(\Delta n) - \frac{Z}{16} \frac{\delta^2 Z}{\Delta n^2} \\
&\times \left[ 5(\Delta n - 2) + 25(\Delta n + 2) \right] \cdots. \tag{A20}
\end{align}

Except when $n^0$ is very small, it suffices to take the leading term in (A18):
\begin{align}
\Delta U_{\Delta n}^{\Delta m} = \beta_{\Delta n}(Z) \beta_{\Delta m}^*(Z). \tag{A21}
\end{align}

Equation (A21) gives a measure of the deviation from unitarity caused by the existence of a finite lower bound in the summation of Eq. (A12) or (A15). Equation (A20) measures the deviation from unitarity [i.e., from the leading term $\delta(\Delta n)$] caused by the variation of $Z$ with $n$.

Similar reductions can be carried out when the $S$ matrix is represented by a product of $\beta$'s. In that case, it must be remembered that each $Z_i$ is generally a function of all the unperturbed quantum numbers $n_i$: $Z_i = Z_i(n_1, n_2, \ldots)$. 


9See, for example, W. H. Miller, J. Chem. Phys. 49, 2373 (1968).


14With regard to the anharmonic oscillator, see also the discussion pertaining to Eqs. (3.94)–(3.100) in W. H. Miller, Adv. Chem. Phys. 25, 69 (1974).