Space-fixed vs body-fixed axes in atom-diatom molecule scattering. Sudden approximations*

Russell T Pack

Group T-6, University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

(Received 4 September 1973)

The Arthurs and Dalgarno space-fixed (SF) axes formulation of the quantum theory of atom-diatom scattering is compared with the body-fixed (BF) axes formulation of Curtiss using consistent notation to facilitate comparison. While equivalent, the two theories are not always equally convenient. When rotation is treated in a sudden approximation, the BF formulation has a tremendous conceptual and computational advantage: it allows an infinite-order sudden approximation, independent of the form of the potential energy, which should be very helpful in vibrationally inelastic and reactive scattering problems. Also, a rapid procedure for calculating WKB phase shifts is presented.

I. INTRODUCTION

The two most common formulations of the quantum theory of molecular scattering are that of Arthurs and Dalgarno and that of Curtiss and co-workers. The essential difference between the two is that, although both start out with the same center of mass-relative coordinate system, Arthurs and Dalgarno always keep their coordinate axes pointed in space-fixed (SF) directions while Curtiss and co-workers transform to body-fixed (BF) axes directed between the molecules. One could choose to put the other apparent differences, such as the degree of generality, the use of integral or differential equations, the incident direction, etc., into either formulation.

Although the BF formulation predates the SF formulation, and although the two approaches are equivalent, virtually all serious attempts at actually computing quantum-mechanical cross sections for molecular scattering have used the SF formulation. The objective of this paper is to show that there are also advantages in the SF formulation in numerical calculations; in particular, for those collisions for which rotational sudden approximations are justified, the BF approach is shown to provide a tremendous simplification and computational advantage.

In the following section, the SF theory of the collision of a structureless atom with a vibrating rotor diatomic molecule is reviewed to provide perspective. Then, in Sec. III, we present and discuss the BF formulation of the same problem using consistent notation to provide easy comparison. The two general approaches are compared in Sec. IV, the simplification obtained in each formalism via a sudden approximation is derived in Sec. V, numerical results on an example problem are compared in Sec. VI, and some conclusions are given in Sec. VII. An Appendix presents a method for the rapid computation of WKB phase shifts.

II. SPACE-FIXED (SF) THEORY

In this section, the generalization of the space-fixed (SF) Arthurs and Dalgarno rigid rotor theory to the scattering of a structureless atom by a Σ-state vibrating rotor diatomic molecule is summarized.

The center of mass (c.m.) coordinate system used for the collision of atom A with diatomic molecule BC is given in Fig. 1. Throughout this section, the angles defining the directions of the vectors R and r are measured from the primed axes whose directions are fixed in the laboratory space.

After separation of the c.m. motion, the Hamiltonian of the system (in cgs units) is

\[
H = -\left(\frac{\hbar^2}{2m_{BC}}\right) \nabla_{\mathbf{R}}^2 + V_{BC}(\mathbf{R}) + V_{IC}(\mathbf{R}),
\]

where \( V \) is the Born-Oppenheimer intermolecular potential, \( \nabla_{\mathbf{R}}^2 \) is the Laplacian operator of \( \mathbf{r} \), \( \mu_{BC} \) is the reduced mass of A relative to BC,

\[
\mu = m_{BC} m_A / (m_{BC} + m_A),
\]

and \( H_{BC} \) is the Hamiltonian governing the nuclear motion of any isolated diatomic molecule BC in a Σ electronic state. That is,

\[
H_{BC} = -\left(\frac{\hbar^2}{2\mu_{BC}}\right) \nabla_{\mathbf{R}}^2 + V_{BC}(\mathbf{R}),
\]

which \( V_{BC} \) is the BC interatomic potential, and \( \mu_{BC} \) is the reduced mass of BC,

\[
\mu_{BC} = m_B m_C / (m_B + m_C).
\]

The eigenfunctions of \( H_{BC} \) satisfy

\[
(H_{BC} - \Delta_{\nu}) \chi_{\nu}(\mathbf{R}) Y_{jm}(\mathbf{\hat{R}}) = 0,
\]

where \( R' = (\theta', \phi') \), \( Y_{jm} \) is a spherical harmonic, \( \chi_{\nu} \) is a vibrational wavefunction, and the \( \Delta_{\nu} \) are rotation-vibration energy levels.

If \( L \) is the angular momentum of A relative to BC, then the eigenfunctions of the operator \( L^2 \) are the \( Y_{jm} \), where \( \hat{R'} = (\theta', \phi'). \)

Since the total angular momentum \( J \),

\[
J = J_{R'} + L,
\]

is conserved, Arthurs and Dalgarno found it convenient to couple the \( Y_{jm} \) and \( Y_{jm} \) to form eigenfunctions of \( J^2 \), \( J_{R'} \), \( J_{\lambda} \), and \( L^2 \) via the Clebsch–Gordan theorem,

\[
y_{jm}^{J_{R'}}(\hat{R'}, \hat{R}) = \sum_{m_{R'}, m_{R}} \sum_{m_L} C(j|m_{R'}; m_{R}, m_{R}, M) y_{jm}^{J_{R'}}(\hat{R}, \hat{R})
\]


Downloaded 18 Apr 2013 to 128.197.27.9. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://jcp.aip.org/about/rights_and_permissions
Then, for given $J$, $M$ the exact solution of the Schrödinger equation for the colliding system,

$$(E - H)\Psi^{J,M}_{IV} = 0,$$  

where the superscripts label the initial values, can be written in the form

$$\Psi^{J,M}_{IV} = \sum_{l''} \sum_{\nu''} r^{-1} G_{l''\nu'' \rightarrow IV}(r) \chi_{l''\nu''}(R),$$

where $G(r)$ are radial channel wavefunctions. This expansion is exact if all $j$ and $l$ and a complete set of bound and unbound vibrational states are included.

Substitution of Eq. (10) into Eq. (9) leads to the set of coupled equations,

$$\frac{d^2}{dr^2} G_{l''\nu'' \rightarrow IV}(r) + k_{l''\nu''} G_{l''\nu'' \rightarrow IV}(r) = (2\mu/k^2) \sum_{l''} \sum_{\nu''} \delta(l'' - l') \delta(\nu'' - \nu') G_{l''\nu'' \rightarrow IV}(r),$$

where the $k_{l''\nu''}$ specify the channel wavenumbers and energies. The matrix elements of the intermolecular potential, are independent of $M$.

If the potential is written in the form

$$V(r, R) = \sum_{n} V_n(r, R) P_n(\cos \theta),$$

these matrix elements take the form

$$\langle j''l''\nu''|V|j'l'\nu'\rangle = \sum_{m_0} V_{n}(j', l', \nu', j, l, \nu) f_{n}(j', l', j''l''\nu''),$$

where

$$v_n = \int_0^\pi R^2 dR \chi_n^* \chi_n \langle j' l' \nu'| j'' l'' \nu'' \rangle,$$

and the $f_n$ are the Percival-Seaton coefficients, $^{1,6}$ analytically known in terms of $3 - j$ and $6 - j$ coefficients.

Solution of Eq. (11) subject to the boundary conditions

$$G_{l''\nu'' \rightarrow IV}(0) = 0,$$

and

$$G_{l''\nu'' \rightarrow IV}(\infty) = \sum_{l'} \sum_{\nu'} \delta(l'' - l') \delta(\nu'' - \nu') \exp[-i(k_{l''\nu''} r - l\pi/2)],$$

defines the scattering matrix $S$.

The complete solution $\Phi$ of the problem is a linear combination of the solutions $\Psi^{J,M}_{IV}$. Choosing the initial relative motion to be in the $z$ direction $^2$ as Arthurs and Dalgarno did, one has

$$\Phi^{J,M}_{IV} = \sum_{l''} \sum_{\nu''} \exp[i(k_{l''\nu''} r - l\pi/2)] \chi_{l''\nu''} Y_{l''\nu''}(\hat{R}) \times \sum_{j''l''\nu''} \sum_{i,j,m} \langle j''l''\nu''|j'l'\nu'\rangle y_{i,j,m}^0(\hat{R})$$

where the $f'$s are scattering amplitudes. By matching the known incident amplitudes from Eqs. (17) and (18), one finds the coefficients of the $\Psi$ in the expansion of $\Phi$, and by matching the outgoing waves, one finds that the scattering amplitudes are given by

$$f(j'm'l'\nu'|jm'l\nu) = \sum_{j''l''\nu''} \sum_{i,j,m} \langle j''l''\nu''|j'l'\nu'\rangle y_{i,j,m}^0(\hat{R}) \times C(jj') m_j M C(j'j'l' M) T_{\nu''\nu}'(j'j'l'|j'i') \times Y_{\nu''\nu'}(\hat{R}),$$

where the sums are over all allowed values (the coefficients are zero unless $M = m_j$ and $m'' = M - m''$, so that the $M$ and $m''$ sums collapse), and $T$ is the transition matrix.
\[ T^j(j',\nu'|j\nu) = \delta_{j,j'} \delta_{\nu,\nu'} - S^j(j',\nu'|j\nu) . \]  

(20)

The degeneracy-averaged scattered intensity ("different-
ferential cross section") is given by

\[ \mathcal{I}(j',\nu' - j|\nu) = (2j + 1)^{-1} k^2 \sum_{j',\nu'} |f(j',m_{j'}',\nu'-j,m_{j}\nu|\nu')|^2 , \]  

(21)

and the integral cross section,

\[ \sigma(j',\nu' - j|\nu) = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta f(j',\nu' - j|\nu') , \]

(22)

simplifies to

\[ \sigma(j',\nu' - j|\nu) = \left( \pi/k^2 \right) \sum_{j',\nu'} (2j + 1) \Omega(j',\nu' - j|\nu') , \]

(23)

where the opacity functions (average transition prob-
abilities) are defined by

\[ \Omega(j',\nu' - j|\nu) = (2j + 1)^{-1} \sum_{m_{j},m_{j'}} \sum_{j'\nu'} |T^j(j',\nu'|j\nu)|^2 . \]  

(24)

Once the \( v_n \) are evaluated for the particular problem of
interest, the major problem in this SF framework is the solution of the set of coupled equations [Eq. (11)].

In actual practice, the most accurate solutions are
presently obtained with the close coupling (CC) method, in which the infinite set is truncated, and the resulting
finite set of coupled equations is solved numerically
with increasing numbers of \( j \) and \( \nu \) values retained until
the desired cross sections converge. In this case, with
the addition of each \( j \) value associated with some \( \nu \),
there are also added (except for \( j < j \) ) \( 2j + 1 \) values of
\( \nu' \(|j - j| \leq \nu' \leq j + j \) ). However, due to the parity selection
rules on the Percival–Seaton coefficients, these resulting channels \( j'\nu' \) are [for any \( \nu'(\nu, R, \theta) \)] coupled into two distinct sets of equations depending on whether \( \nu' \) is even or odd. Addition of state \( j \) adds \( j + 1 \) equa-
tions to one set and \( j \) equations to the other.

III. BODY-FIXED (BF) THEORY

In this section, we derive the equations of the body-
fixed (BF) axes theory of Curtiss and associates\(^8\) for
the problem of the previous section using consistent
notation to allow easy comparison. The derivation is
given in a little more detail in the hope of encouraging
understanding and use of the BF theory.

We begin again from the c.m. coordinates of Fig. 1
with the components of \( \mathbf{R} \) and \( \mathbf{r} \) initially measured from
the same space-fixed (primed) axes. Equations (1)–(7)
and (9) apply as before, except that now we write Eq.
(1) in the form

\[ H = -h^2/2\mu \frac{d^2}{dr^2} + \mathbf{\mathbf{L}}^2/2\mu r^2 + H_{BC} + V , \]

(25)

remember that \( L = -J + \mathbf{J}_R \), and write Eq. (9) as

\[ (E - H) \Psi^{j\nu j\nu'} = 0 , \]

(26)

so that \( \Psi^{j\nu j\nu'} \) now labels the incident channel. Now, instead of coupling spherical harmonics together, one
rotates the coordinate axes to make the new \( z \) axis point
along \( \nu \) as in the unprimed set in Fig. 1. Choosing the Euler angles \( (\alpha, \beta, \gamma) \) of this transformation to be

\[ (\phi', \theta', 0) \] accomplishes the desired rotation and leaves the
new \( y \) axis in the old \( x' y' \) plane.

The details of the effect of the rotation on \( \Psi^{j\nu j\nu'} \) have
been discussed in Ref. 2 and (in the present notation) in
one of our publications,\(^9\) where it is shown that carry-
ning out the rotation is equivalent to letting

\[ \Psi^{j\nu j\nu'} = \sum_{j',\nu'} \sum_{j',\nu'} D_{j',\nu'}^{j\nu} (\phi', \theta', 0) \Psi_{j',\nu'}^{j\nu} (\mathbf{R}, \gamma) . \]  

(27)

Here, the \( D_{j',\nu'}^{j\nu} \) are the coefficients of the irreducible
presentations of the rotation group\(^10\) \( \Omega' \) is the com-
ponent of \( j \) along the BF \( z \) axis, and the \( \Psi_{\Omega'} \) are func-
tions of coordinates measured from the BF axes. By
substitution of Eq. (27) into Eq. (26) or by formal argu-
ments,\(^8\) it is found that the \( \Psi_{\Omega} \) satisfy a set of coupled
equations of the form

\[ -H_{\Omega,\nu} - \Omega_{\nu} - \nu - \nu - 1) \Psi_{\Omega,\nu} = 0 , \]

(28)

where

\[ H_{\Omega,\nu} = -h^2/2\mu \frac{d^2}{dr^2} + \mathbf{\mathbf{L}}^2/2\mu r^2 - H_{BC} + V(\nu, R, \theta) , \]

(29)

and

\[ H_{\Omega,\nu} = -h \lambda_{\nu}(J, \Omega) J_{\Omega}/2\mu r^2 \]

(30)

In these equations, \( H_{BC} \) is given by Eq. (4) with coordi-
mates understood to be body-fixed. The raising and
lowering operators\(^11\)

\[ J_{\Omega} = J_{\Omega,\nu} \pm \Omega_{\nu}, \]

(31)

have their usual definitions, and the \( \lambda_{\nu} \) are numbers de-
FINED by

\[ \lambda_{\nu}(J, \Omega) = [(J \pm \Omega + 1)/(J \mp \Omega)]^{1/2} . \]

(32)

Now let us expand the \( \Psi_{\Omega} \) in the complete set

\[ \Psi_{\Omega,\nu} = \sum_{j',\nu'} \sum_{j',\nu'} \lambda_{\nu}(J, \Omega) \chi_{j',\nu'}(\mathbf{R}) \chi_{j',\nu}(\mathbf{R}) , \]

(33)

where \( \bar{R} = (\theta_{\Omega}, \phi_{\Omega}) \) are the angles of \( \bar{R} \) in the BF system.
Substituting Eq. (33) into Eq. (28), multiplying by
\( (2\mu/h^2) \chi_{j',\nu'} \chi_{j',\nu'} \), and integrating over \( R \) and \( \bar{R} \), one
obtains the set of coupled radial equations

\[ h_{\Omega,\nu}^{j',\nu} G_{j',\nu j',\nu'}^{j\nu}(r) + h_{\nu}^{j',\nu} G_{j',\nu}^{j\nu}(r) + h_{\nu}^{j',\nu} G_{j',\nu}^{j\nu}(r) = (2\mu/h^2) \sum_{j',\nu'} \langle j' \Omega' \nu' | V | j'' \Omega' \nu'' \rangle G_{j''\nu''}^{j',\nu'}(r) , \]

(34)

where

\[ h_{\nu}^{j',\nu} = \frac{d^2}{dr^2} + \frac{h^2}{2\mu r^2} - \left[ (J + 1)/2\Omega^2 \right] , \]

(35)

with \( h_{\nu}^{j',\nu} \) as defined in Eq. (12),

\[ h_{\nu}^{j',\nu} = \lambda_{\nu}(J, \Omega) \lambda_{\nu}(J, \Omega + 1)/r^2 , \]

(36)

and

\[ \langle j' \Omega' \nu' | V | j'' \Omega' \nu'' \rangle = \int_0^\infty R^2 dR \int d\Omega \chi_{j',\nu'} \cdot \chi_{j',\nu}(r) , \]

(37)

When \( V \) is written in the form of Eq. (14), these matrix
elements take the form,
\[
\langle j'\Omega'd'| V | j\Omega'v' \rangle = \sum_n v_n \langle j'\Omega'n' | V | j\Omega'v' \rangle .
\]
where the \(v_n\) are again given by Eq. (16), but the \(d_n\) are given simply by
\[
d_n(j'\Omega'n') = \int d\tilde{R} Y_{j'n'\Omega'}(\tilde{R}) P_n(\cos \theta) Y_{j'\Omega'}(\tilde{R}) ,
\]
and
\[
d_n(j'\Omega'n') = \frac{1}{2} (2j'+1)(2j+1) \sqrt{C(j'\Omega'v'); \Omega\Omega} 
\]
\[
\times C(j'n'\Omega'v') \times 000 .
\]
This simplification (no \(6-j\) coefficients) occurs because \(\theta = \theta_R\) in the BF coordinates.

Solution of the coupled Eqs. (34), subject to the boundary conditions, \(G_{j'M'j'v'}(0) = 0\), and
\[
G_{j'M'j'v'}(R) = k_{j'v'}^{1/2} \sum_{j'\Omega'v'} \delta_{jm, j'n'} \delta_{Mn} \delta_{M'v'} \phi_{j'M'j'v'}(R) Y_{j'n'\Omega'}(\tilde{R})
\]
\[
- S_{j'\Omega'v'}(j', -\Omega, v) \exp \left[ \frac{i}{2} \left( k_{j'v'} R - (j + j') \pi/2 \right) \right],
\]
defines a scattering matrix appropriate to this formulation. The reason for this particular choice will become apparent below.

We again choose the incident relative motion to be in the \(z'\) direction, \(7\) so that \(\Phi\) again satisfies Eq. (18), expand \(\Phi\) in the form,
\[
\Phi_{j'M'j'v'}^{jm} = \sum_{J, M} A(JMjm, j'Mv) \Phi_J^{JMj'Mv} ,
\]
determine the coefficients \(A\) by equating the incident parts of Eqs. (18) and (42). To do so, one first puts the plane wave part of Eq. (18) into a convenient form by making the usual expansion of the plane wave as a sum over \(l\) of Legendre polynomials, \(P_l\), and spherical Bessel functions, \(j_l\), notes that \(P_l = D_{jv}^{l} \Phi\) uses the asymptotic form of the \(j_l\) and, Eq. (27) to change \(Y_{jMjMv}(\tilde{R})\) to BF coordinates, couples the two resulting \(D's\) together (noting that \(m_j\) is the only component of \(m\)) to get \(D_{j'v'}^{M}\), changes the order and limits of the \(l\) and \(J\) sums, and uses the properties of the Clebsch–Gordan coefficients to sum over \(l\), to obtain
\[
\exp \left( i k_{j'v'} r \right) \chi_{j'v'} Y_{j'MjMv}(\tilde{R}) = (2k_{j'v'} r) \sum_l \sum_{M} \sum_{J} (i)^{J+1}(2J+1) \delta_{m_j, -J} \chi_{j'v'}(\tilde{R})
\]
\[
\times D_{j'v'}^{lM} Y_{j'MjMv}(\tilde{R}) \times \delta_{J, -J} \exp \left[ \frac{i}{2} \left( k_{j'v'} R - (J + j') \pi/2 \right) \right] .
\]
Comparing the incident parts of this equation with those of Eq. (42) after substitution of Eqs. (27), (33), and (41), one finds that
\[
A(JMjm, j'Mv) = \frac{1}{2} (i)^{J+1}(2J+1) \delta_{m, -J} \delta_{Mn} \delta_{M'v'} k_{j'v'}^{1/2} .
\]
This reason that all the incident waves have \(\Omega' = \Omega = -M = -m_j\) is because the \(z\) axis points in the \(-z'\) direction on the incident side of the collision.

Next, one equates Eq. (42) and Eq. (18) to solve for the scattering amplitudes. To do this conveniently, one uses Eq. (43) to remove the equal incident parts, transforms the outgoing parts of Eq. (43) to the other side of the equation, sums over \(\Omega\), and defines the transition matrix by
\[
T_{j'\Omega'v'}(jMv) = \delta_{v', v} \delta_{j', j} \delta_{M, M} - S_{j'\Omega'v'}(jMv) .
\]
Thus, the definition [Eq. (41)] of \(S'\) makes \(S'\) become the unit matrix and \(T'\) become zero in the limit of no scattering (\(V = 0\)) as they ought. Now, using the inverse of Eq. (27) to convert \(Y_{j'MjMv}(\tilde{R})\) back to SF coordinates, and using the properties of the \(D\) coefficients to couple the resulting \(D's\) together, one sees that the scattering amplitudes are given by
\[
f(j'm', j'n') = \sum_{j'M'j'v'} \langle jj'v' | j'M'j'v' \rangle \delta_{m, m'} \delta_{m', m'} \delta_{M', M'} \delta_{M, M'} \times C(jj'L; j'n'L; M, -m', M) Y_{j'MjMv}(\tilde{R}) .
\]
Again the sums are over all allowed values in the indicated order, and, like Eq. (19), this is really a three-fold sum.

The degeneracy-averaged scattered intensity is again given by Eq. (21), and, using the properties of the Clebsch–Gordan coefficients, one easily shows that the integral cross sections reduce to Eq. (23),
\[
\sigma(j'v' - jv) = (\pi/k_{j'v'}^2) \sum_{j0} (2J+1) \phi_j(j'v' - jv) .
\]
However, the opacity functions are now given by
\[
\phi_{j'v' - jv} = (2j + 1)^{-1} \times \sum_{M' = -J} \frac{1}{2} \sum_{M = -J} | T_{j'\Omega'v'}(jMv) |^2 ,
\]
where \(j_k\) is the lesser of \(j\) and \(J\), and \(j_k'\) is the lesser of \(j'\) and \(J'\).

The major problem in this coordinate system is now the solution of the set [Eq. (34)] of coupled equations. Addition of each rotor state \(j'\) adds \(2j' + 1\) channels \(j'\Omega'(-j' \leq \Omega' \leq j')\). As formulated, all of these appear to be coupled together. However, as we have shown elsewhere, the inversion parity of the Hamiltonian allows BF solutions of definite reflection parity and solutions of Eq. (34) of definite parity under a change in sign of \(\Omega'\). The functions \(G_{j'Mj'v'}\) defined by Eq. (41) are neither even nor odd under this change. We therefore define functions satisfying Eq. (34),
\[
S_{j'Mj'v'}^{JMj'Mv} = G_{j'Mj'v'}^{JMj'Mv} + G_{j'Mj'v'}^{JMj'Mv} ,
\]
and
\[
\tau_{j'Mj'v'}^{JMj'Mv} = G_{j'Mj'v'}^{JMj'Mv} - G_{j'Mj'v'}^{JMj'Mv} ,
\]
which are, respectively, symmetric and unsymmetric under this reflection. Since \(\tau_{j'Mj'v'}^{JMj'Mv} = 0\), the equations for \(\tau\) with positive \(\Omega\) are not coupled to those for negative \(\Omega\) and one need solve the coupled equations for \(\tau\) only for the \(j'\) positive values of \(\Omega'(1 \leq \Omega' \leq j')\) for each \(j'\).
added. In the coupled equations for $s$ with $\Omega' = 0$, one has $s_j^{\text{Br}} = s_j^{\text{CC}}$, and $h_{\alpha\Omega}$ is $h_{\Omega\Omega}$, so that the left-hand side of Eq. (34) becomes $h_{\Omega\Omega} s_j^{\text{Br}}(r) + 2h_{\Omega\Omega} s_j^{\text{CC}}(r)$, and the $j' + 1$ equations with $0 < \Omega' \leq j'$ are not coupled to those with negative $\Omega'$.

If the equations for $s$ and $u$ are not solved for $\Omega' = 0$ subject to the boundary conditions,

$$ s_j^{\text{Br}}(0) = \sum_{j' \Omega'} s_j^{\text{CC}}(0) = 0, $$

then the elements of the scattering matrix needed are

$$ S_j^{\text{Br}} = \sum_{j' \Omega'} S_j^{\text{CC}}(r), $$

and

$$ S_j^{\text{CC}} = \sum_{j' \Omega'} S_j^{\text{Br}}(r). $$

Then, if one has $N$ rotational channels strongly coupled together in Eq. (11) for each vibrational state, then, he can:

1. approximate all the $l'' (l'' + 1)$ terms by $J(J + 1)$, and
2. all the $k''_{j'' \Omega''}$ by $k''_{j''}$ (both approximations are necessary to achieve any kind of simplification) and without further approximation, reduce Eq. (11) to sets of coupled equations in which the number of coupled channels is equal to the number of vibrational states that must be retained (usually only a few). This is done by numerically finding at each $J$ the $r$ and $\nu$-independent $N \times N$ unitary transformation which diagonalizes the matrix of Percival–Seaton coefficients which Eq. (15) generates from Eq. (52). Solving the few state vibrational equations by any desired method and transforming back gives the IOS scattering matrix. This IOS approximation is orders of magnitude faster than doing full CC calculations and has been found to give good results for small $J$ collisions where the rotational states are strongly coupled. Also, it can easily be reduced to the usual first-order sudden (FOS) approximation. However, it should also be pointed out that the IOS approximation is well defined and can be used independent of the form of the potential in problems of pure rotational scattering when the energy is high enough to allow a sudden approximation on rotational energies also.

B. BF theory

Because the $\Omega$ and $j$ couplings in Eq. (34) occur in separate terms, the two sudden approximations made together above can be made separately in the BF approach. The equivalent of setting $l'' (l'' + 1)$ to $J(J + 1)$ is to set $L^2 = J^2$ in Eq. (25). The result is that the $\Omega$ coupling disappears and Eqs. (34) reduce to

$$ [d^2/dr^2 + k''_{j'' \Omega''} - J(J + 1)/r^2] G^{\text{CC}}_{j'' \Omega''}, $$

This approximation is justified when $J$ and/or $j''$ are small. Note that it can be made independent of the form of $V$. One has immediately and analytically obtained a drastic reduction of the problem to many fewer than $N$ coupled rotational channels.

Since all $\Omega$ coupling has been neglected, it is clear from Eq. (41) that the scattering matrix of this approximation has the form

$$ S''(j'' \Omega'' | j, -\Omega, \nu) = \delta_{\Omega \Omega'} S''(j'' \Omega'' | j - \Omega, \nu). $$

Since this cannot become diagonal [see Eq. (45)] in the large $J$, weak coupling limit, it is clear why the IOS approximation is well defined and can be used independent of the form of the potential in problems of pure rotational scattering when the energy is high enough to allow a sudden approximation on rotational energies also.
approximation becomes poor at large $J$. It should also
be noted that in this approximation, one does not need
the functions $s$ and $u$ of Eq. (49) but only the boundary
condition [Eq. (41)].

One could now proceed to solve Eqs. (54) by a CC
method, and we expect such an approach to prove very
useful in vibrationally inelastic and reactive scattering
problems where most of the contribution to the cross
sections comes at the small $J$ at which this IOS ap­proxi­mation is valid.

If conditions of Eqs. (52) and (53) are satisfied, one
can also obtain further simplification by making a sec­ond
sudden approximation, $k^2_{j 
u'} = k^2_{j 
u}$, in Eq. (54).
Then by finding the unitary transformation [of much
smaller dimension than $N \times N$, typically of $O(N^{1/2} \times N^{1/2})$]
that diagonalizes the appropriate matrix of $d_{j}$ coeffi­
cients of Eq. (38) (which is independent of $J$), one can
remove all coupling except that in $\nu$. At the thermal
energies of primary interest to this author, vibrational
energy spacings are too large to admit a sudden approx­
imation on $\nu$ except in the special case of almost re­s­
onant transitions. However, the number of vibra­tional
states appreciably coupled together is usually
small enough that the resulting equations can be eco­
nomically solved by new efficient CC methods.23 Inverting
the transformation then gives the scattering matrix.

Hence, the primary conclusion of this section is that
the BF formulation allows IOS approximations to be
made far more generally and numerically much more
simply than the SF formulation. This is further de­
monstrated in the next section.

VI. NUMERICAL EXAMPLES. RIGID ROTOR

In a previous paper,19 using empirical potentials of
the simple form,

$$V(r, \theta) = V_0(r) + V_2(r) P_2(\cos \theta), \tag{56}$$

which allows a full IOS approximation to be defined in
either SF or BF coordinates, and using the SF rigid
rotor model of Arhurs and Dalgarno,1 we calculated the
FOS, IOS, and CC rotationally inelastic cross sec­tions
$\sigma(j'-j)$ for the $2-0$ and $4-0$ transitions in ther­
mal Ar $+$ TIF and Ar $+$ N$_2$ collisions. The CC program
used was that of Gordon,23 and the relative compute­ing
times of the many-state SF $-$ FOS : IOS : CC programs
used in that work was 1 : 2 : 90.

In beginning this work, we first improved the pro­
cedure for calculating the WKB phase shifts needed in
the IOS method. Use of the Gauss– Mehler quadrature
discussed in the Appendix was found to decrease the
time needed to calculate many-state IOS integral cross
sections by a factor of 2. (Similar methods could also
decrease the time of the FOS method somewhat.)

Then, we converted the IOS program to the BF for­
mulation and repeated the IOS calculations to compare
results and running times. The results were identical,
but there was a dramatic difference in run times. For
example, in the Ar $+$ TIF problem, it was necessary at
small $J$ to include the rotor states $j = 0, 2, 4, \ldots 14$ to get
convergence. In the SF formulation, this makes a 64-
channel problem, and the SF $-$ IOS program must di­
agonalize a $64 \times 64$ matrix of $f_{j}$ coefficients and evaluate
64 WKB phase shift integrals at each $J$. However, to
calculate the same cross sections for the same prob­
lem, the BF $-$ IOS program only need diagonalize one
$8 \times 8$ matrix of $d_{j}$ coefficients which is independent of $J$
and at each $J$ evaluate only 8 phase shift integrals.
As a result, typical relative running times of our present
BF $-$ IOS : SF $-$ IOS : SF $-$ CC programs are 1 : 100 : 9000,
and the many-states IOS integral cross sections reported
in our previous paper can all be recalculated for less
than one dollar’s worth of computing time on the Los
Alamos Scientific Laboratory’s CDC 7600 computer.

VII. CONCLUSIONS

From this work, we conclude that, while the BF and
SF formulations of the quantum theory of atom–diatom
scattering are equivalent, the SF approach is more con­
venient for weak collisions, and the BF approach is
more convenient for strong collisions. In particular,
the BF formulation allows rotational sudden approxima­
tions with much greater directness, simplicity, and
generality, doing much of the work analytically. This
should prove very helpful in reducing the complexity
of vibrationally inelastic and reactive scattering prob­
lems where the main contribution comes from the small
$J$ region in which rotational sudden approximations are
valid.

ACKNOWLEDGMENTS

I thank Associated Western Universities for the
Faculty Research Participation fellowship under which
this work was completed, and the staff of the Los
Alamos Scientific Laboratory for their hospitality,
stimulating environment, and use of facilities.

APPENDIX: RAPID CALCULATION OF WKB PHASE
SHIFTS

The common WKB phase shift formula is

$$\eta = \lim_{R \to \infty} \left\{ \int_{r_{c}}^{R} \left[ k^2 - (l+\frac{1}{2})^2/r^2 - U \right]^{1/2} \, dr - kR + (l+\frac{1}{2})\pi/2 \right\}, \tag{A1}$$

where $k$ ($k^2 = 2\mu E/\hbar^2$) is the wavenumber, $V$ ($U = 2\mu V/\hbar^2$)
the potential energy, and $r_{c}$ the classical turning point.
(We are here using the Langer modification24 $[(l+1)$
$- (l+\frac{3}{2})^2]$.)

Noting the success of Tellinghuisen25 and Dickinson26
in evaluating somewhat similar RKR integrals with
Gauss–Mehler quadratures, we now put this integral
in a form convenient for the same methods by writing
it in the form

$$n = \lim_{R \to \infty} \left\{ \int_{r_{c}}^{R} \left[ k^2 - (l+\frac{1}{2})^2/r^2 - U \right]^{1/2} \, dr \\
- \int_{r_{c}}^{R} \left[ k^2 - (L+\frac{1}{2})^2/r^2 - U \right]^{1/2} \, dr + (l+L)\pi/2 \right\}, \tag{A2}$$

$$= \int_{r_{c}}^{R} \left[ k^2 - (l+\frac{1}{2})^2/r^2 - U \right]^{1/2} - \left( k^2 - (L+\frac{1}{2})^2/r^2 \right]^{1/2} \, dr$$
\[ \eta_i(E) = kr_i \int_0^1 f(x)(1 - x^2)^{1/2} dx + (l + \frac{1}{2} - kr_i)\pi/2, \]

where \( f(x) = x^{-2} \{ 1 - (l + \frac{1}{2})^2 x^2 k^2 r_i^2 - U(x)/k^2 \}^{1/2} \)

is smooth and well behaved. The weight function \((1 - x^2)^{1/2}\) has removed the singularity in the slope at the turning point.

The \( N \) point Gauss–Mehler approximation to this integral is given by

\[ \eta_i(E) = kr_i \sum_{j=1}^N w_j f(x_j) + (l + \frac{1}{2} - kr_i)\pi/2, \]

and Kopal\(^{27}\) gives the points \( x_j \) and weights \( w_j \) appropriate to the weighting function \((1 - x^2)^{1/2}\) as

\[ x_j = \cos \left( \frac{j\pi}{2(N+1)} \right), \]

and

\[ w_j = (1 - x_j^2)\pi/(2N+1). \]

Since the \( x_j \) and \( w_j \) are so simply calculated, a Fortran subroutine with arbitrary \( N \) was easily written which evaluates the \( x_j \) and \( w_j \) on the first pass through it. It was tested using a Lennard-Jones 12–6 potential and a wide range of \( k, l, \) and potential depths. The results for \( N \) up to 64 were compared with each other and with Simpson’s rule results. It was found that the approximation converges very rapidly with \( N: \) \( N = 4 \) gave an average of 5 significant figure accuracy, \( N = 6 \) an average of 6 significant figures, and \( N = 8 \) an average of 7 significant figures. \( N = 6 \) was actually used in the calculations reported herein. It often gave 7 figure accuracy, and in none of the tests did it give less than 5 figure accuracy, which was more than adequate for our purposes.

However, it should be noted that in deriving (A5) we started with the formulas\(^{25}\) for a \( 2N \)-point quadrature on the interval \((-1,1)\) and used the \( N \) points with \( x_j > 0 \) to estimate an integral on \((0,1)\). If \( f(x) \) is an even function of \( x \), \( U(x) \) an even function of \( r_i \), as is true for the \( 12–6 \) potential, this is rigorous. But if \( f \) is not even, the points and weights used are not optimum, and the estimate may converge slowly. We thank the referee for pointing this out. In practice, if it is the short range potential which is not an even function of \( r_i \), the method still converges rapidly; in test calculations with an \( N = 6 \) potential, 6 significant figures were obtained with \( N = 7 \) or 8. However, one can readily show that if the leading term in the long-range potential is an odd function of \( r_i \), the method converges much more slowly. The worst possible case for the method for neutral molecule scattering is to have the \( r^3 \) dipole–dipole term in the potential; test calculations with an \( N = 3 \) potential gave only 4 to 5 significant figures with \( N = 24 \). In such a case (and for even functions also) one could obtain rapid convergence by using the weighting function \((1 - x)^{1/2}\) instead of \((1 - x^2)^{1/2}\); the appropriate weights and points on \((0,1)\) are known.\(^{28}\)

\(^{*}\)Work performed under the auspices of the U. S. Atomic Energy Commission.

\(^{1}\)Associated Western Universities Faculty Research Participant, Summer 1973. On sabbatical leave from the Department of Chemistry, Brigham Young University, Provo, UT 84602.


\(^{27}\)This notation is that of M. E. Rose, Elementary Theory of Angular Momentum (Wiley, New York, 1957).


\(^{29}\)See, for example, A. Messiah, Quantum Mechanics (Wiley, New York, 1961), p. 497.

\(^{30}\)Reference 5, p. 58.

\(^{31}\)Reference 5, pp. 35, 38, 39.

\(^{32}\)Reference 5, pp. 54, 58, 60.

\(^{33}\)R. T Pack and J. O. Hirschfelder, J. Chem. Phys., 49, 4009 (1968); 52, 521 (1970). In the present paper, \( R \) is being treated as the electronic coordinates were and \( \mathbf{r} \) as the internuclear distance was in those papers.

\(^{34}\)The \( D \) used here are equal to the \( D_\Pi \) of Ref. 5. If that notation difference is remembered, all of Rose's formulas for them can be used.

\(^{35}\)Reference 5, p. 24.

\(^{36}\)Reference 5, p. 62.

\(^{37}\)See, for example, A. Messiah, Quantum Mechanics (Wiley, New York, 1961), p. 497.

\(^{38}\)Reference 5, p. 38.

\(^{39}\)Reference 5, pp. 54, 58, 60.


\(^{47}\)R. E. Langer, Phys. Rev., 51, 669 (1937). This modification makes \( s \rightarrow 0 \) properly as \( u \rightarrow 0 \) or \( u \rightarrow \infty \). In unpublished work, we have made a uniform asymptotic derivation that avoids need of this modification by giving a formula like Eq. (A11), but with \( U(u) \) under the integral and \( 1/2 + 1/2) \) replaced by \( 1/4 + 1/4 \).


