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Polarization and electronic excitation in nonreactive collisions: Basic formulation for quantum calculations of collisions between ^2P-state alkali-metal atoms and H_2 or D_2

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The inelastic scattering of two structured systems—for example, an excited atom and a molecule—is considered in the case of nonreactive collisions. Explicit formulas are presented for cross sections corresponding to transitions between arbitrary eigenstates of the two isolated systems. These formulas are then used to derive cross sections for polarization transfer and multipole relaxation in one system when the other system is unpolarized. Both space-fixed and body-fixed formulations are given. Explicit matrix elements are worked out for interactions such as occur between model alkali-metal atoms and rigid-rotor diatomic molecules. An effective interaction method is also discussed and related to an adiabatic-state approach.

I. INTRODUCTION

There is evidence[1–4] that in collisions of excited atoms with molecules, the cross sections for transitions among atomic energy levels are sometimes sensitive to the rotational degrees of freedom of the molecule. Thus transitions between fine-structure levels can be enhanced by the presence of rotational transitions which are nearly resonant with the fine-structure splitting.[1,2] Most calculations of such effect in the past have relied on classical trajectories in a time-dependent calculation[1] or on computations in which the molecule is treated as a classical object of fixed orientation with respect to the atom.[5] It has also been suggested that anisotropy effects are often more important than rotational degrees of freedom.[6]

As realistic potential energy surfaces become available[7] which include both short-range overlap effects and long-range correlation for the interaction of excited atoms and molecules, it is important to calculate the cross sections in a scattering theory with a fully quantum treatment of both the internal degrees of freedom of the colliding partners and of their relative motion. The calculations by Fowler and Launay[3] of fine-structure transitions in C^+ in collisions with H_2 are of this type, although as discussed more fully in a following paper,[8] they neglected an important part of the interaction. Rebentrost and Lester[4] have reported close-coupling calculations of $F(^2P)$ collisions with H_2 in an adiabatic-state basis. Like Fowler and Launay,[3] other recent calculations[9] of the $F+H_2$ system, and the general formulation of DeVries and George,[10] Rebentrost and Lester direct their attention to total cross sections summed over magnetic sublevels, whereas we need to consider both differential cross sections and total cross sections for the multipole relaxation and transfer of atomic polarization, as well.

To calculate inelastic cross sections for excited atoms with molecules, we use the time-independent scattering theory of composite systems in a fairly general form. The essential concepts are well understood.[4,11] The coupled equations which result from the energy eigenvalue equation for the system are practical to solve only if rotation and inversion symmetries are exploited to reduce the coupled equations to blocks of given J, M, and π_t, the eigenvalues representing the total angular momentum $\mathbf{J}$, its projection on the space-fixed quantization axis $\hat{\mathbf{z}}$, and the total parity. Two convenient bases in which J, M, and π_t are eigenvalues are a space-fixed (SF) basis with eigenvalues j_1, j_2, j, l, J, M, and π_t, and a body-fixed (BF) basis with eigenvalues j_1, j_2, j, Ω, J, M, and π_t. Here $\mathbf{j}_1$ and $\mathbf{j}_2$ are the angular momenta of the interacting systems, $\mathbf{j}$ is their sum, and $\mathbf{l}$ is the orbital angular momentum of the relative motion of the two systems about their center of momentum (CM),

$$\mathbf{j}=\mathbf{j}_1+\mathbf{j}_2=\mathbf{J}-\mathbf{l} . \tag{1}$$

The eigenvalue Ω is the magnitude of the eigenvalue for the projection of $\mathbf{j}$ onto $\mathbf{R}$, which locates the CM of system 2 with respect to that of 1. The SF basis is the natural choice for investigating collisionally induced transitions between sublevels with magnetic quantum numbers m_1,m_2 corresponding to the SF projections $\mathbf{j}_1\cdot\hat{\mathbf{z}},\mathbf{j}_2\cdot\hat{\mathbf{z}}$. It also allows the simplest derivation of the scattering equations. The BF basis, on the other hand, takes advantage of the symmetry of the interaction V with respect to rotations about $\mathbf{R}$ and the consequent diagonality of the interaction matrix in Ω, but it also contains potentials pitfalls in the proper application of the commutation relations of $\mathbf{j}$ with $\mathbf{J}$ when the basis states are eigenstates of $\mathbf{j}\cdot\hat{\mathbf{R}}$ and $\mathbf{J}\cdot\hat{\mathbf{z}}$, but not of l^2.

The scattering theory required is a generalization of the theories for collisions of ^{2}P-state atoms with structureless ground-state atoms or ions as used by Reid[12] in an SF formulation and by Mies[13] in an adiabatic-state, BF formulation. Furthermore, just as Reid's work was an extension of an earlier theory of rotational excitation in rigid rotors due to collisions with structureless atoms,[14] so our theory may be obtained as an extension of theories for rotational energy transfer between diatomic molecules.[15] Launay has presented some of the theory needed in a BF formulation,[16] whereas Rebentrost and Lester[4] have extended the adiabatic-state approach of Mies.[13]

We believe it is conceptually simpler to derive the scattering equations first in the SF frame and then to transform them to the rotating BF frame if needed. However, since the results are fully equivalent to what can be obtained by the BF-frame derivations of Launay[16] and of Rebentrost and Lester,[4] we present (Sec. II) only a brief summary of the SF-frame derivation and then give the transformation to the BF frame (Sec. III). Next, reduced expressions for total cross sections are derived for multipole transfer and relaxation when one of the systems is initially unpolarized (Sec. IV). With the form of the interaction potential introduced in Sec. V, results are immediately applicable to rotational transfer and relaxation between rigid diatomic molecules, to interactions between two possibly excited atoms, each with a single valence electron (but with spin-spin interactions, charge exchange, and photon transfer ignored), or to the problem of specific concern to us, the interaction of such an atom with a rigid diatomic molecule. Finally, we discuss calculations in bases of adiabatic molecular states of the combined system and relate such calculations to a type of effective interaction approximation.

II. SCATTERING EQUATIONS IN THE SF FRAME

Consider interacting systems 1 and 2 with internal coordinates represented by $\mathbf{r}_i$, $i=1,2$, with respect to their individual centers of mass. Each *isolated* system i has a total Hamiltonian $H_i + P_i^2/(2M_i)$ where $\mathbf{P}_i$ and M_i are, respectively, the total momentum operator and the total mass, and H_i is the Hamiltonian of system i in its center-of-momentum (CM) frame with eigenstates $|a_i m_i\rangle$:

$$H_i\,|a_i m_i\rangle = E_{a_i}\,|a_i m_i\rangle \ . \tag{2}$$

Since we take the isolated systems to be invariant under rotations and inversions, H_i commutes with both the angular momentum operator $\mathbf{j}_i$ and the parity operator Π_i, so that the energy eigenstates can be taken to be eigenstates also of j_i^2, $\mathbf{j}_i\cdot\hat{\mathbf{z}}$, and Π_i, where $\hat{\mathbf{z}}$ is the SF quantization axis, with eigenvalues $j_i(j_i+1)$, m_i, and π_i, respectively, in units with $\hbar=1$. The energies are independent of m_i which labels the "sublevels" of the system. Other relevant quantum numbers (j_i, π_i, etc.) are represented by a_i.

The total Hamiltonian of the interacting systems in the CM frame is

$$H = P^2/(2\mu) + H_1 + H_2 + V(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R}) \ , \tag{3}$$

where $\mu = M_1M_2/(M_1+M_2)$ and $\mathbf{P} = -i\nabla_{\mathbf{R}}$. The interaction potential V depends on the internal coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ as well as on the separation $\mathbf{R}$ of system 2 from system 1. Of course, H commutes with the total angular momentum $\mathbf{J} = \mathbf{j} + \mathbf{l} = \mathbf{j}_1 + \mathbf{j}_2 + \mathbf{l}$ and the total parity $\Pi_t = \Pi_1\Pi_2\Pi_{\mathbf{R}}$, but not generally with the orbital angular momentum $\mathbf{l}$ of the two systems in the CM frame.

The scattering equations arise from the eigenvalue equation $(H-E)\psi = 0$ when the wave function ψ of the interacting systems is constrained to satisfy appropriate boundary conditions. They are most simply derived in a simple product basis of isolated-system states, with antisymmetrization of electrons to include exchange effects between systems 1 and 2, if desired:[17]

$$|a_1a_2m_1m_2\rangle = \mathcal{A}_{12}\,|a_1m_1\rangle\,|a_2m_2\rangle \ .$$

The resulting radial equation, although formally simple, is impractical to solve because all states and all l values are coupled together. The matrices involved need to be reduced to block-diagonal form with blocks labeled by the conserved quantum numbers J, M, and π_t. The reduction is accomplished by a unitary transformation changing the basis to one comprising eigenstates of J^2, $\mathbf{J}\cdot\hat{\mathbf{z}}$, and Π_t. Thus in the basis of states

$$|\Phi_{\alpha l}^{JM}\rangle = \sum_{m_1,m_2,m} |\beta\rangle\, Y_{lm}(\hat{\mathbf{R}})\, X(\beta l m,\alpha J M) \ , \tag{4}$$

where α represents a_1a_2j, β represents $a_1a_2m_1m_2$, and the matrix elements of the unitary transformation are[18]

$$X(\beta l m,\alpha l J M) = \sum_n (-1)^{j_1-j_2+n+j-l+M} \times[(2j+1)(2J+1)]^{1/2} \times \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -n \end{pmatrix} \begin{pmatrix} j & l & J \\ n & m & -M \end{pmatrix} , \tag{5}$$

one finds matrix equations

$$\left[\underline{\mathbb{1}}\frac{d^2}{dR^2} + \underline{k}'^2 - \frac{\underline{l}'^2}{R^2}\right]\underline{F}^J(R) = 2\mu\underline{V}^J(R)\underline{F}^J(R) \tag{6}$$

for each block of radial wave functions $\underline{F}^J(R)$. Here $\underline{k}'^2$ and $\underline{l}'^2$ are the diagonal matrices with elements $k_{12}'^2 = 2\mu(E - E_{a_1'} - E_{a_2'})$ and $l'(l'+1)$, respectively, and the matrix elements of $\underline{V}^J(R)$ are

$$\langle \Phi_{\alpha' l'}^{JM}\,|\,V(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\,|\,\Phi_{\alpha l}^{JM}\rangle \ ,$$

which from $[H,\mathbf{J}]=0$ are easily shown to be independent of M for $-J \le M \le J$. The matrix blocks are limited to l values lying in the range $|J-j| \le l \le J+j$ and yielding a given total parity $\pi_t = \pi_1\pi_2(-1)^l$.

The differential equations (6) are solved for each J, M, and π by starting with a square matrix $\underline{F}^J(R)$ near $R=0$ in which each column represents a bounded, linearly independent solution and numerically integrating outward and matching the open-channel component (for which $k_{12}^2 \ge 0$) to the asymptotic form

$$\underline{F}^J = \underline{j}\,\underline{A}^J - \underline{n}\,\underline{B}^J \ , \tag{7}$$

where $\underline{j}$ and $\underline{n}$ are diagonal matrices with elements given in terms of spherical Bessel functions of the first and second kind[19] by $k_{12}^{1/2}Rj_l(k_{12}R)$ and $k_{12}^{1/2}Rn_l(k_{12}R)$, respectively. The real square matrices $\underline{A}^J$ and $\underline{B}^J$ are easily combined to give the T matrix (or closely related S matrix)

$$\underline{T}^J=\underline{1}-\underline{S}^J=2\underline{B}^J(\underline{B}^J+i\underline{A}^J)^{-1}\ , \tag{8}$$

with matrix elements $T^J_{\alpha' l',\alpha l}=\langle \Phi^{JM}_{\alpha' l'} \mid T \mid \Phi^{JM}_{\alpha l}\rangle$ where, as above, α represents a_1a_2j. From these, one can find the differential cross section for the transition from SF sublevel $\beta=(a_1a_2m_1m_2)$ to sublevel $\beta'=(a'_1a'_2m'_1m'_2)$ by transforming back to the SF product basis:

$$\frac{d}{d\Omega_{\hat{\mathbf{R}}}}\sigma_{\beta'\leftarrow\beta}(\hat{R},\hat{k}) = \left| \frac{2\pi}{k_{12}} \sum_{l,m,l',m'} Y^{(\hat{R})}_{l'm'}Y^{(\hat{k})}_{lm} i^{\,l-l'} \times T(\beta' l' m' \leftarrow \beta l m) \right|^2 , \tag{9}$$

where k_{12} is associated with the initial states,

$$T(\beta' l' m' \leftarrow \beta l m)= \sum_{j,j',J,M} X(\beta' l' m',\alpha' JM) \times T_{\alpha' l',\alpha l}X^{*}(\beta l m,\alpha JM)\ , \tag{10}$$

and $\hat{\mathbf{k}}$ and $\hat{\mathbf{R}}$ are the incident and scattered directions, respectively. If $\hat{\mathbf{k}}$ is chosen as the quantization axis, Eq. (9) can be simplified by the identity $Y_{lm}(\hat{\mathbf{z}})=\delta_{m0}[(2l+1)/(4\pi)]^{1/2}$.

III. TRANSFORMATION TO THE BF FRAME

Calculations of molecular structure are usually made in a BF frame in which $\hat{\mathbf{R}}$ is taken as the quantization axis. The symmetry of the interaction V with respect to rotations of the interacting systems about $\hat{\mathbf{R}}$, namely, $[V,\mathbf{j}\cdot\hat{\mathbf{R}}]=0$, can be exploited by calculating matrix elements in the BF basis of states

$$|\,\alpha n\,\rangle_{\mathrm{BF}}= \sum_{m_1,m_2} |\,\beta\rangle_{\mathrm{BF}}(-1)^{j_1-j_2+n}(2j+1)^{1/2} \times \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -n \end{pmatrix} , \tag{11}$$

where $\alpha=a_1a_2j$ and $\beta=a_1a_2m_1m_2$.

To use the symmetry in scattering calculations, one looks for linear combinations of the $|\,\Phi^{JM}_{\alpha l}\rangle$ which are simultaneous eigenstates of j_1^2, j_2^2, j^2, $\mathbf{j}\cdot\hat{\mathbf{R}}$, J^2, J_z, and Π_t. It may be shown[16] that the unitary transformation

$$|\,\alpha\Omega JM\pi_t\,\rangle= \sum_{l} |\,\Phi^{JM}_{\alpha l}\rangle \xi^{jJ}_{l\Omega} \tag{12}$$

gives such linear combinations, where l is summed over the range $|\,J-j\,| \le l \le J+j$ with the restriction that $(-1)^l=\pi_t\pi_1\pi_2$ and the matrix elements of the transformation are

$$\xi^{jJ}_{l\Omega}=(-1)^{l-j-\Omega}\left[\frac{4l+2}{1+\delta_{\Omega 0}}\right]^{1/2}\begin{pmatrix} j & l & J \\ \Omega & 0 & -\Omega \end{pmatrix} . \tag{13}$$

Note that there are two possible parities $\pi_t=\pm 1$ for allowed values of $\Omega>0$, namely, for $0<\Omega\le j_<$, where $j_<$ is the smaller of $\{j,J\}$, but only one possible parity $\pi_t=\pi_1\pi_2(-1)^{J-j}$ for the case $\Omega=0$. When j and J are half-integral, there are $j_<+\frac{1}{2}$ states of each parity, whereas when j and J are integral, there are $j_<$ states of parity $\pi_t=\pi_1\pi_2(-1)^{J-j+1}$ and $j_<+1$ states of parity $\pi_t=\pi_1\pi_2(-1)^{J-j}$. The inverse of Eq. (12) is

$$|\,\Phi^{JM}_{\alpha l}\rangle= \sum_{\Omega} |\,\alpha\Omega JM\pi_t\,\rangle\xi^{jJ}_{l\Omega}\ , \tag{14}$$

where Ω is summed over the range $0\le\Omega\le j_<$.

Matrix elements of the interaction V in the basis $\{\,|\,\alpha\Omega JM\pi_t\,\rangle\}$ are particularly simple, because they are diagonal not only in J, M, and π_t, but also in Ω. In terms of the BF states $|\,\alpha n\,\rangle_{\mathrm{BF}}$ defined in Eq. (11),

$$\langle \alpha'\Omega' J' M' \pi'_t \mid V \mid \alpha\Omega M\pi_t\,\rangle =\delta_{JJ'}\delta_{MM'}\delta_{\Omega\Omega'}\langle \alpha\Omega \mid V \mid \alpha'\Omega\,\rangle_{\mathrm{BF}}\ . \tag{15}$$

However, the orbital angular momentum operator l^2 is not diagonal in the basis. As may be shown from Eqs. (12) and (13), the nonvanishing matrix elements of l^2 are

$$\langle \alpha\Omega JM\pi_t \mid l^2 \mid \alpha\Omega JM\pi_t\,\rangle =J(J+1)+j(j+1)-2\Omega-(-1)^{J-j-l}\lambda_{+}\delta_{\Omega,1/2}\ , \tag{16a}$$

$$\langle \alpha\Omega JM\pi_t \mid l^2 \mid \alpha\Omega+1JM\pi_t\,\rangle = -\lambda_{-}(1+\delta_{\Omega 0})^{1/2}=\langle \alpha\Omega+1JM\pi_t \mid l^2 \mid \alpha\Omega JM\pi_t\,\rangle\ , \tag{16b}$$

where

$$\lambda_{\pm}=[J(J+1)-\Omega(\Omega\pm 1)]^{1/2}[j(j+1)-\Omega(\Omega\pm 1)]^{1/2}\ .$$

[These matrix elements are in agreement with results of Launay[16] except for a fairly obvious error in one of the Kronecker δ functions of his equation (A.8).]

The procedure for finding cross sections in the BF basis $\{\,|\,\alpha\Omega JM\pi_t\,\rangle\}$ is identical to that in the SF basis $\{\,|\,\Phi^{JM}_{\alpha l}\rangle\}$. The sizes of the coupled equations (6) for a specified J are the same; only the coupling is distributed differently. Whereas in the SF basis all the coupling originates in the interaction matrix $\underline{V}^J$, in the BF basis, many more of the off-diagonal elements of $\underline{V}^J$ vanish and the coupling is transferred to the l^2 matrix. The concept of rotational coupling[20] is seen to be meaningful only in BF systems. The $\underline{T}$ matrices in the two systems are related by the transformation $\underline{\xi}^{jJ}$ of Eq. (12):

$$\underline{T}^J=\underline{\xi}^{jJ}\underline{T}^{J\pi_t}(\underline{\xi}^{jJ})^{\dagger}\ , \tag{17}$$

where $\underline{T}^J$ represents the matrix connecting states of total parity $\pi_t = \pi_1 \pi_2 (-1)^l$ in the SF system, with elements $T^J_{\alpha' l', \alpha l}$, and $\underline{T}^{J\pi_t}$ represents that in the BF basis, with elements $T^{J\pi_t}_{\alpha'\Omega', \alpha\Omega}$. The differential cross sections for any transition can be calculated by substituting Eq. (17) into Eq. (10) and then using Eq. (9).

Of course, other unitary transformations besides (17) may be desirable. For example, one might want to diagonalize the interaction matrix $\underline{V}$ at every R. The resulting transformation would then be to the Born-Oppenheimer molecular basis. It would be R dependent so that the radial kinetic energy matrix would generally acquire significant off-diagonal elements and give rise to radial coupling among the adiabatic states.[20] In his calculation of fine-structure transitions in F(^{2}P) due to collisions with protons,[13] Mies used an adiabatic molecular basis but found he could ignore the radial-coupling terms. (See also Sec. VI.)

IV. TOTAL CROSS SECTIONS WHEN ONE SYSTEM IS UNPOLARIZED

Results are greatly simplified when total cross sections are calculated and one system, say, system 2, is unpolarized. First consider the more general total cross sections. By integrating Eq. (9) over scattered directions $\hat{R}$, one obtains the total cross section for a fixed incident direction of relative velocity $\hat{\mathbf{k}}$:

$$\sigma_{\beta' \leftarrow \beta}(\hat{\mathbf{k}}) = \sum_{l', m'} \left| \frac{2\pi}{k_{12}} \sum_{l,m} i^l Y_{l,m}(\hat{\mathbf{k}}) \times T(\beta' l' m' \leftarrow \beta l m) \right|^2 . \quad (18)$$

If one averages over $\hat{\mathbf{k}}$, the total cross section for transitions from sublevel β $[=(a_1 a_2 m_1 m_2)]$ to sublevel β' is obtained under conditions of isotropic collisions:

$$\sigma_{\beta' \leftarrow \beta} = \frac{\pi}{k_{12}^2} \sum_{l,m,l',m'} | T(\beta' l' m' \leftarrow \beta l m) |^2 . \quad (19)$$

Now, if system 2 is unpolarized before collision, we can average Eq. (19) over the initial values m_2. If in addition any polarization of system 2 after collision remains uncorrelated to measurements on system 1, we can also sum over final values m'_2, so that the relevant total cross sections are

$$\sigma_{a'_1 \bar{a}'_2 m'_1 \leftarrow a_1 \bar{a}_2 m_1} = (2j_2+1)^{-1} \sum_{m_2, m'_2} \sigma_{\beta' \leftarrow \beta} , \quad (20)$$

where bars over a_2 and a'_2 indicate that we have averaged over the initial sublevels and summed over the final sublevels of the asymptotic states of system 2.

All such cross sections can be conveniently expressed in terms of the 2^x-multipole relaxation (if $a'_1 = a_1$) or intrasystem transfer (if $a'_1 \neq a_1$) cross sections for system 1, defined by[21]

$$\sigma^{(x)}_{a'_1 \bar{a}'_2 \leftarrow a_1 \bar{a}_2} = \sum_{m_1, m'_1} (-1)^{j'_1 - j_1 - m'_1 + m_1} (2x+1) \times \begin{pmatrix} j'_1 & x & j'_1 \\ -m'_1 & 0 & m_1 \end{pmatrix} \begin{pmatrix} j_1 & x & j_1 \\ -m_1 & 0 & m_1 \end{pmatrix} \times \sigma_{a'_1 \bar{a}'_2 m'_1 \leftarrow a_1 \bar{a}_2 m_1} . \quad (21)$$

One can combine Eqs. (5), (10), and (19)–(21) with some Racah algebra[17] to express the $\sigma^{(x)}_{a'_1 \bar{a}'_2 \leftarrow a_1 \bar{a}_2}$ directly in terms of the SF T-matrix elements:

$$\sigma^{(x)}_{a'_1 \bar{a}'_2 \leftarrow a_1 \bar{a}_2} = \frac{\pi}{k_{12}^2} \sum_{\substack{l,l',J,J' \\ j,j',j'',j'''}} (-1)^s \frac{(2J+1)(2J'+1)}{(2j_2+1)} [(2j+1)(2j'+1)(2j''+1)(2j'''+1)]^{1/2} \times \begin{Bmatrix} j'_1 & j'_1 & x \\ j' & j''' & j'_2 \end{Bmatrix} \begin{Bmatrix} j' & j''' & X \\ J' & J & l' \end{Bmatrix} \begin{Bmatrix} j & j'' & x \\ J' & J & l \end{Bmatrix} \begin{Bmatrix} j_1 & j_1 & x \\ j & j'' & j_2 \end{Bmatrix} T^J_{\alpha' l' \leftarrow \alpha l} T^{J^*}_{\alpha''' l' \leftarrow \alpha'' l} , \quad (22)$$

where $\alpha'' = a_1 a_2 j''$ and $\alpha''' = a'_1 a'_2 j'''$, and where the sign factor is determined by $s = j' - j''' - j + j'' - l' + l + j'_2 - j_2 + j'_1 - j_1$. The transformation to the BF basis, Eq. (12), does not simplify the result further. All sublevel- (or Zeeman-) transition cross sections, Eq. (20), are easily obtained from the multipole cross sections of Eq. (22) by the inverse of Eq. (21):[21]

$$\sigma_{a'_1 \bar{a}'_2 m'_1 \leftarrow a_1 \bar{a}_2 m_1} = (-1)^{j_1 - j'_1 + m_1 - m'_1} \sum_{x\,(\geq 0)} (2x+1) \begin{pmatrix} j'_1 & x & j'_1 \\ -m'_1 & 0 & m_1 \end{pmatrix} \begin{pmatrix} j_1 & x & j_1 \\ -m_1 & 0 & m_1 \end{pmatrix} \sigma^{(x)}_{a'_1 \bar{a}'_2 \leftarrow a_1 \bar{a}_2} , \quad (23)$$

where the sum over multipoles is limited by the 3-j symbols to x less than or equal to the smaller of j_1 and j'_1. The total cross section for transitions $a'_1 a'_2 \leftarrow a_1 a_2$ is found by averaging Eq. (23) over m_1 and summing over m'_1,

$$\sigma_{\bar{a}'_1 \bar{a}'_2 \leftarrow \bar{a}_1 \bar{a}_2} = (2j_1+1)^{-1} \sum_{m_1, m'_1} \sigma_{a'_1 \bar{a}'_2 m'_1 \leftarrow a_1 \bar{a}_2 m_1} = \left[\frac{2j'_1+1}{2j_1+1} \right]^{1/2} \sigma^{(0)}_{a'_1 \bar{a}'_2 \leftarrow a_1 \bar{a}_2} = \frac{\pi^2}{k_{12}^2} \sum_{j',j,J} \frac{(2J+1)}{(2j_1+1)(2j_2+1)} \times \sum_{l',l} | T^J_{\alpha' l', \alpha l} |^2 . \quad (24)$$

From the unitarity of the transformation, Eq. (17), from the SF to the BF basis, we also note

$$\sum_{l',l} | T^{J}_{\alpha' l',\alpha l} |^2 = \sum_{\Omega,\Omega',\pi_t} | T^{J\pi_t}_{\alpha'\Omega',\alpha\Omega} |^2 \; . \tag{25}$$

A similar reduction can be effected in cases of *inter*-system polarization transfer. If one starts with system 1 polarized and system 2 unpolarized, and then measures the polarization of system 2 after collisional interaction, without correlating the results to the final polarization of system 1, the relevant cross sections are

$$\sigma_{\bar{a}'_1 a'_2 m'_2 \leftarrow a_1 \bar{a}_2 m_1} = (2j_2+1)^{-1} \sum_{m'_1 m_2} \sigma_{\beta' \leftarrow \beta} \; . \tag{26}$$

In analogy with Eq. (21), one puts

$$\sigma^{(x)}_{\bar{a}'_1 a'_2 \leftarrow a_1 \bar{a}_2} = \sum_{m_1, m'_2} (-1)^{j'_2 - m'_2 - j_1 + m_1} (2x+1) \times \begin{bmatrix} j'_2 & x & j'_2 \\ -m_2 & 0 & m_2 \end{bmatrix} \begin{bmatrix} j_1 & x & j_1 \\ -m_1 & 0 & m_1 \end{bmatrix} \times \sigma_{\bar{a}'_1 a'_2 m'_2 \leftarrow a_1 \bar{a}_2 m_1} \tag{27}$$

and finds

$$\sigma^{(x)}_{\bar{a}'_1 a'_2 \leftarrow a_1 \bar{a}_2} = \frac{\pi}{k^2_{12}} \sum_{\substack{l,l',J,J' \\ j,j',j'',j'''}} (-1)^{s'} \frac{(2J+1(2J'+1)}{(2j_2+1)} [(2j+1)(2j'+1)(2j''+1)(2j'''+1)]^{1/2} \times \begin{Bmatrix} j'_2 & j'_2 & x \\ j' & j'' & j'_1 \end{Bmatrix} \begin{Bmatrix} j' & j''' & x \\ J' & J & l' \end{Bmatrix} \begin{Bmatrix} j & j'' & x \\ J' & J & l \end{Bmatrix} \begin{Bmatrix} j_1 & j_1 & x \\ j & j'' & j_2 \end{Bmatrix} T^{J}_{\alpha' l',\alpha l} T^{J'*}_{\alpha''' l',\alpha'' l} \tag{28}$$

with $s' = j'' - j + l - l' + j'_1 + j'_2 - j_1 - j_2$.

V. INTERACTION MATRIX ELEMENTS

Use of either the SF or BF formulation above requires the interaction matrix $\underline{V}$ in the appropriate basis. We consider here a spin-free interaction depending on only two internal coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and the separation $\mathbf{R}$ of the center of masses of the interacting systems: $V = V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R})$. This could represent the interaction between a model atom with a single valence electron and rigid-rotor approximation to a diatomic molecule, or between two such atoms or two such molecules. The interaction can be expanded in spherical harmonics. Because of the symmetry of V under rotations of the entire scattering system, the expansion takes the form

$$V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = \sum_{\substack{k_1,k_2,k_3, \\ q_1,q_2,q_3}} A_{k_1 k_2 k_3}(r_1, r_2, R) \begin{bmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & q_3 \end{bmatrix} \times Y_{k_1 q_1}(\hat{\mathbf{r}}_1) Y_{k_2 q_2}(\hat{\mathbf{r}}_2) Y_{k_3 q_3}(\hat{\mathbf{R}}) \; . \tag{29}$$

From the invariance of V with respect to spatial inversion and from the parity $(-1)^k$ of $Y_{kq}(\hat{\mathbf{r}})$, it follows that $A_{k_1 k_2 k_3}$ vanishes unless $k_1 + k_2 + k_3$ is even.

If $\hat{\mathbf{R}} = \hat{\mathbf{z}}$, Eq. (29) can be simplified to

$$V(\mathbf{r}_1, \mathbf{r}_2, R\hat{\mathbf{z}}) = 4\pi \sum_{k_1 k_2 q} v_{k_1 k_2 q}(r_1, r_2, R) \times Y_{k_1 q}(\hat{\mathbf{r}}_1) Y_{k_2 -q}(\hat{\mathbf{r}}_2) \; , \tag{30}$$

which expresses the interaction in terms of the function[22]

$$v_{k_1 k_2 q}(r_1, r_2, R) = \sum_{k_3} (4\pi)^{-3/2} (2k_3+1)^{1/2} \begin{bmatrix} k_1 & k_2 & k_3 \\ q & -q & 0 \end{bmatrix} \times A_{k_1 k_2 k_3}(r_1, r_2, R) \; . \tag{31}$$

By inverting Eq. (31) and substituting for $A_{k_1 k_2 k_3}$ in Eq. (29) we find

$$V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = \sum_{k_1,k_2,k_3,q} (2k_3+1)^{1/2} v_{k_1 k_2 q}(r_1, r_2, R) \times Z^{(q)}_{k_1 k_2 k_3}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}) \; , \tag{32}$$

where q is summed over both positive and negative values and

$$Z^{(q)}_{k_1 k_2 k_3}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}) = (4\pi)^{3/2} \frac{1}{2} \left[\begin{bmatrix} k_1 & k_2 & k_3 \\ q & -q & 0 \end{bmatrix} + \begin{bmatrix} k_1 & k_2 & k_3 \\ -q & q & 0 \end{bmatrix} \right] \times \sum_{q_1,q_2,q_3} \begin{bmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & q_3 \end{bmatrix} Y_{k_1 q_1}(\hat{\mathbf{r}}_1) Y_{k_2 q_2}(\hat{\mathbf{r}}_2) Y_{k_3 q_3}(\hat{\mathbf{R}}) = Z^{(-q)}_{k_1 k_2 k_3}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}) \; . \tag{33}$$

From Eq. (32), the desired matrix elements of V are easily obtained from those for $Z^{(q)}_{k_1k_2k_3}$.

From the definition, Eq. (4), of the basis states $\Phi^{JM}_{\alpha l}$ and assuming $\mathbf{j}_1$ and $\mathbf{j}_2$ have both spin ($\mathbf{S}_i$) and orbital ($\mathbf{L}_i$) parts $\mathbf{j}_i=\mathbf{S}_i+\mathbf{L}_i$ (of course, S_i may be zero), one obtains directly the SF matrix elements

$$\begin{aligned}
\langle \Phi^{J'M'}_{\alpha' l'} \,|\, Z^{(q)}_{k_1k_2k_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{R}}) \,|\, \Phi^{JM}_{\alpha l}\rangle = \tfrac{1}{2}\delta_{S_1S_1'}\delta_{S_2S_2'} & \left[\begin{pmatrix} k_1 & k_2 & k_3 \\ q & -q & 0 \end{pmatrix} + \begin{pmatrix} k_1 & k_2 & k_3 \\ -q & q & 0 \end{pmatrix} \right] \\
& \times [(2k_1+1)(2k_2+1)(2k_3+1)(2j_1+1)(2j_1'+1)(2j_2+1) \\
& \times (2j_2'+1)(2L_1+1)(2L_1'+1)(2L_2+1)(2L_2'+1) \\
& \times (2l+1)(2l'+1)(2j+1)(2j'+1)]^{1/2} \\
& \times \begin{pmatrix} L_1' & k_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_2' & k_2 & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k_3 & l \\ 0 & 0 & 0 \end{pmatrix} \\
& \times \begin{Bmatrix} L_1' & L_1 & k_1 \\ j_1 & j_1' & S_1 \end{Bmatrix} \begin{Bmatrix} L_2' & L_2 & k_2 \\ j_2 & j_2' & S_2 \end{Bmatrix} \Theta_{\mathrm{SF}} ,
\end{aligned} \tag{34}$$

where Θ_{SF} is a sum of products of eight 3-j symbols which with Racah algebra can be reduced to the product of a 6-j with a 9-j symbol,[17]

$$\Theta_{\mathrm{SF}}=(-1)^{j_1+j_2+j-S_1-S_2-J} \begin{Bmatrix} l' & l & k_3 \\ j & j' & J \end{Bmatrix} \begin{Bmatrix} j_1' & j_2' & j' \\ j_1 & j_2 & j \\ k_1 & k_2 & k_3 \end{Bmatrix} \delta_{JJ'}\delta_{MM'} . \tag{35}$$

The matrix elements of V in the BF basis $\{\,|\alpha\Omega JM\pi_t\rangle\}$ can be found either by unitary transformation with ξ^{jJ}, Eqs. (12) and (13), or by applying Eq. (15) directly. Either way, one finds

$$\begin{aligned}
& \langle \alpha'\Omega' J' M' \pi_t' \,|\, Z^{(q)}_{k_1k_2k_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{R}}) \,|\, \alpha\Omega JM\pi_t \rangle \\
& \quad = \tfrac{1}{2}\delta_{S_1S_1'}\delta_{S_2S_2'}\delta_{\Omega\Omega'}\delta_{\pi_t\pi_t'} \left[\begin{pmatrix} k_1 & k_2 & k_3 \\ q & -q & 0 \end{pmatrix} + \begin{pmatrix} k_1 & k_2 & k_3 \\ -q & q & 0 \end{pmatrix} \right] \\
& \qquad \times [(2k_1+1)(2k_2+1)(2k_3+1)(2j_1+1)(2j_1'+1)(2j_2+1)(2j_2'+1)(2L_1+1)(2L_1'+1) \\
& \qquad \times (2L_2+1)(2L_2'+1)(2j+1)(2j'+1)]^{1/2} \\
& \qquad \times \begin{pmatrix} L_1' & k_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_2' & k_2 & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & k_3 & j \\ -\Omega & 0 & \Omega \end{pmatrix} \begin{Bmatrix} L_1' & L_1 & k_1 \\ j_1 & j_1' & S_1 \end{Bmatrix} \begin{Bmatrix} L_2' & L_2 & k_2 \\ j_2 & j_2' & S_2 \end{Bmatrix} \Theta_{\mathrm{BF}} ,
\end{aligned} \tag{36}$$

where

$$\Theta_{\mathrm{BF}}=(-1)^{j_1+j_2+j'+S_1+S_2-\Omega} \times \begin{Bmatrix} j_1' & j_2' & j' \\ j_1 & j_2 & j \\ k_1 & k_2 & k_3 \end{Bmatrix} \delta_{JJ'}\delta_{MM'} . \tag{37}$$

The BF result is in agreement with Launay.[16]

VI. EFFECTIVE INTERACTION METHODS

The complexity of the scattering calculation, together with the fact that it must normally be repeated at many incident energies and J values and that the computation time grows roughly as the cube of the size of the basis, usually means that the number of states employed is much smaller than for a calculation of molecular potential energy surfaces. The resultant restriction of the basis set introduces a truncation error which may be severe if important real or virtual transitions are thereby neglected. The role of *real* transitions is fairly obvious. Various dimension-reducing approximations[11] carefully divide the invariant spaces $\mathscr{E}^{JM\pi_t}$ into subspaces with only weak coupling among them. Thus the j_z-conserving approximation ignores the nonadiabatic coupling between states of different Ω. The role of *virtual* transitions is in determining the energies and characteristics of the adiabatic states. When virtual transitions are ignored, the eigenvalues of the interaction within the truncated basis may deviate substantially from those of the true adiabatic energy surfaces in regions which make a substantial contribution to the transition under investigation.

One approach to the possible loss of *real* transitions is to average the interaction over the m levels of the interacting systems to obtain "effective potentials" in a reduced basis with only one sublevel for each j_1 and j_2.[15] The neglect of *virtual* transitions can also be corrected with the use of an effective interaction. The usual suggestion is to use a truncated basis of adiabatic molecular states as briefly discussed at the end of Sec. III. The interaction $\underline{V}$ is diagonal in such a basis and the coupling arises from off-diagonal terms of the kinetic energy operator. To compute these coupling terms one needs to express the molecular adiabatic states as a linear combination of SF states. The coupling strength will depend on the total energy E and total angular momentum J as well as on the size of the SF basis to which the adiabatic states are referred. To ensure that the interaction Hamiltonian is Hermitian and the S matrix unitary, one generally restricts the SF reference basis to be the same size as the adiabatic basis. The result is to approximate the nonadiabatic coupling and of course to ignore transitions outside the restricted set of adiabatic states, but at least the adiabatic energy surfaces and the resultant adiabatic phase shifts are correct.

A fully equivalent formulation can be carried through in the SF basis by transforming the adiabatic basis, with its accurate energy surfaces, back to the *restricted* SF basis. The kinetic energy matrix is again diagonal so that the coupling occurs only through the interaction matrix. However, this interaction matrix is not the same as $\underline{V}$ in the SF basis. Rather, it is an effective interaction $\underline{V}_{\text{eff}}$ which has the adiabatic potential energies as its eigenvalues. In other words, V_{eff} is the interaction which would have to occur among the restricted set of SF states in order to reproduce from them the accurate adiabatic energies. Although there are generally many effective interactions $\underline{V}_{\text{eff}}$ which have the adiabatic energies as eigenvalues, the procedure of establishing a unitary transformation by renormalization of the projection of the adiabatic states onto the restricted SF basis produces a unique choice.

The same method can of course be applied in the BF basis as well. We also refer to this technique, whether applied to an SF basis or to an R-dependent BF basis, as an "effective interaction method." It has been used previously to calculate fine-structure transitions and depolarization in alkali-metal atoms in collisions with noble gases[12,23] and molecules.[3]

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