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Propensity rules in rotationally inelastic collisions of diatomic molecules in $^3\Sigma$ electronic states

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The formalism for the treatment of rotationally inelastic collisions of molecules in $^3\Sigma$ electronic states is exposed, for the general case of intermediate coupling. The reduced matrix elements of the T operator are expressed in a Hund's case (a) basis. Within the infinite-order-sudden (IOS) limit, the symmetry of the reduced T -matrix elements and the large- J limit of certain vector coupling coefficients can be used to derive several propensity rules bearing on changes in the F_i ($i = 1-3$) label. In particular, for large J only the F_i conserving transitions will have large cross sections. From a physical viewpoint this propensity rule implies that the scattering, at least in the IOS limit at large J , is independent of Σ , the spin projection quantum number. The experimental study by Caughey and Crosley [J. Chem. Phys. **71**, 736 (1979)] of rotational relaxation in the $B^3\Sigma_u^-$ state of S_2 confirms our theoretical propensity rules, although the experimental rate constants for the $F_1 \rightarrow F_2, F_3$ transitions are considerably larger than would be predicted theoretically.

I. INTRODUCTION

In recent years there has been some theoretical interest¹⁻¹¹ in describing rotationally inelastic collisions of diatomic molecules in open-shell electronic states, where the manifold of rotational levels is split by interactions with the other angular momenta of the molecule (spin, electronic orbital). Some experimental work,¹²⁻¹⁷ initially by Crosley and co-workers^{12,13} has indicated that certain transitions between the various symmetry and parity multiplets are more favored than others. Gottscho¹⁸ has discussed this work and developed several simple explanations for the existence of these symmetry propensity rules. In a series of papers we have shown⁷⁻¹⁰ how these rules could be derived from the fully quantum description of the collision dynamics, in particular within the first-order Born¹⁹ and infinite order sudden²⁰⁻²³ (IOS) or energy sudden²³⁻²⁷ limits. In these papers,⁷⁻¹⁰ we have discussed principally molecules in electronic states ($^2\Sigma$, $^1\Pi$, $^2\Pi$) in which the rotational levels are split into doublets,²⁸ which are designated spectroscopically as e or f .²⁹ The propensity rules we have developed⁷⁻¹⁰ imply that collision induced transitions which conserve e/f symmetry will be strongly favored, in agreement with the experimental findings.¹²⁻¹⁷

In this paper we extend our theoretical analysis to collisions of molecules in $^3\Sigma$ electronic states, in which there exist three levels for each total angular momentum,²⁸ two of which have the same e/f symmetry.²⁹⁻³¹ An additional complication is that for many $^3\Sigma$ states the molecular wave functions lie intermediate between Hund's case (a) and case (b). In our previous work⁷⁻¹⁰ only pure case (a) or pure case (b) wave functions were considered.

The organization of this paper is as follows: In the next section we discuss the rotational wave functions of a $^3\Sigma$ molecule. Then we review the quantum formulation of the collision dynamics, using the irreducible

tensor expansion first introduced by Grawert³² into the field of atomic collisions and which Alexander and Davis have recently applied^{10,33} to collisions of open-shell diatomics. Explicit expressions for the important reduced T -matrix elements^{10,33,34} appropriate to a $^3\Sigma$ molecule in an intermediate coupling limit are derived within the IOS limit. In Sec. IV several collisional propensity rules are derived, both for degeneracy averaged and M -state resolved cross sections. In the former case we base our development on semiclassical expressions for the key vector coupling coefficients,³⁵⁻³⁸ rather than on the asymptotic expressions³⁹ used previously.^{7,8} These semiclassical expressions are discussed in the Appendix to the present paper. In Sec. V the derived propensity rules are compared with the experimental cross sections for rotational energy transfer in the $B^3\Sigma_u^-$ state of S_2 , reported by Caughey and Crosley,¹³ and are related to the previous qualitative discussions by these authors and by Gottscho.¹⁸ A brief conclusion follows.

II. $^3\Sigma$ WAVE FUNCTIONS

In a Hund's case (a) basis the wave function for a diatomic molecule in a $^3\Sigma_\Omega$ electronic state can be written as^{30,31,40}

$$|JM\Omega v\Sigma\rangle = |JM\Omega\rangle |v\Sigma\rangle, \quad (1)$$

where J denotes the total angular momentum with projection along space- and body-fixed axes of M and Ω , respectively; S and Σ denote the spin angular momentum and its body-fixed projection, respectively; and v is the vibrational quantum number. With no loss of generality we shall restrict ourselves to collisions which are vibrationally elastic, so that the v index can be suppressed for simplicity. In addition, S , which equals one, will be suppressed. The rotational wave functions $|JM\Omega\rangle$ are proportional to rotation matrix elements.³⁹⁻⁴¹

For a $^3\Sigma$ molecule the index Ω can equal 0 or ± 1 . In the latter case it is convenient to use the definite parity states defined by

$$|JM1\epsilon\rangle = 2^{-1/2} [|JM, \Omega = 1\rangle | \Sigma = 1\rangle + \epsilon |JM, \Omega = -1\rangle | \Sigma = -1\rangle], \quad (2)$$

where the index ϵ can take on the values ± 1 and has been denoted previously by Alexander^{7,8} as a "parity index". The total parity of the $|JM1\epsilon\rangle$ functions is given by⁴¹

$$i|JM1\epsilon\rangle = \epsilon(-1)^{J-1+s}|JM1\epsilon\rangle, \quad (3)$$

where $s = 1$ for Σ^- states and $s = 0$ for Σ^+ states. The parity of the $\Omega = 0$ states is given by

$$i|JM0\rangle = (-1)^{J-1+s}|JM0\rangle. \quad (4)$$

In contemporary spectroscopic notation²⁹ the $\Omega = 0$ and $\Omega = 1, \epsilon = 1$ levels are labeled f for Σ^+ states and e for Σ^- states; the $\Omega = 1, \epsilon = -1$ levels are labeled e for Σ^+ states and f for Σ^- states.

The $\Omega = 0$ and $\Omega = 1, \epsilon = 1$ levels are mixed by the nuclear rotation and spin-rotation terms in the molecular Hamiltonian.^{30,31} The resulting two levels are designated F_1 and F_3 and in the case (b) limit can be labeled by the value of N , the nuclear rotational angular momentum,^{28,30,31} where $N = J - 1$ for the F_1 levels and $N = J + 1$ for the F_3 levels. The wave functions can be written as^{31,42}

TABLE I. Expansion coefficients of $|JMF_i\rangle$ states of a $^3\Sigma$ molecule in terms of Hund's case (a), definite parity states.^a

F_i	$C_{JF_i}^{\Omega\epsilon}$		
	$\Omega = 1, \epsilon = 1$	$\Omega = 1, \epsilon = -1$	$\Omega = 0, \epsilon = 1$
F_1	$\sin \theta_J$	0	$\cos \theta_J$
F_2	0	1	0
F_3	$\cos \theta_J$	0	$-\sin \theta_J$

^aSee Eq. (7); for a discussion of the angle θ_J see the text immediately following Eqs. (5) and (6).

$$|JMF_1\rangle = \sin \theta_J |JM1, \epsilon = 1\rangle + \cos \theta_J |JM0\rangle \quad (5)$$

and

$$|JMF_3\rangle = \cos \theta_J |JM1, \epsilon = 1\rangle - \sin \theta_J |JM0\rangle, \quad (6)$$

where θ_J is an angle ranging from 0 to $\pi/2$ whose value depends on the magnitude of J , and of the rotational constant B , the spin-rotation constant γ , and the spin-spin constant λ . If the latter is much larger in magnitude than $(B - \frac{1}{2}\gamma)[J(J+1)]^{1/2}$ then θ_J approaches 0 if λ is positive or $\pi/2$ if λ is negative. The F_1 and F_3 wave functions then become equal to the pure case (a) states. On the other hand, if $(B - \frac{1}{2}\gamma)[J(J+1)]^{1/2}$ is much greater than $|\lambda|$, then θ_J approaches $\pi/4$ and the F_1 and F_3 wave functions become equal to pure case (b) states, with equal mixing of the $\Omega = 0$ and $\Omega = 1, \epsilon = 1$ states at high J .

The $\Omega = 1, \epsilon = -1$ levels are not mixed with either of the other two levels and are designated F_2 levels, with $N = J$ in the case (b) limit.^{30,31} Figure 1 presents the energies of the lowest rotational levels for two $^3\Sigma$ states, the $X^3\Sigma_g^- v = 0$ state of O_2 and the $B^3\Sigma_u^- v = 4$ state of S_2 . These were chosen as representative of the case (b) and (a) limits, respectively.

For the purposes of the development in the succeeding sections it will be convenient to summarize the preceding paragraphs in the following expression:

$$|JMF_i\rangle = \sum_{\Omega=0}^1 \sum_{\epsilon=-1}^{+1} C_{JF_i}^{\Omega\epsilon} |JM\Omega\epsilon\rangle, \quad (7)$$

where the values of the coefficients are given in Table I and where only the $\epsilon = +1$ index contributes for $\Omega = 0$.

In the particular case of a homonuclear diatomic, the e and f levels, for a given J , are associated with nuclear spin states of opposite inversion symmetry, which will not be interconverted by collisions unless the interaction potential contains nuclear spin dependent terms.

III. COLLISION DYNAMICS

The collision of a molecule in a particular $|JMF_i\rangle$ state with a structureless target is usually treated by expanding the overall wave function in eigenfunctions of the total angular momentum \mathcal{J} , namely^{4,7,8,11}

$$|JLF_i\mathcal{J}\mathcal{M}\rangle = \sum_{MM_L} (JMLM_L | \mathcal{J}\mathcal{M} \rangle | LM_L \rangle | JMF_i \rangle. \quad (8)$$

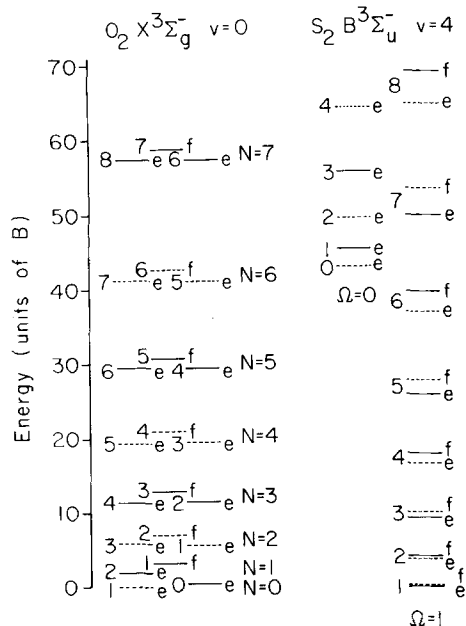


FIG. 1. Rotational energy levels of two $^3\Sigma$ states: $X^3\Sigma_g^- v = 0$ of O_2 and $B^3\Sigma_u^- v = 4$ of S_2 . Spectroscopic constants taken from K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979). The total angular momentum J is indicated at the left of each level. The zero of energy is at the lowest rotational level. The e/f parity designation (Ref. 29) as given for each state. Because of nuclear spin statistics, the dashed levels are absent in $^{16}O_2$ and $^{32}S_2$. The B state of S_2 is perturbed so that the actual level positions may be shifted somewhat from those plotted.

Here $(\dots | \dots)$ is a Clebsch-Gordan coefficient,³⁹ \mathfrak{M} is the projection of \mathcal{J} along the space-fixed z axis, L is the relative orbital angular momentum quantum number, and $|LM_L\rangle$ is the wave function for the angular motion of the structureless particle. The radial expansion coefficients of the $|JMF_i\rangle$ functions are solutions to the so-called close-coupled (CC) equations.^{4,7,8,11,43} The asymptotic behavior of these coefficients defines the S matrix, indexed in \mathcal{J} and in the indices of the initial and final rotational states. The T -matrix is defined as $T = 1 - S$.

The scattering amplitude for a transition from the $|JMF_i\rangle$ state to the $|J'M'F'_i\rangle$ state is given by¹⁰

$$f_{JMF_i \rightarrow J'M'F'_i} = (-1)^{-J-M} \sum_{KQ} (2K+1)^{1/2} (-1)^{K-Q} \times \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix} f_{JF_i, J'F'_i}^{KQ}, \quad (9)$$

where (\dots) is a $3j$ symbol³⁹ and^{9,33}

$$f_{JF_i, J'F'_i}^{KQ} = 2\pi(2K+1)^{1/2} \sum_{L'M'_L} i^{L-L'} (-1)^{M_L} Y_{L'M'_L}^*(\hat{R}') Y_{L'M'_L}(\hat{R}) \times \begin{pmatrix} L & L' & K \\ M_L & -M'_L & -Q \end{pmatrix} (J' L' F'_i | T_K | J L F_i). \quad (10)$$

Here \hat{R} describes the scattering in the collision frame, with z axis along the initial relative velocity vector \mathbf{v}_{rel} ; and \hat{R}' describes the orientation of the collision frame with respect to an external z axis to which the M and M' quantum numbers refer. In Eq. (10) the reduced matrix element of the T operator is defined by³⁴

$$(J' L' F'_i | T_K | J L F_i) = (-1)^{-J-L'} (2K+1) \sum_{\mathcal{J}} (-1)^{-\mathcal{J}} (2\mathcal{J}+1) \begin{Bmatrix} L' & J' & \mathcal{J} \\ J & L & K \end{Bmatrix} \times T_{JLF_i, J'L'F'_i}^{\mathcal{J}}, \quad (11)$$

where $\{\dots\}$ is a $6j$ symbol³⁹ and $T_{JLF_i, J'L'F'_i}^{\mathcal{J}}$ is a matrix element of the T operator in the $|JLF_i\rangle$ basis.

If one squares Eq. (9), integrates over \hat{R} , and averages over all possible values of \hat{R}' , then one obtains, exactly as in our previous papers,^{10,33} an expression for the integral M -state resolved cross section appropriate to collision cell experiments, where the distribution of relative velocity vectors is isotropic with respect to the axis of quantization. We find

$$\sigma_{JMF_i \rightarrow J'M'F'_i} = \frac{\pi}{k_{JF_i}^2} \sum_{KQ} \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2 P_{JF_i, J'F'_i}^K, \quad (12)$$

where k_{JF_i} is the wave vector in the initial channel and the tensor opacity $P_{JF_i, J'F'_i}^K$ is defined by^{10,33}

$$P_{JF_i, J'F'_i}^K = \frac{1}{2K+1} \sum_{L'L'} |(J' L' F'_i | T_K | J L F_i)|^2. \quad (13)$$

Independent of the choice of quantization axis the degeneracy-averaged integral cross section is given by the expression

$$\sigma_{JF_i \rightarrow J'F'_i} = \frac{\pi}{(2J+1)k_{JF_i}^2} \sum_K P_{JF_i, J'F'_i}^K. \quad (14)$$

As discussed in Sec. II the $|JMF_i\rangle$ states of a $^3\Sigma$ molecule can be expressed as a linear combination of the Hund's case (a), definite parity states [Eq. (7)]. Thus we can write the crucial reduced matrix elements [Eq. (11)] as

$$(J' L' F'_i | T_K | J L F_i) = \sum_{\Omega\Omega'} \sum_{\epsilon\epsilon'} C_{JF_i}^{\Omega\epsilon} C_{J'F'_i}^{\Omega'\epsilon'} (J' L' \Omega' \epsilon' | T_K | J L \Omega \epsilon), \quad (15)$$

where the reduced T -matrix elements on the right-hand side refer to the pure case (a) electronic states. If the intermolecular potential does not contain any spin-dependent terms, which is usually the case, then the spin projection quantum number Σ must be conserved. Thus, from the discussion in Sec. II, $\Omega = 0 \rightarrow 1$ transitions will not occur, so that Eq. (15) can be simplified to

$$(J' L' F'_i | T_K | J L F_i) = \sum_{\Omega\Omega'} C_{JF_i}^{1\Omega} C_{J'F'_i}^{1\Omega'} \times (J' L', \Omega = 1, \epsilon' | T_K | J L, \Omega = 1, \epsilon) + C_{JF_i}^{01} C_{J'F'_i}^{01} (J' L', \Omega = 0 | T_K | J L, \Omega = 0). \quad (16)$$

Alexander and Davis have shown¹⁰ how the case (a) reduced T -matrix elements can be written within the infinite-order-sudden (IOS) limit²⁰⁻²³ as

$$(J' L' \Omega \epsilon' | T_K | J L \Omega \epsilon) = (-1)^{J'-\Omega} [(2J+1)(2J'+1)]^{1/2} \times F_{J\Omega\epsilon, J'\Omega\epsilon'}^K R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^K, \quad (17)$$

where

$$F_{J\Omega\epsilon, J'\Omega\epsilon'}^K = \frac{1}{2} [1 + \epsilon\epsilon' (-1)^{J+J'+K+2\Omega}]. \quad (18)$$

Here^{10,44}

$$R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^K = -i^{L+L'-2\bar{L}} (-1)^{-L'} [(2L+1)(2L'+1)]^{1/2} \times \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & K & J \\ -\Omega & 0 & \Omega \end{pmatrix} S_{\bar{K}}^{\bar{L}}, \quad (19)$$

where $S_{\bar{K}}^{\bar{L}}$ is a coefficient arising from the expansion of the fixed-orientation S function. The index \bar{L} designates the orbital angular momentum which appears in the fixed-orientation scattering problem and is a function of L and L' . For the purposes of the present paper it will not be necessary to specify the exact form of this function.

Equations (16)–(19) imply that the reduced T -matrix elements for collisions of a $^3\Sigma$ molecule can be written in the IOS limit as

$$(J' L' F'_i | T_K^{\text{IOS}} | J L F_i) = i^{L+L'-2\bar{L}} (-1)^{J'-L'} [(2J+1)(2J'+1) \times (2L+1)(2L'+1)]^{1/2} \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} [\mathfrak{B}_{JF_i, J'F'_i}^K + \mathfrak{C}_{JF_i, J'F'_i}^K + \mathfrak{D}_{JF_i, J'F'_i}^K] S_{\bar{K}}^{\bar{L}}. \quad (20)$$

Here

$$\mathfrak{B}_{JF_i, J'F'_i}^K = \frac{1}{2} [1 + (-1)^{J+J'+K}] \begin{pmatrix} J' & K & J \\ -1 & 0 & 1 \end{pmatrix} B_{JF_i, J'F'_i}, \quad (21)$$

$$\mathfrak{C}_{JF_i, J'F'_i}^K = \frac{1}{2} [1 - (-1)^{J+J'+K}] \begin{pmatrix} J' & K & J \\ -1 & 0 & 1 \end{pmatrix} C_{JF_i, J'F'_i}, \quad (22)$$

TABLE II. Values of expansion coefficients for reduced T -matrix elements: intermediate coupling.^a

	F'_1	F'_2	F'_3
	$B_{JF_i, J'F'_i}$		
F_1	$\sin \theta_J \sin \theta_{J'}$	0	$\sin \theta_J \cos \theta_{J'}$
F_2	0	1	0
F_3	$\cos \theta_J \sin \theta_{J'}$	0	$\cos \theta_J \cos \theta_{J'}$
	$C_{JF_i, J'F'_i}$		
F_1	0	$\sin \theta_J$	0
F_2	$\sin \theta_J$	0	$\cos \theta_J$
F_3	0	$\cos \theta_J$	0
	$D_{JF_i, J'F'_i}$		
F_1	$-\cos \theta_J \cos \theta_{J'}$	0	$\cos \theta_J \sin \theta_{J'}$
F_2	0	0	0
F_3	$\sin \theta_J \cos \theta_{J'}$	0	$-\sin \theta_J \sin \theta_{J'}$

^aSee Eqs. (21)–(23).

and

$$D_{JF_i, J'F'_i}^K = \begin{pmatrix} J' & K & J \\ 0 & 0 & 0 \end{pmatrix} D_{JF_i, J'F'_i}, \quad (23)$$

and the coefficients $B_{JF_i, J'F'_i}$, $C_{JF_i, J'F'_i}$, and $D_{JF_i, J'F'_i}$ are listed in Table II for the general situation of intermediate coupling.

IV. PROPENSITY RULES

The propensity rules we have previously derived^{7,8,10} for collision induced transitions between various symmetry doublets are all based on the properties of the $3j$ symbols which appear in the expressions for the inelastic cross sections, similar to Eqs. (9), (12), and (21)–(23). We shall now carry out a similar analysis for collisions of $^3\Sigma$ molecules.

From Table II we observe that only the $C_{JF_i, J'F'_i}$ coefficients lead to coupling between the F_2 levels and the F_1 or F_3 levels. This fact, taken together with the phase factor in Eq. (22), implies that only tensor orders for which $(J + J' + K)$ is odd will contribute to $F_2 - F_1$, F_3 transitions. For transitions in which $M = M' = 0$, the $3j$ symbol in Eq. (9) vanishes unless the same $(J + J' + K)$ factor is even. Thus, the $M = 0 - M' = 0$ transition will be forbidden for $F_2 - F_1$, F_3 processes, at least within the IOS limit. In an earlier paper Davis and Alexander⁹ derived an identical selection rule for $^3\Sigma$ molecules within the case (b) limit and for quantization along \mathbf{v}_{rel} . The derivation was completely general, independent of any dynamical limit. We see here that within the IOS limit, the $M = 0 - M' = 0$ selection rule applies to all possible choices of quantization axis, and, consequently to laboratory quantization in a collision cell experiment.

Davis and Alexander discussed⁹ how a similar $M = 0 - M' = 0$ selection rule in a $^1\Pi$ electronic state could be experimentally verified by an optical-optical double resonance experiment similar to that performed by

Silvers, Gottscho, and Field.⁴⁵ Equivalent experiments could be carried out on a $^3\Sigma$ molecule. This would involve pumping, with a plane-polarized laser, into the $J = 1$, F_1 or $J = 1$, F_3 level in an electronically excited state from $J = 0$ of another electronic state. Only the $M = 0$ projection levels would be populated. Collisions could transfer population to the neighboring $J' = 1$, F_2 level, but, because of the selection rule derived in the preceding paragraph, only the $M' = \pm 1$ projection levels would be populated. This nonisotropic M -level distribution in the final state could be easily seen by probing with a second plane-polarized laser⁹ or by polarized fluorescence detection.⁴⁶

A similar selection rule applies to transitions out of the $J = 0$ level. For this particular value of the total angular momentum only the F_3 or F_1 level exists, depending on whether λ is positive or negative, respectively. Coupling to the other levels occurs only through the $D_{JF_i, J'F'_i}$ coefficients, since the $3j$ symbols in Eq. (21) and (22) vanish for $J = 0$. But from Table II we see that D coefficients vanish for $F_3 - F_2$ transitions. Thus collisions will not transfer population from the unique $J = 0$ level of a $^3\Sigma$ state to any of the F_2 rotational levels.

In several previous papers Alexander^{7,8,47} has derived a class of symmetry selection rules by examining the asymptotic behavior of $3j$ symbols similar to those which appear in Eqs. (21)–(23). We shall carry out a similar analysis here, but making use of more general semiclassical expressions for the $3j$ symbols, which are derived in the Appendix. In particular, for $J, J' > K > 1$ we have, for $(J + K + J')$ even,

$$\begin{pmatrix} J' & K & J \\ 0 & 0 & 0 \end{pmatrix} \approx (-1)^{G/2} [\pi j j' \Delta (JKJ')]^{-1/2} \quad (24)$$

and

$$\begin{pmatrix} J' & K & J \\ -1 & 0 & 1 \end{pmatrix} \approx -(-1)^{G/2} (\pi j j' \Delta)^{-1/2} (1 - \frac{1}{2} \Delta^2), \quad (25)$$

and, for $(J + K + J')$ odd,

$$\begin{pmatrix} J' & K & J \\ -1 & 0 & 1 \end{pmatrix} \approx -(-1)^{(G-1)/2} (\pi j j' \Delta)^{-1/2} \Delta, \quad (26)$$

where $j = J + \frac{1}{2}$, $j' = J' + \frac{1}{2}$, $G = (J + J' + K)$, and

$$\Delta^2 (JKJ') = [(K + \frac{1}{2})^2 - (J - J')^2] / j j'. \quad (27)$$

This limit ($J, J' > K > 1$) will usually apply at large J, J' since the S_K^L coefficients [Eq. (19)] are usually largest for small K . In this limit the reduced T -matrix elements will be given by, for $(J + J' + K)$ even,

$$\lim_{J, J' > K > 1} \langle J' L' F'_i | | T_K | | J L F_i \rangle = i^{L+L'-2L} (-1)^{J'-L'} \times [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \times (-1)^{G/2} (\pi j j' \Delta)^{-1/2} [E_{JF_i, J'F'_i} - \frac{1}{2} \Delta^2 B_{JF_i, J'F'_i}] S_K^L, \quad (28)$$

and, for $(J + J' + K)$ odd,

$$\lim_{J, J' > K > 1} \langle J' L' F'_i | | T_K | | J L F_i \rangle = i^{L+L'-2L} (-1)^{J'-L'}$$

TABLE III. Values of expansion coefficients $E_{JF_i, J'F'_i}$ [Eq. (28)] for reduced T -matrix elements in large J limit.

	F'_1	F'_2	F'_3
F_1	$\cos(\theta_J - \theta_{J'})$	0	$\sin(\theta_J - \theta_{J'})$
F_2	0	1	0
F_3	$-\sin(\theta_J - \theta_{J'})$	0	$\cos(\theta_J - \theta_{J'})$
$\theta_J \approx \theta_{J'}$			
F_1	$1 - \frac{1}{2}(\theta_J - \theta_{J'})^2$	0	$(\theta_J - \theta_{J'})$
F_2	0	1	0
F_3	$-(\theta_J - \theta_{J'})$	0	$1 - \frac{1}{2}(\theta_J - \theta_{J'})^2$

$$\begin{aligned} & \times [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \\ & \times (-1)^{(G-1)/2} (\pi j j')^{-1/2} \Delta C_{JF_i, J'F'_i} S_K^L, \end{aligned} \quad (29)$$

where the $E_{JF_i, J'F'_i}$ coefficients are given in Table III. If the angle θ_J , which corresponds, as we have seen in Sec. II, to the relative mixing of the $\Omega = 1$, $\epsilon = 1$, and $\Omega = 0$ case (a) wave functions in the F_1 and F_3 wave functions, is not greatly changed between the initial and final rotational states, then the $E_{JF_i, J'F'_i}$ coefficients can be further simplified, as shown also in Table III.

The quantity $\Delta(JKJ')$ [Eq. (27)] is typically a small number and goes to zero as $J, J' \gg K$. In this limit we see from Eqs. (28) and (29) and from Table III, that out of the nine-possible $F_i - F'_i$ transitions only the three " F_i -conserving" ($F'_i = F_i$) transitions will have large reduced T -matrix elements and, consequently, large cross sections. The magnitude of the reduced T -matrix element for the $F_2 - F_2$ transition will be only slightly larger than those for the $F_1 - F_1$ and $F_3 - F_3$ transitions, themselves equal. For the weaker, F_i -changing transitions ($F_i - F_j$ with $j \neq i$) the reduced T -matrix elements will vary as

$$(\theta_J - \theta_{J'}) - \frac{1}{2}\Delta^2 \sin \theta_J \cos \theta_{J'}, \quad F_1 - F_3, \quad (30)$$

$$\Delta \sin \theta_J, \quad F_1 - F_2, \quad (31)$$

$$\Delta \cos \theta_J, \quad F_3 - F_2. \quad (32)$$

We point out that this derivation of a propensity toward conservation of the F_i quantum number does not depend on a particular choice of θ_J , so it will be equally valid for all $^3\Sigma$ electronic states, regardless of the degree of intermediate coupling between Hund's case (a) and case (b). We see from Eqs. (30)–(32) that if $\theta_J \approx \theta_{J'}$, then, since $\Delta < 1$, the reduced T -matrix elements for $F_1 - F_3$ transitions can be smaller than those for F_1 , $F_3 - F_2$ transitions. Since both the F_1 and F_3 levels have the same e or f labels (see Sec. II), while the F_2 levels have the opposite symmetry label, the conclusion in the preceding sentence implies that cross sections for the e/f conserving $F_1 - F_3$ transitions can be smaller than those for the e/f changing F_1 , $F_3 - F_2$ transitions, contrary, perhaps, to an intuitive prediction.

Because the propensity for conservation of the F_i label, as derived above, is present in the reduced T -matrix elements, it will also, because of Eqs. (9) and (10), be present in the differential M dependent cross sections, regardless of the orientation of the collision frame with respect to the quantization axis. Consequently, the propensity rule will also apply to M dependent integral cross sections [Eq. (12)] and, also, to the degeneracy averaged integral cross sections. At the beginning of this section we demonstrated that the $M = 0 \rightarrow M' = 0$ transition will be forbidden for $F_2 - F_1(F_3)$ processes, for all values of J and J' . We see here that at large J , J' all the $JMF_i \rightarrow J'M'F'_i$ transitions will become forbidden for $F'_i \neq F_i$, regardless of the initial and final M quantum numbers.

As derived in the preceding paragraphs the propensity against $F_1 - F_3$ transitions is strictly valid for large J, J' . In the case (a) coupling limit (Sec. II) this propensity will extend to all values of J , since the $B_{JF_i, J'F'_i}$, $C_{JF_i, J'F'_i}$, and $D_{JF_i, J'F'_i}$ coefficients (Table II), all vanish for $F_1 - F_3$ transitions when $\theta_J = 0$ or $\theta_J = \pi/2$, which defines the two case (a) limits.

In the case of a homonuclear diatomic the scattering, in the fixed-orientation IOS model, will be unchanged under a rotation of the molecule by 180° , so that only even terms will occur in the expansion of the IOS S function. From Eqs. (21)–(23) and Table II, we see that $F_i - F_j$ transitions for $i = 1, 3$ and $j = 2$ will occur only if $(-1)^J = -(-1)^{J'}$, and, for $i, j = 1, 3$ will occur only if $(-1)^J = (-1)^{J'}$. This, of course, is just the rigorous selection rule for conservation of nuclear spin state, discussed in Sec. II.

The physical origin of the $F_i - F_i$ propensity rule can be understood by examination of the matrix elements of the atom-molecule potential in an unsymmetrized case (a) basis [Eq. (1)]. Since the electronic wave function of a Σ electronic state is cylindrically symmetric, these potential matrix elements can be written in the total \mathcal{J} basis as

$$\begin{aligned} \langle J' L' \Omega' \mathcal{J} \mathcal{M} | V | J L \Omega \mathcal{J} \mathcal{M} \rangle &= \delta_{\Omega \Omega'} (-1)^{J+J'+\mathcal{J}-\Omega} [(2J+1)(2J'+1) \\ &\times (2L+1)(2L'+1)]^{1/2} \sum_l \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & \mathcal{J} \\ L' & J' & l \end{Bmatrix} \\ &\times \begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix} A_l(R), \end{aligned} \quad (33)$$

where $A_l(R)$ arises from the standard expansion^{43,48} of the potential in Legendre polynomials. Equation (33) has been derived by Alexander,⁷ for collisions of molecules in $^2\Sigma^+$ electronic states, by Dixon and Field,⁴ and recently by Corey and McCourt,¹¹ for the general case of a molecule in a $^{2S+1}\Sigma$ electronic state.

The restriction that $\Omega' = \Omega$ in Eq. (33) arises because a purely electrostatic potential cannot lead to changes in the spin projection quantum number Σ . The only dependence on Ω occurs in the phase factor and in the $3j$ symbol. For $(J' + l + J)$ even, the symmetry of this $3j$ symbol implies that the matrix elements will be independent of the sign of Ω , and, for large $J(J, J' > l)$, Eqs. (24) and (25) imply that the matrix elements will become

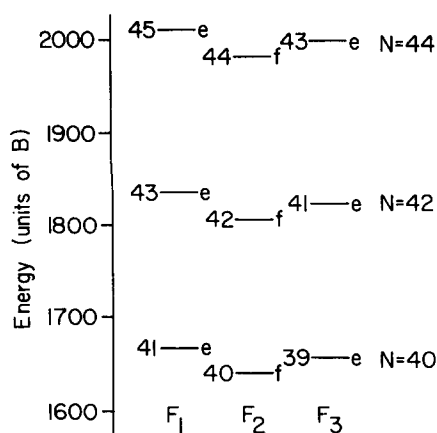


FIG. 2. Rotational energy levels of the $B^3\Sigma_u^- v=4$ state of S_2 near $J=41, F_1$ ($N=40$). The zero of energy is at the largest rotational level (Fig. 1).

independent of the magnitude of Ω . For $(J' + l' + J)$ odd, the matrix elements will become vanishingly small, from Eq. (26). Thus no changes in $\Sigma(\Omega)$ will occur, and, at high J , the scattering will be independent of Σ .

Because of the restriction that Σ remain unchanged, the collisional coupling between the F_2 and F_1 or F_3 levels will occur through the $\Omega = 1$ terms in the F_1 and F_3 wave functions. However, because the $\Sigma = 1$ and $\Sigma = -1$ terms occur equally with the same sign in the F_1 and F_3 wave functions [Eq. (2) with $\epsilon = +1$], but with opposite sign in the F_2 wave functions ($\epsilon = -1$), the collisional $F_2 \rightarrow F_1, F_3$ coupling will vanish at high J , since the scattering is independent of the sign of Σ . Because the F_1 and F_3 wave functions are orthonormal mixtures of the $\Omega = 1, \epsilon = 1$, and $\Omega = 0$ case (a) states [Eqs. (5) and (6)], the collisional coupling between these two levels will also vanish at high J , since the scattering is independent of the magnitude of $\Sigma(\Omega)$.

V. COMPARISON WITH EXPERIMENT

Caughey and Crosley^{13,49} have investigated collisional energy transfer in the $B^3\Sigma_u^-$ excited state of S_2 . Transitions between the initial rotational state $J = 41, F_1$ ($N = 40$)⁵⁰ of the $v = 4$ vibrational level excited by radiation from an atomic Zn lamp, and a number of nearby rota-

tional levels were studied for collisions with several rare gas scattering partners.¹³ The state-to-state rate constants were obtained by observations of the spectrally resolved fluorescence as a function of scattering gas pressure. To our knowledge, this work represents the only state-resolved study of rotational transfer in a $^3\Sigma$ state. Figure 2 presents the energies of rotational levels near the initially excited level. It can be seen that $S_2 B^3\Sigma_u^-$ is approaching the case (b) limit at these values of J .

An interesting analysis of the experiments of Caughey and Crosley¹³ can be carried out using Eqs. (13), (14), and (20) to write the degeneracy averaged cross section for the $JF_i \rightarrow J'F'_i$ transition as

$$\sigma_{JF_i \rightarrow J'F'_i} = \frac{\pi}{(2J+1)k_{JF_i}^2} \sum_K A_{JF_i, J'F'_i}^K G^K, \quad (34)$$

where

$$G^K = \sum_{LL'} (2L+1)(2L'+1) \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix}^2 |S_K^{\bar{L}}|^2, \quad (35)$$

and

$$A_{JF_i, J'F'_i}^K = \frac{(2J+1)(2J'+1)}{(2K+1)} \times [\mathcal{Q}_{JF_i, J'F'_i}^K + \mathcal{C}_{JF_i, J'F'_i}^K + \mathcal{D}_{JF_i, J'F'_i}^K]^2, \quad (36)$$

with the quantities on the right-hand side of Eq. (36) defined by Eqs. (21)–(23) and Table II. Consider now transitions out of the $J = 41, F_1$ ($N = 40$) level into the fine structure levels of the $N' = 40, 42, 44$ manifolds of $S_2 B^3\Sigma_u^-$. Because this molecule is homonuclear, as discussed in Sec. IV, only even values of the tensor order K will contribute, with $K \geq |J' - J|$. For the $F_1 \rightarrow F_3$ transition with $J' = J$, the $K = 0$ term cancels identically since $\mathcal{Q}_{JF_1, JF_3}^0 = -\mathcal{D}_{JF_1, JF_3}^0$. Explicit evaluation of the $3j$ symbols in Eq. (21)–(23) and the mixing parameters θ_J and $\theta_{J'}$ appropriate to the $v = 4$ manifold of $B^3\Sigma_u^-$ yield the values of the $A_{JF_i, J'F'_i}^K$ coefficients listed in Table IV.

Since the G^K terms are independent of J, F_i, J' , and F'_i , the relative sizes of the degeneracy averaged cross sections will be roughly proportional to the relative sizes of the $A_{JF_i, J'F'_i}^K$ coefficients. Thus, from Table

TABLE IV. Expansion coefficients $A_{JF_i, J'F'_i}^K$ [Eq. (36)] for transitions out of the $J = 41, F_1$ ($N = 40$) level of the $S_2 B^3\Sigma_u^- v = 4$ manifold.

$J'F'_i$	$A_{JF_i, J'F'_i}^K$			
	$K=2$	4	6	8
$J' = 40, F_2(N' = 40)$	9.49×10^{-3}	9.88×10^{-3}	9.96×10^{-3}	9.97×10^{-3}
$J' = 39, F_3(N' = 40)$	3.39×10^{-4}	1.27×10^{-4}	1.03×10^{-4}	1.06×10^{-4}
$J' = 43, F_1(N' = 42)$	6.37	1.47	0.663	0.377
$J' = 42, F_2(N' = 42)$	9.27×10^{-3}	9.65×10^{-3}	9.72×10^{-3}	9.74×10^{-3}
$J' = 41, F_3(N' = 42)$	2.87×10^{-6}	9.98×10^{-6}	2.12×10^{-5}	3.66×10^{-5}
$J' = 45, F_1(N' = 44)$... ^a	2.64	0.817	0.426
$J' = 44, F_2(N' = 44)$... ^a	7.34×10^{-3}	8.56×10^{-3}	8.98×10^{-3}
$J' = 43, F_3(N' = 44)$	2.55×10^{-4}	2.94×10^{-5}	1.57×10^{-6}	2.37×10^{-6}

^aThere is no $K=2$ term for transitions with $\Delta J > 2$.

TABLE V. Experimental cross sections for transitions out of the $J=41$, $F_1(N=40)$ level of the $v=4$ manifold of $S_2 B^3\Sigma_u^-$.^a

$J' F'_i$	$\sigma_{J=41, F_1 \rightarrow J' F'_i} (\text{\AA}^2)$		
	He ^b	Ar ^b	Xe ^b
$J' = 40, F_2(N' = 40)$	0.6 ± 0.6
$J' = 39, F_3(N' = 40)$	1.2 ± 0.7	2.0 ± 1.0	1.0 ± 0.5
$J' = 43, F_1(N' = 42)$	5.4 ± 0.8	9.0 ± 1.6	5.8 ± 1.0
$J' = 42, F_2(N' = 42)$	0.33 ± 0.25	0.7 ± 0.7	1.1 ± 1.1
$J' = 41, F_3(N' = 42)$	1.8 ± 0.3	3.1 ± 1.0	1.1 ± 0.5
$J' = 45, F_1(N' = 44)$	2.6 ± 0.7	3.7 ± 1.3	2.7 ± 0.8
$J' = 43, F_3(N' = 44)$	2.4 ± 0.4	3.3 ± 0.9	1.3 ± 0.5

^aReference 13, temperature 900 K.^bCollision partner.

IV we would expect the cross section for the $F_1 \rightarrow F_1$ transition to be ~ 100 times larger than that for the $F_1 \rightarrow F_2$ transition and ~ 10000 times larger than that for the $F_1 \rightarrow F_3$ transition. While it is perhaps counter-intuitive, the e/f conserving $F_1 \rightarrow F_3$ transitions are predicted to be much smaller than the e/f changing $F_1 \rightarrow F_2$ transitions, as anticipated by the discussion in Sec. IV.

For these transitions experimental cross sections reported by Caughey and Crosley¹³ are listed in Table V. In agreement with the predictions in Table IV, the $F_1 \rightarrow F_1$ cross sections are found to be the largest. However, the $F_1 \rightarrow F_2$, F_3 cross sections are much larger than predicted by the present theoretical analysis, and, furthermore, the $F_1 \rightarrow F_2$ cross sections are found to be smaller than the $F_1 \rightarrow F_3$ cross sections, contrary to the theoretical prediction. The IOS approximation, on which Eqs. (34)–(36) are based, would be expected to apply here, especially for the light helium target, since the energy spacings (35 and 72 cm^{-1} for $\Delta N = 2$ and 4, respectively) are small compared to kT . Indeed, the ratio of the $F_1 \rightarrow F_2$ to $F_1 \rightarrow F_1$ cross section for $N = 42$ is the smallest for He.

A more likely explanation for the observed enhancement of the “forbidden” $F_i \rightarrow F_j$ ($i \neq j$) transitions is the fact that the $S_2 B^3\Sigma_u^-$ state is known to be perturbed.^{51–56} The perturbing state has been identified^{53,54} as $B''^3\Pi_u$. This state has been observed in spectroscopic studies of S_2 isolated in rare gas matrices.⁵⁷ Recently, Patiño and Barrow⁵⁴ have deperturbed the $v = 1$ level of $B^3\Sigma_u^-$ and derived a set of constants for the perturbing $B''^3\Pi_u$ state.

Patiño and Barrow⁵⁴ find that the off-diagonal $^3\Pi \sim ^3\Sigma^-$ spin-orbit matrix element⁵⁸ is much larger than that for the rotation-electronic interaction. This implies that the Ω components are mixed into the e/f parity $^3\Sigma^-$ levels to different degrees. Specifically, the f parity levels should acquire mainly $^3\Pi_1$ character, while the e levels should have an admixture of mostly $^3\Pi_0$. This $^3\Pi$ character of the F_1 and F_3 e levels will facilitate collisional transfer between them since e/f symmetry- and Ω -conserving transitions in a $^3\Pi$ state are expected to be facile.⁵⁹ Thus, the perturbed nature of the $B^3\Sigma_u^-$ state of S_2 is likely the explanation for Caughey and Crosley's

observation¹³ of significant $F_1 \rightarrow F_3$ forbidden collisional transitions. By contrast, since $e/f \rightarrow f/e$, $\Omega = 0 \rightarrow 1$ transitions in a $^3\Pi$ state are strongly forbidden,⁵⁹ the perturbation induced mixing with the $B''^3\Pi_u$ state should not enhance the $e \rightarrow f$ $F_1 \rightarrow F_2$ transitions within the $B^3\Sigma_u^-$ state.

VI. CONCLUSION

In the present paper we have presented a formal treatment of rotationally collision inelastic collisions of a diatomic molecule in a $^3\Sigma$ electronic state, valid in the general case of intermediate Hund's coupling. Examination of the infinite-order-sudden (IOS) limit of the key reduced matrix elements of the T operator, and of semiclassical expressions for certain $3j$ symbols allowed us to extract the following propensity rules, valid for both differential and integral cross sections:

(1) $M = 0 \rightarrow M' = 0$ transitions will be forbidden for $F_2 \rightarrow F_1$, F_3 processes at all values of J and J' . (2) Transitions from the unique $J = 0$ level to any F_2 level will be forbidden. (3) For J and J' large, compared to the tensor orders which make a significant contribution, the $JMF_i \rightarrow J'M'F'_i$ transition will be weak unless $F'_i = F_i$. (4) In the case (a) limit, corresponding to large values of the spin-spin constant λ , the propensity against $F_1 \rightarrow F_3$ transitions will be valid at all values of J and J' . The physical origin of these propensities lies in the fact that a purely electrostatic potential can not lead to changes in the spin projection quantum number Σ , and, furthermore, within the IOS limit the scattering, at high J , is independent of the value of Σ .

Obviously, these propensity rules are, strictly speaking, valid only in the IOS limit. In our previous work on similar systems we showed^{8,10,47} how the symmetry propensity rules, analogous to those derived here, were equally valid within the first Born limit, since the expression for the $R_{fL\Omega e, J' L' \Omega' e'}$ factor [Eq. (19)] is formally identical, except with the expansion coefficient of the IOS S function replaced¹⁰ by a term involving the expansion of the interaction potential. An entirely equivalent argument could be made here to demonstrate that propensity rules (1)–(4) above are also valid in the Born limit. The IOS and Born limits represent two very different collision regimes: the first valid when the collisions are impulsive and short in duration; the second valid when the collisions are weak. It is intriguing to speculate whether the propensity rules will be valid in other collision regimes. The discussion at the end of Sec. IV might indicate that the necessary condition for the validity of these propensity rules is that for collisions involving molecules in $^3\Sigma$ states, the scattering be independent of Σ , the spin projection quantum number. As we have shown, a sufficient condition is for J and J' to be large and for the scattering to be described well by either the Born or IOS approximations. Clearly, additional work should be devoted to delimiting the complete range of validity of the propensity rules derived here.

A comparison was made with the results of an experimental study by Caughey and Crosley¹³ of energy transfer within the $v = 4$ rotational manifold of the $B^3\Sigma_u^-$ state

of S_2 . The $J = 41$, $F_1 - J' F_1$ rate constants were found to be larger than those for the $F_1 - F_2$, F_3 transitions, in good qualitative agreement with our propensity rule for conservation of the F_i label. However, the experimental $F_1 - F_2$, F_3 rates were found to be much larger, relative to the $F_1 - F_1$ rates, than the predictions of our theoretical analysis, based on the IOS treatment of the dynamics. Also the $F_1 - F_3$ rates were found to be larger than the $F_1 - F_2$ rates, in contrast with the theoretical prediction. Possibly the known mixing between the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states of S_2 will tend to wash out the large variation between the $F_1 - F_1$ and $F_1 - F_2$, F_3 rates.

It would be very interesting to investigate rotational transfer from other initial levels of S_2 , particularly at lower J , and also to study other $^3\Sigma$ electronic states unaffected by local perturbations. For the latter, the second-order spin-orbit interaction with $^3\Pi$,⁶⁰ and other states⁶¹⁻⁶³ mimics the first-order spin-spin interaction $\mathcal{H}_{ss}^{(1)}$ in the $^3\Sigma$ effective Hamiltonian and is much larger than $\mathcal{H}_{ss}^{(1)}$ for heavier molecules.⁶⁴ Thus, the resulting small admixtures of other states in these "unperturbed" $^3\Sigma$ electronic states may significantly enhance the forbidden $F_i - F_j$ ($i \neq j$) transitions over the very small predicted values (see Table IV).

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APPENDIX: SEMICLASSICAL LIMIT OF CERTAIN $3j$ SYMBOLS

Using the known semiclassical limit of the $3j$ symbol,³⁵⁻³⁸ we can write⁶⁵

$$\begin{pmatrix} J_1 & l & J_2 \\ -M & 0 & M \end{pmatrix} = (-1)^{J+l+J_2} (2\pi A)^{-1/2} \cos[\Theta(j_1 \lambda j_2 M)], \quad (\text{A1})$$

where $j_1 = J_1 + \frac{1}{2}$, $\lambda = l + \frac{1}{2}$, $j_2 = J_2 + \frac{1}{2}$ and

$$A = \frac{1}{4} [\mathcal{A}(j_1 \lambda j_2) + 4\lambda^2 M^2]^{1/2}, \quad (\text{A2})$$

where

$$\mathcal{A}(j_1 \lambda j_2) = 2(j_1^2 \lambda^2 + j_1^2 j_2^2 + j_2^2 \lambda^2) - (j_1^4 + j_2^4 + \lambda^4). \quad (\text{A3})$$

The angle $\Theta(j_1 \lambda j_2 M)$ is given by

$$\Theta(j_1 \lambda j_2 M) = (j_1 \theta_1 + \lambda \theta + j_2 \theta_2 - \phi M + \pi/4), \quad (\text{A4})$$

where

$$\cos \theta_1 = M(j_1^2 + \lambda^2 - j_2^2) [(j_1^2 - M^2) \mathcal{A}(j_1 \lambda j_2)]^{-1/2}, \quad (\text{A5})$$

$$\cos \theta = -2\lambda M \mathcal{A}(j_1 \lambda j_2)^{-1/2}, \quad (\text{A6})$$

$$\cos \theta_2 = M(j_2^2 - j_1^2 + \lambda^2) [(j_2^2 - M^2) \mathcal{A}(j_1 \lambda j_2)]^{-1/2}, \quad (\text{A7})$$

and

$$\cos \phi = \frac{1}{2} (\lambda^2 - j_1^2 - j_2^2 + 2M^2) [(j_1^2 - M^2)(j_2^2 - M^2)]^{-1/2}. \quad (\text{A8})$$

One can expand [Eq. (A4)] as a power series in M . With a little algebra the results can be shown to be

$$\Theta(M) = (j_1 + \lambda + j_2 + \frac{1}{2})\pi/2 + M(\omega_{12} - \pi) + O(M^3/j_{\min}^2), \quad (\text{A9})$$

where $j_{\min} = \min(j_1, \lambda, j_2)$ and where ω_{12} is the angle between the classical angular momentum vectors \mathbf{j}_1 and \mathbf{j}_2 in the triangle formed by the three vectors \mathbf{j}_1 , λ , and \mathbf{j}_2 , that is

$$\cos \omega_{12} = (j_1^2 + j_2^2 - \lambda^2)/(2j_1 j_2). \quad (\text{A10})$$

From plane trigonometry the area of this triangle is given by $\frac{1}{2} j_1 j_2 \sin \omega_{12}$. From Eqs. (A2), (A3), and (A10) we see that this area is equal to $A(M=0)$ and thus equal to $\frac{1}{4} \mathcal{A}(j_1 \lambda j_2)^{1/2}$.

Substitution of this equality and Eq. (A9) into Eq. (A1) gives the following results for $M = 0 - 2$ when $(J_1 + l + J_2)$ is even:

$$\begin{pmatrix} J_1 & l & J_2 \\ -M & 0 & M \end{pmatrix} = (-1)^{M+G/2} \{ \pi j_1 j_2 [\sin^2 \omega_{12} + (M\lambda/j_1 j_2)^2]^{1/2} \}^{-1/2} \cos(M\omega_{12}), \quad (\text{A11})$$

and, when $(J_1 + l + J_2)$ is odd:

$$\begin{pmatrix} J_1 & l & J_2 \\ -M & 0 & M \end{pmatrix} = (-1)^{M+(G-1)/2} \{ \pi j_1 j_2 [\sin^2 \omega_{12} + (M\lambda/j_1 j_2)^2]^{1/2} \}^{-1/2} \sin(M\omega_{12}), \quad (\text{A12})$$

where

$$G = J_1 + l + J_2. \quad (\text{A13})$$

We note that Eq. (A12) correctly predicts the vanishing of the $3j$ symbol when $M = 0$ and $(J_1 + l + J_2)$ is odd.

Equation (A11) for $M = 0$ is already known.³⁸ If we neglect the $(\lambda/j_1 j_2)^2$ term in Eq. (A11), which is justified if all three angular momenta are large, then we predict, for $(J_1 + l + J_2)$ even,

$$\begin{pmatrix} J_1 & l & J_2 \\ -1 & 0 & 1 \end{pmatrix} = -\cos \omega_{12} \begin{pmatrix} J_1 & l & J_2 \\ 0 & 0 & 0 \end{pmatrix}, \quad (\text{A14})$$

which we see from Eq. (A10) is the semiclassical equivalent of the known quantum-mechanical relation^{38,39}

$$\begin{pmatrix} J_1 & l & J_2 \\ -1 & 0 & 1 \end{pmatrix} = \frac{l(l+1) - J_1(J_1+1) - J_2(J_2+1)}{2[J_1(J_1+1)J_2(J_2+1)]^{1/2}} \begin{pmatrix} J_1 & l & J_2 \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{A15})$$

Since the derivation of Eqs. (A11) and (A12) depends on the power series expansion of $\Theta(j_1 \lambda j_2 M)$ [Eq. (A4)], it would probably be unwarranted to use them for $M > 2$, except for very large values of all three angular momenta.

When $J_1, J_2 \gg l$, so that the angle ω_{12} is small, then we can use the small angle limits for $\cos \omega_{12}$ and $\sin \omega_{12}$ to write, for $(J_1 + l + J_2)$ even,

$$\begin{pmatrix} J_1 & l & J_2 \\ -M & 0 & M \end{pmatrix} = (-1)^{M+G/2} [\pi j_1 j_2 \Delta(J_1 l J_2)]^{-1/2} [1 - (M\Delta)^2/2], \quad (\text{A16})$$

and, for $(J_1 + l + J_2)$ odd,

$$\begin{pmatrix} J_1 & l & J_2 \\ -M & 0 & M \end{pmatrix} = (-1)^{M+(G-1)/2} (\pi j_1 j_2 \Delta)^{-1/2} (M\Delta), \quad (\text{A17})$$

where

$$\Delta^2(J_1 J_2) = [\lambda^2 - (j_1 - j_2)^2] / j_1 j_2. \quad (\text{A18})$$

Because of the triangle relation $0 < \Delta^2 \leq 1$. As an example of the accuracy of Eqs. (A16) and (A17), numerical tests indicate that for $2 \leq l \leq 6$ and $M = 1$, these expressions are accurate to within 10% whenever $J_1, J_2 \geq 8$. For $M = 2$ the same accuracy can be achieved only when $J_1, J_2 \geq 15$.

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