

DIATOMIC MOLECULAR SPECTROSCOPY WITH STANDARD AND ANOMALOUS COMMUTATORS

CHRISTIAN G. PARIGGER AND JAMES O. HORNKOHL

The University of Tennessee Space Institute, Tullahoma, Tennessee 37388, U.S.A.

Abstract: In this review, we address computation of diatomic molecular spectra. An overview of the theory is discussed based on symmetries of the diatomic molecule. The standard quantum theory of angular momentum fully accounts for the rotational states of the diatomic molecule. Details are elaborated in view of standard versus anomalous commutators for generation of a synthetic spectrum. Specific example spectra are presented for selected diatomic molecules in view of diagnostic applications in laser-induced optical breakdown spectroscopy.

Keywords: Molecular Spectra (PACS 33.20), Intensities and Shapes of Molecular Spectral Lines and Bands (PACS 33.70), Plasma Diagnostics (PACS 52.70), Laser-Induced Optical Breakdown.

1. INTRODUCTION

Although Van Vleck's reversed angular momentum technique [1] is little used today, the anomalous angular momentum commutators [2] upon which it was based still appear in current texts [3–5]. In this review, we show that the standard quantum theory of angular momentum fully accounts for the rotational states of the diatomic molecule. We find that the commutators which define angular momentum are not changed in a transformation from a laboratory coordinate system to one which rotates with the molecule, and the seemingly anomalous behavior of the rotated angular momentum operators J'_\pm and N'_\pm is simply the result of their operating on the complex conjugate of rotation matrix elements.

A rotation is a unitary transformation and, therefore, preserves the commutation relationships which define angular momentum. Also, operation of the raising and lowering operators on standard angular momentum states is the same in all coordinate systems connected by proper rotations. Two approaches are presented to show that proper rotations preserve the angular momentum commutators. The frequently applied nonstandard behavior of the raising and lowering operators on diatomic states is illustrated as a result of the operators acting on elements of the rotation operator matrix instead

of standard angular momentum eigenfunctions. A specific element of the rotation matrix cannot represent a standard angular momentum state because the rotation matrix element carries two magnetic quantum numbers. A fundamental property of angular momentum is that the square of the total angular momentum and only one of its components are constants of motion. An equation giving operation of the raising and lowering operators on the rotation matrix is derived. Some matrix elements of the rotational Hamiltonian are calculated to demonstrate that standard results can be obtained without resorting to Van Vleck's argument [1] that the unexpected behavior of J'_\pm and N'_\pm is the result of the anomalous commutators. Specifically, we show below that:

$$J'_\pm |J\Omega\rangle = \sqrt{J(J+1) - \Omega(\Omega \pm 1)} |J, \Omega \pm 1\rangle \quad \dots (1)$$

$$\begin{aligned} J'_\pm D_{M\Omega}^{J*}(\alpha\beta\gamma) \\ = \sqrt{J(J+1) - \Omega(\Omega \mp 1)} D_{M, \Omega \mp 1}^{J*}(\alpha\beta\gamma) \end{aligned} \quad \dots (2)$$

Notice the molecule-fixed operator J'_\pm acts on the state whose magnetic quantum number Ω is referenced to the molecule-fixed z' axis as expected, but that J'_+ lowers Ω

when operating on the complex conjugate of the rotation matrix element while J'_- raises Ω of $D_{M\Omega}^{J'*}(\alpha\beta\gamma)$.

The fully standard formalism of angular momentum is applicable without modification to the theory of diatomic spectra as will be demonstrated here: (i) An exact equation for the *total* angular momentum states of the diatomic molecule will be derived. (ii) The Hund's cases (a) and (b) basis sets will be obtained from the exact equation. (iii) The effects of J_+ , J_- , J'_+ , and J'_- on $D_{M\Omega}^J(\alpha\beta\gamma)$ and its complex conjugate will be calculated. (iv) Some case (a) matrix elements of the rotational Hamiltonian will be evaluated to show that the standard angular momentum formalism gives the accepted results. Also, Hönl-London factors for all n -photon $a \leftrightarrow a$ and $b \leftrightarrow b$ transitions obeying the $\Delta S = 0$ selection rule will be calculated. Applications will be illustrated in the study of molecular spectra recorded following laser-induced optical breakdown.

1.1 Review of Standard and Anomalous Angular Momentum Commutators

The customary starting point for the quantum theory of angular momentum is the commutation formula for the cartesian components of the angular momentum operator \mathbf{J} ,

$$\mathbf{J}_j \mathbf{J}_j - \mathbf{J}_j \mathbf{J}_i = i \epsilon_{ijk} \mathbf{J}_k \quad \dots (3)$$

where

$$\epsilon_{ijk} = \begin{cases} +1 & i, j, k \text{ in cyclic order} \\ -1 & i, j, k \text{ not in cyclic order} \\ 0 & \text{if any indices equal} \end{cases}$$

The above commutator property usually defines the angular momentum operator. Coordinate transformations leave the angular momentum operator definition invariant. The conservation law for angular momentum is fundamental. The definition of angular momentum, Eq. (3), is, of course, invariant under specifically spatial translations and rotations. Furthermore, Eq. (3) is invariant under coordinate inversion and time reversal.

Van Vleck's reversed angular momentum method starts with Eq. (3) but then utilizes change of sign of i for angular momentum when a transformation of coordinates to a system attached to a rotating molecule is made,

$$\mathbf{J}'_i \mathbf{J}'_j - \mathbf{J}'_j \mathbf{J}'_i = -i \epsilon_{i'j'k'} \mathbf{J}'_{k'} \quad \dots (4)$$

Here, the primed index denotes a rotated coordinate. This equation containing the reversed sign of i is known as Klein's [2] anomalous commutation formula.

Two approaches are debated in this work, namely an operator and an algebraic approach, without utilizing Klein's anomalous commutation formula. Each approach begins with the standard commutator formula, Eq. (3). We point out that in principle, Eq. (4) can be utilized in building angular momentum theory. However, in analogy to distinction between right- and left- handed coordinate systems, different signs occur. We only use the *standard* sign as indicated in Eq. (3) in computation of a molecular diatomic spectrum [6], i.e., without resorting to use of Klein's anomaly and Van Vleck's reversed angular momentum method.

Here, the reversal of the sign in Eq. (3) is briefly investigated for an unitary and an anti-unitary transformation. The Euler rotation matrix is a real, unitary matrix (see Eq. (11) below). The determinate of the Euler rotation matrix is +1 meaning that the sign of vectors is preserved under rotations. A spatial rotation of coordinates is a proper transformation.

Conversely, the inversion or parity operator constitutes an improper rotation—this transformation cannot be described exclusively in terms of the Euler angles. However, angular momentum is a pseudo or axial vector, preserving the sign of \mathbf{J} under improper rotations. The parity operator is also unitary and Eq. (3) is preserved by the parity operator. Time reversal (time inversion or reversal of motion) changes the sign of \mathbf{J} and it complex-conjugates the imaginary unit due to time reversal being anti-unitary. Thus, Eq. (3) is invariant under time reversal. As shown in texts (e.g. Messiah [7]), the time reversal operator has been designed to be anti-unitary for the very purpose of preserving the sign of i in commutation formulae.

1.2 Effect of Unitary Transformation on Angular Momentum Commutators

In a brief review we show that unitary transformations preserve commutation formulae. Consider the operators A , B , and C which satisfy the commutation formula

$$AB - BA = iC, \quad \dots (5)$$

and subject these operators to the unitary transformation U . That is,

$$A' = U A U^\dagger \quad \dots (6)$$

and

$$A = U^\dagger A' U, \quad \dots (7)$$

with similar equations holding for B' and C' . The operator U is unitary, i.e., $U^\dagger = U^{-1}$, so

$$\begin{aligned} U^\dagger A' U U^\dagger B' U - U^\dagger B' U U^\dagger A' U \\ = U^\dagger A' B' U - U^\dagger B' A' U = i U^\dagger C' U, \quad \dots (8) \end{aligned}$$

or

$$A' B' - B' A' = i C' \quad \dots (9)$$

The above textbook discussion (e.g. Davydov [8]) confirms that the angular momentum quantum commutators, Eq. (3), are preserved under unitary transformations. The Euler rotation matrix, Eq. (11) below, is easily demonstrated to be unitary.

An algebraic approach is used in the following to show that the commutator Eq. (3) remains invariant when proper rotation of coordinates is applied. The laboratory referenced \mathbf{J} is transformed to the rotated coordinate system by application of the rotation matrix $\mathbf{D}(\alpha\beta\gamma)$,

$$\mathbf{J}' = \mathbf{D}(\alpha\beta\gamma) \mathbf{J}, \quad \dots (10)$$

where α , β , and γ are the Euler angles and $\mathbf{D}(\alpha\beta\gamma)$ is an orthogonal matrix whose determinant is +1, Goldstein [9],

$$\begin{aligned} \mathbf{D}(\alpha\beta\gamma) = \\ \begin{pmatrix} \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma & -\sin \beta \cos \gamma \\ -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma & -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma & \sin \beta \sin \gamma \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & \cos \beta \end{pmatrix} \\ \dots (11) \end{aligned}$$

The Euler angles and the matrix $\mathbf{D}(\alpha\beta\gamma)$ used here are those normally used in quantum mechanics, Messiah [7], Davydov [8], Goldstein [9], Rose [10], Brink and Satchler [11], Tinkham [12], Varshalovich et al. [13], Gottfried [14], Baym [15], and Shore and Menzel [16]. This same set of Euler angles is also used by some authors of books on the theory of diatomic spectra, Judd [17], Mizushima [18], Brown and Carrington [3], and Lefebvre-Brion and Field [4]. Evaluation of the angular momentum commutation formulae in the rotated system of coordinates gives

$$\mathbf{J}_i \mathbf{J}_j - \mathbf{J}_j \mathbf{J}_i = i \epsilon_{ijk} \mathbf{J}_k \quad \dots (12)$$

This result is obtained from Eqs (3), (10), and (11). The calculation is simplified somewhat if one notes that for an orthogonal matrix the cofactors, i.e., signed minor

determinants, are equal to the corresponding matrix elements of $\mathbf{D}(\alpha\beta\gamma)$ labeled m_{ij} , i.e., m_{ij} is its own cofactor. For example,

$$\begin{aligned} J_x' J_y' - J_y' J_x' \\ = i [(m_{12} m_{23} - m_{13} m_{22}) (J_y J_z - J_z J_y) + \\ (m_{13} m_{21} - m_{11} m_{23}) (J_x J_z - J_z J_x) + \\ (m_{11} m_{22} - m_{12} m_{21}) (J_x J_y - J_y J_x)], \quad \dots (13) \end{aligned}$$

and since

$$\begin{aligned} m_{12} m_{23} - m_{13} m_{22} &= m_{31}, \\ m_{13} m_{21} - m_{11} m_{23} &= -m_{32}, \\ m_{11} m_{22} - m_{12} m_{21} &= m_{33}, \quad \dots (14) \end{aligned}$$

the right side of the Eq. (12) reduces to $i J_z'$.

Comparison with Van Vleck's [1] treatment of Klein's anomalous formula, given between his Eqs (4) and (5), shows that we do not require reversal of sign in our approach. The anomalous sign in Eq. (4) does not reveal a novel aspect of the nature of diatomic molecules. Noteworthy is that the anomalous commutation formula remains today a time honored tradition in the theory of molecular spectra, e.g., see Refs. [2–5, 14–22]. Klein's anomalous commutators are means by which matrix elements of various operators in the molecular Hamiltonian, in particular those expressed in terms of angular momentum raising and lowering operators, are obtained.

1.3 Effect of Raising and Lowering Operators on Standard States $|JM\rangle$ and on Elements of the Rotation Matrix $\mathbf{D}_{M\Omega}^{J*}(\alpha\beta\gamma)$

The angular momentum raising and lowering operators have the following effects on the standard $|JM\rangle$ states,

$$J_\pm |JM\rangle = C_\pm(J, M) |J, M \pm 1\rangle, \quad \dots (15)$$

where

$$\begin{aligned} C_\pm(J, M) &= \sqrt{J(J+1) - M(M \pm 1)} \\ &= \sqrt{(J \mp M)(J \pm M - 1)} \quad \dots (16) \end{aligned}$$

This general equation is of course applicable to the diatomic molecule. However, as a result of approximation, one deals with approximate diatomic eigenfunctions. Contained in Van Vleck's method is his discovery that the above standard results are not directly

applicable to approximate diatomic eigenfunctions. Typically two magnetic quantum numbers occur for approximate diatomic eigenfunctions, M and Ω in Hund's case (a) or M_N and Λ in case (b).

In modern notation, approximate diatomic angular momentum states are represented by elements of the rotation matrix, $D_{M\Omega}^{J*}(\alpha\beta\gamma)$, which carry two magnetic quantum numbers, one more than allowed by the nature of angular momentum. Only \mathbf{J}^2 and one of its components, by usual convention J_z , commute with the Hamiltonian. It will be important in our approach to find the effects of the raising and lowering operators on elements of the rotation matrix while applying standard theory.

The rotated raising operator, J'_+ ,

$$J'_+ = J_x + iJ_y, \quad \dots (17)$$

lowers the Ω quantum number on Hund's case (a) states. See, for example, Van Vleck [1], Judd [17], Mizushima [18], Freed [19], Kovacs [20], Hougen [21], Carrington et al. [22], Zare et al. [23], Brown and Howard [24], and Lefebvre-Brion and Field [4]. Similarly, the rotated raising operator N'_+ lowers the Λ quantum number on case (b) kets. Agreement between eigenvalues of Hamiltonian matrices built using these results and experimentally measured term values has firmly established their correctness. Klein's anomalous commutators are often referenced in debating the reason why J'_+ lowers Ω and why N'_+ lowers Λ . However, of interest will be the following equation

$$J'_\pm D_{M\Omega}^{J*}(\alpha\beta\gamma) = -C_\mp(J, \Omega) D_{M, \Omega \mp 1}^{J*}(\alpha\beta\gamma) \quad \dots (18)$$

which will be derived below. Note that J'_+ lowers Ω , that J'_- raises Ω , and that an unexpected minus sign occurs.

The nature of angular momentum does not allow M and Ω both to be rigorously good quantum numbers. This is equivalent to stating that J_z and $J_{z'}$ do not commute. According to definition of angular momentum, Eq. (3), J_z does not commute with J_x or J_y , but it is, perhaps, not obvious that J_z and $J_{z'}$ fail to commute. One can easily show, Gottfried [14],

that:

$$[J_z, J_{z'}] = i \sin(\beta) J_\beta \quad \dots (19)$$

$$= i \sin(\beta) [-\sin(\alpha) J_x + \cos(\alpha) J_y] \quad \dots (20)$$

where $J_\beta = \partial/\partial\beta$ is the angular momentum operator for rotation about the first intermediate y-axis. In general, J_z

and $J_{z'}$ do not commute. Thus, $D_{M,\Omega}^{J*}(\alpha\beta\gamma)$ cannot represent a state of angular momentum of a molecule or any other system. The rotation matrix connects two different states of angular momentum.

2. ANGULAR MOMENTUM OPERATORS

Angular momentum operator representations in terms of Euler angles are elaborated. A rotation provides a particularly simple way of expressing a component of angular momentum. The three Euler rotations give the following three components,

$$J_\alpha = -i \frac{\partial}{\partial\alpha} = J_z, \quad \dots (21)$$

$$J_\beta = -i \frac{\partial}{\partial\beta}, \quad \dots (22)$$

$$J_\gamma = -i \frac{\partial}{\partial\gamma} = J_{z'}. \quad \dots (23)$$

Each of these operators is referenced to a different coordinate system. That is, $J_\alpha = J_z$ in the laboratory system, $J_\beta = J_{y_1}$ in the first intermediate system, and $J_\gamma = J_{z'}$ in the fully rotated system. Applying the first Euler rotation to the vector operator \mathbf{J} results in

$$\begin{pmatrix} J_{x_1} \\ J_{y_1} \\ J_{z_1} \end{pmatrix} = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} \quad \dots (24)$$

From this one finds

$$J_{y_1} = J_\beta = -\sin \alpha J_x + \cos \alpha J_y, \quad \dots (25)$$

giving J_β in terms of the laboratory coordinates of \mathbf{J} . Similarly, using the full rotation matrix, Eq. (11), one can express J_γ in laboratory coordinate system,

$$\mathbf{J}' = D(\alpha\beta\gamma) \mathbf{J}, \quad \dots (26)$$

$$J_{z'} = J_\gamma = \cos \alpha \sin \beta J_x + \sin \alpha \sin \beta J_y + \cos \beta J_z, \quad \dots (27)$$

where the substitution $J_z = J_\alpha$ has been made. Equations (25) and (27) can be inverted for J_x and J_y :

$$J_x = -i \left(-\cos \alpha \cot \beta \frac{\partial}{\partial\alpha} - \sin \alpha \frac{\partial}{\partial\beta} + \frac{\cos \alpha}{\sin \beta} \frac{\partial}{\partial\gamma} \right), \quad \dots (28)$$

$$J_y = -i \left(-\sin \alpha \cot \beta \frac{\partial}{\partial \alpha} + \cos \alpha \frac{\partial}{\partial \beta} + \frac{\sin \alpha}{\sin \beta} \frac{\partial}{\partial \gamma} \right), \quad \dots (29)$$

$$J_z = -i \frac{\partial}{\partial \gamma}. \quad \dots (30)$$

The method in obtaining these results included evaluation of J_β and J_γ in terms of the laboratory components of J . Similarly, $J_{x'}$, $J_{y'}$, and $J_{z'}$ can be obtained by expressing J_α and J_β in terms of the components of \mathbf{J}' . The inverse of the full rotation matrix is applied to the rotated vector \mathbf{J}' ,

$$\mathbf{J} = D^{-1}(\alpha\beta\gamma) \mathbf{J}' = D^\dagger(\alpha\beta\gamma) \mathbf{J}', \quad \dots (31)$$

to find J_α in terms of the rotated coordinates of \mathbf{J} ,

$$J_z = J_\alpha = -\sin \beta \cos \gamma J_{x'} + \sin \beta \sin \gamma J_{y'} + \cos \beta J_{z'}. \quad \dots (32)$$

The Euler β -rotation is taken about the first intermediate y -axis meaning that the first intermediate and second intermediate y -axes coincide. Thus J_β can be evaluated in fully rotated coordinates by applying the inverse of the γ rotation matrix to \mathbf{J}' ,

$$\begin{pmatrix} J_{x_2} \\ J_{y_2} \\ J_{z_2} \end{pmatrix} = \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} J_{x'} \\ J_{y'} \\ J_{z'} \end{pmatrix} \quad \dots (33)$$

$J_{y2} = J_{y1} = J_\beta$, therefore, we find

$$J_\beta = \sin \gamma J_{x'} + \cos \gamma J_{y'}. \quad \dots (34)$$

The two equations in two unknowns are inverted as before. We find for $J_{x'}$ and $J_{y'}$

$$J_{x'} = -i \left(\cos \gamma \cot \beta \frac{\partial}{\partial \gamma} + \sin \gamma \frac{\partial}{\partial \beta} - \frac{\cos \gamma}{\sin \beta} \frac{\partial}{\partial \alpha} \right), \quad \dots (35)$$

$$J_{y'} = -i \left(-\sin \gamma \cot \beta \frac{\partial}{\partial \gamma} + \cos \gamma \frac{\partial}{\partial \beta} + \frac{\sin \gamma}{\sin \beta} \frac{\partial}{\partial \alpha} \right), \quad \dots (36)$$

$$J_{z'} = -i \frac{\partial}{\partial \gamma} \quad \dots (37)$$

The raising and lowering operators are then constructed using the results above:

$$J_+ = -ie^{i\alpha} \left(-\cot \beta \frac{\partial}{\partial \alpha} + i \frac{\partial}{\partial \beta} + \frac{1}{\sin \beta} \frac{\partial}{\partial \gamma} \right), \quad \dots (38)$$

$$J_- = -ie^{-i\alpha} \left(-\cot \beta \frac{\partial}{\partial \alpha} - i \frac{\partial}{\partial \beta} + \frac{1}{\sin \beta} \frac{\partial}{\partial \gamma} \right), \quad \dots (39)$$

$$J_{x'} = -ie^{-i\gamma} \left(\cot \beta \frac{\partial}{\partial \gamma} + i \frac{\partial}{\partial \beta} - \frac{1}{\sin \beta} \frac{\partial}{\partial \alpha} \right), \quad \dots (40)$$

$$J_{y'} = -ie^{i\gamma} \left(\cot \beta \frac{\partial}{\partial \gamma} - i \frac{\partial}{\partial \beta} - \frac{1}{\sin \beta} \frac{\partial}{\partial \alpha} \right). \quad \dots (41)$$

These general results also apply to systems composed of any number of particles. A modification or better simplification is required for a system consisting of a single particle (or two particles, since the two-body reduction can always be applied to a system of two particles). The third Euler angle, γ , is superfluous for a single particle, i.e., $\partial/\partial\gamma = 0$. Choosing the first Euler angle to be azimuthal angle ϕ , and the second Euler angle to be the polar angle θ , then Eqs (28–30) reduce to the familiar textbook equations for the angular momentum operators of a single particle.

Comparison of Eqs (28–30) with Eqs (35–37) shows the components of angular momentum are changed by a coordinate transformation. However, Eq. (3) defines the angular momentum in terms of its cartesian components. This defining relationship among the components remains invariant, although the individual components differ. We note that Eqs (21), (38), and (39) agree with Judd's [17] Eq. (1.22), but (23), (40), (41) differ in sign from Judd's Eq. (1.23) presumably due to the use of the anomalous commutator formula. It appears that Judd obtained his rotated operators in a manner which guaranteed they would obey Klein's anomalous commutation formula.

3. ANGULAR MOMENTUM STATES OF THE DIATOMIC MOLECULE

Fundamental symmetries including special geometrical symmetries of the diatomic molecule allow us to derive a general equation for the angular momentum states of the molecule. In the laboratory system of coordinates the eigenfunction for the diatomic molecule can be written as

$$\begin{aligned} \Psi_{nJM}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b) \\ = \langle \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b | nJM \rangle \quad \dots (42) \end{aligned}$$

Here, $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$ are the spatial coordinates of N electrons, and \mathbf{R}_a and \mathbf{R}_b are nuclear coordinates. J is the

quantum number for the total angular momentum that includes spin, M is the quantum number for the z -component of J , and n represents all other required quantum numbers. The symbol $|n\rangle$ reflects the complexity of the system. Moreover, the angular momentum quantum numbers J and M contain also electronic and nuclear spins, thereby adding complexity.

In principle, the total eigenfunction for the system consisting of the molecule and the radiation fields should be constructed so that energy, linear and angular momentum is formally conserved. However, the probability of quantum transitions is controlled by matrix elements connecting initial and final states. The interaction occurs at some intermediate instant. One can consider independent states of the molecule and the radiation field for the initial and final states of the complete system. The system state at these times is the product of two independent states. Conservation laws can be met by requiring that conserved quantities lost or gained by the molecule are correspondingly gained or lost by the radiation field.

3.1 Conservation of Energy

The first fundamental symmetry considered is conservation of energy. Energy is the quantity conserved under a translation of time. The evolution operator generates a translation in time of the eigenfunction. Given an eigenfunction at time t_0 , one can find the eigenfunction at some later time t by applying the evolution operator,

$$\begin{aligned} \langle \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b | U(t, t_0) | nJM t_0 \rangle \\ = \langle \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b | nJM t \rangle \quad \dots (43) \end{aligned}$$

The evolution operator is unitary. Also, $U(t, t) = 1$. Conservation of energy and aspects of the evolution operator are not further discussed here. They were mentioned to demonstrate the common features they share with the following conservation laws and their associated unitary operators.

3.2 Conservation of Linear Momentum

The second fundamental symmetry considered is the homogeneity of space, that is, conservation of linear momentum. The total linear momentum is conserved under a translation of coordinates. Again, an operator is devised to produce the spatial translation. For homogeneous space, a translation of coordinates to some new origin \mathbf{R}_0 :

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0, \quad \dots (44)$$

leave the state of the molecule unchanged. Translation merely takes us to another vantage point from which to view the molecule. As was the case of the time translation operator, the spatial translation operator, $T(\mathbf{R}_0)$, is defined by its effect upon the eigenfunction:

$$\begin{aligned} \langle \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b | T(\mathbf{R}_0) | nJM \rangle \\ = \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r}_a, \mathbf{r}_b | nJM \rangle. \quad \dots (45) \end{aligned}$$

The translation operator is unitary like the unitary evolution operator. The unitarity of $T(\mathbf{R}_0)$ can be explored by expanding into Taylor series the original eigenfunction about \mathbf{R}_0 . One finds:

$$\begin{aligned} \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r}_a, \mathbf{r}_b | nJM \rangle \\ = \langle \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b | e^{-i\mathbf{R}_0 \cdot \mathbf{P}/\hbar} | nJM \rangle \quad \dots (46) \end{aligned}$$

where \mathbf{P} is the total linear momentum of the molecule. A comparison of Eqs (45) and of (46) yields:

$$T(\mathbf{R}_0) \equiv e^{-i\mathbf{R}_0 \cdot \mathbf{P}/\hbar} \quad \dots (47)$$

The Schrödinger (or x -) representation of the adjoint translation operator (in practice, its complex conjugate) can be interpreted as the total linear momentum eigenfunction. This can be elucidated by rewriting Eq. (45) as:

$$\begin{aligned} \Psi_{nJM}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b) \\ = T^\dagger(\mathbf{R}_0) \Psi_{nJM}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r}_a, \mathbf{r}_b) \quad \dots (48) \end{aligned}$$

An analogous situation occurs with the temporal evolution of quantum states. One defines the unitary evolution operator by its action on the eigenfunction. Yet the evolution operator satisfies the time dependent Schrödinger equation, again showing the interplay of eigenfunction and operator. A similar connection arises when the rotation of coordinates is considered. A sum over matrix elements of the rotation operator become the angular momentum eigenfunctions of the system.

Before exploring conservation of angular momentum we first find the optimal origin of coordinates about which to make rotations. The geometrical symmetry of the diatomic molecule guides us in finding this optimal origin, that is, how to choose \mathbf{R}_0 .

A geometrical symmetry is implied for a diatomic molecule. There are precisely two nuclei and their motion

can be reduced to that of a single, fictitious particle having reduced mass μ ,

$$\mu = \frac{m_a m_b}{m_a + m_b} \quad \dots (49)$$

when we choose the location of \mathbf{R}_0 to be the center of mass of the nuclei, \mathbf{R}_{cmn} ,

$$\mathbf{R}_0 = \mathbf{R}_{\text{cmn}} = \frac{m_a \mathbf{R}_a + m_b \mathbf{R}_b}{m_a + m_b} \quad \dots (50)$$

This two-body reduction replaces the six coordinates of \mathbf{R}_a and \mathbf{R}_b with the three coordinates of \mathbf{R}_{cmn} and the three coordinates of \mathbf{r} ,

$$\mathbf{r} = \mathbf{R}_a - \mathbf{R}_b, \quad \dots (51)$$

the internuclear vector. Note that $T^\dagger(\mathbf{R}_{\text{cmn}})$ represents the total linear momentum, not the linear momentum of only the nuclei. The total eigenfunction can now be written:

$$\Psi_{nJM}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b) = T^\dagger(\mathbf{R}_{\text{cmn}}) \Psi_{nJM}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r}) \quad \dots (52)$$

in which the internal eigenfunction, $\Psi_{nJM}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r})$, is a function of $3N + 3$ spatial coordinates, not the total $3N + 6$. Because we are interested here in only the internal states of the molecule, the total linear momentum \mathbf{P} is set equal to zero giving $T^\dagger(\mathbf{R}_{\text{cmn}}) = 1$.

The center of mass of the nuclei is the origin of the internuclear vector, \mathbf{r} , and this vector, which defines the internuclear axis, is an axis of symmetry of the diatomic molecule. Any axis about which a rotation is made is an axis of symmetry because space is isotropic, but this rotation does not necessarily induce a dynamical variable. While it is true that the ratio of nuclear to electronic masses is large, meaning that \mathbf{R}_{cmn} nearly coincides with the center of total mass and that nuclear motions are approximately separable from electronic motions, the motivation for choosing the origin to lie on the internuclear axis is that the rotation about this axis can be used as a dynamical variable of the molecule, not the simplifying approximations which result from the large ratio of nuclear to electronic masses.

In passing, it is noted that one who regards conservation of linear momentum as a formal nicety which can be skipped in practice will miss the mass

polarization term which appears in the Hamiltonian. This term is comparable in magnitude to the terms dropped in the Born-Oppenheimer approximation, see for example Bunker [25] or Bransden and Joachain [26].

3.3 Conservation of Angular Momentum

The third fundamental symmetry considered is the isotropy of space, that is, conservation of angular momentum. As before, the operator associated with this symmetry, the rotation operator $\mathcal{R}(\alpha\beta\gamma)$, is defined by its effect on the eigenfunction:

$$\begin{aligned} \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | \mathcal{R}(\alpha\beta\gamma) | nJM \rangle \\ = \langle \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, \mathbf{r}' | nJM \rangle \end{aligned} \quad \dots (53)$$

where, for example:

$$\mathbf{r}' = \mathbf{D}(\alpha\beta\gamma) \mathbf{r}, \quad \dots (54)$$

with similar equations holding for $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$. Below, one will see examples showing that the rotation operator produces translations of angular coordinates just like the evolution operator translates time and the translation operator translates Cartesian coordinates. The rotation operator is unitary like the translation operator, but angular momentum states are discrete whereas linear momentum states are continuous. The effect of the rotation operator can also be expressed as a unitary transformation of the kets:

$$\begin{aligned} \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | \mathcal{R}(\alpha\beta\gamma) | nJM \rangle \\ = \sum_{\Omega=-J}^J \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | nJ\Omega \rangle D_{\Omega M}^J(\alpha\beta\gamma) \dots \end{aligned} \quad (55)$$

in which the matrix elements of the rotation operator are defined by:

$$D_{\Omega M}^J(\alpha\beta\gamma) = \langle J\Omega | \mathcal{R}(\alpha\beta\gamma) | JM \rangle. \quad \dots (56)$$

The quantum number M represents the z -component of \mathbf{J} , and the quantum number Ω represents the z' -component of \mathbf{J} . Equation (53) is written in terms of the eigenfunction $\langle \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, \mathbf{r}' | nJM \rangle$ showing rotated coordinates and the quantum number M which is referenced to the laboratory coordinate system. Similarly, Eq. (55) is written in terms of the eigenfunction $\langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | nJ\Omega \rangle$ showing laboratory coordinates and the quantum number Ω which is referenced to the rotated

coordinate system. Equations (53) and (55) serve to define the rotation operator and its matrix elements. However, we seek an identity with transparent interpretation as follows: Operate on the laboratory eigenfunction with $\mathcal{R}^\dagger(\alpha\beta\gamma)$ (i.e., in Eq. (53) replace the rotation operator with its adjoint) and follow this with operation by $\mathcal{R}(\alpha\beta\gamma)$ to obtain:

$$\langle r_1, r_2, \dots, r_N, r | nJ\Omega \rangle = \sum_{\Omega=-J}^J \langle r'_1, r'_2, \dots, r'_N, r' | nJ\Omega \rangle D_{\Omega M}^{J*}(\alpha\beta\gamma) \dots \quad (57)$$

in which the eigenfunctions are now either referenced purely to the laboratory coordinate system or rotated coordinate system. This equation reveals the effect on the eigenfunction from a rotation of coordinates. In general, the rotation of coordinates changes the direction of the z -axis and, therefore, a new magnetic quantum number, Ω , appears. A general property of angular momentum is that only one of its components is a constant of the motion. If M is a *good* quantum number, Ω cannot be. A version of Eq. (57) can be written in which Ω is a *good* quantum number but then the equation contains a summation over all M (see Eq. (71) below).

3.4 Inclusion of Special Symmetry for Diatomic Molecules

An origin of coordinates lying on the internuclear axis was chosen above. This choice allows us to take advantage of the axial symmetry of the molecule. Equation (57) is valid for arbitrary Euler rotations. Let us choose specific Euler angles which simplify the analysis.

First, we write the internuclear vector, \mathbf{r} , in terms of its spherical polar coordinates:

$$\mathbf{r} = r(\theta\phi) \dots \quad (58)$$

The Euler angle α and the azimuthal angle ϕ both represent counterclockwise rotations about the z -axis. If ϕ is the azimuthal angle of the internuclear vector in the laboratory coordinate system, after the Euler rotation α the azimuthal angle has a new value $\phi' = \phi - \alpha$. We are at liberty to choose the value of α which makes $\phi' = 0$ (i.e., $\alpha = \phi$). Similarly, we are at liberty to choose $\beta = \theta$. These choices force the z' -axis to coincide with the internuclear axis. The Euler angles α and β now serve dual purposes. They are parameters of the rotation of coordinates and they are dynamical variables of the molecule.

Second, we model the two nuclei as point masses lying on the internuclear axis. Hence, the third Euler angle, γ , cannot represent motion of the nuclei. If it is to be made a dynamical variable, γ must be made an electronic coordinate. This is accomplished by letting the third Euler angle γ describe rotation of one of the electrons, say the N th electron, about the internuclear axis [27]. The molecule-fixed cartesian coordinates x'_N, y'_N, z'_N of the N th electron are replaced by the cylindrical coordinates ρ', χ', ξ' ,

$$x'_N = \rho'_N \cos(\chi'_N) \dots \quad (59)$$

$$y'_N = \rho'_N \sin(\chi'_N) \dots \quad (60)$$

$$z'_N = \xi'_N \dots \quad (61)$$

where, because the laboratory rotation χ_N and γ are both counterclockwise rotations about the same axis,

$$\chi'_N = \chi_N - \gamma \dots \quad (62)$$

we may choose $\chi_N = \gamma$, that is, choose $\chi'_N = 0$. Equation (57) can now be rewritten to read

$$\langle r_1, r_2, \dots, r_N, r | nJM \rangle = \sum_{\Omega=-J}^J \langle r'_1, r'_2, \dots, r'_{N-1}, \rho'_N \zeta'_N | n_{J\Omega} \rangle D_{M\Omega}^{J*}(\alpha\beta\gamma) \dots \quad (63)$$

where the scalar r is the internuclear distance. Primes on ρ and ζ have been dropped for the same reason that the internuclear distance r is not primed. Like r , ρ and ζ are scalar invariants, distances whose value is the same in all coordinate systems. The ket $|n_{J\Omega}\rangle$ is not an angular momentum state but it is a function of J and Ω . This behavior is analogous to the radial eigenfunction of the hydrogen atom which is not an angular momentum eigenfunction but does depend on the orbital angular momentum quantum number l (see Eq. (64) below).

With the chosen Euler angles, the rotation matrix element has replaced the angular momentum eigenfunction of the diatomic molecule. The eigenfunction

$\langle r'_1, r'_2, \dots, r'_{N-1}, \rho'_N \zeta'_N | nJ\Omega \rangle$ is not a function of the Euler angles. If one of the nuclei and all but one of the electrons were removed from Eq. (42), then following the above procedure one would find, separating off the electron's spin:

$$\begin{aligned} \langle r_1 | nlm \rangle &= \langle r_1 | nl \rangle \sqrt{\frac{2l+1}{4\pi}} D_{m0}^{l*}(\alpha\beta 0) \\ &= \psi_{nl}(r_1) Y_{lm}(\theta = \beta, \phi = \alpha) \dots \quad (64) \end{aligned}$$

The change of variables indicated in Eq. (58) is familiar, and θ and ϕ are dynamical variables of the problem. We demonstrated above that γ can be made a dynamical variable of the diatomic molecule. The difference between Eqs (64) and (63) is that γ is not relevant to a spherically symmetric hydrogenic atom, but γ is relevant to the axially symmetric diatomic molecule.

3.5 Inclusion of Spin

In accord with standard diatomic notation, Eq. (63) should be written in terms of the quantum numbers F , M_F and Ω_F that in the standard notation represent the total angular momentum,

$$\mathbf{F} = \mathbf{R} + \mathbf{L} + \mathbf{S} + \mathbf{T}, \quad \dots (65)$$

where \mathbf{R} is the total orbital angular momentum of the nuclei, \mathbf{L} is the total orbital angular momentum of the electron, \mathbf{S} is the total spin of the electrons, and \mathbf{T} is the total spin of the nuclei. However, Eq. (63) follows the usage of J in the literature of angular momentum where J , and M , and Ω represent the *total* angular momentum. Derivation of Eq. (63) was based on the isotropy of space, and therefore holds only if J , M , and Ω represent the total angular momentum including all orbital momenta and all spins. The electronic and nuclear spin in Eq. (63) can be revealed by application of the inverse Clebsch-Gordan series to the rotation matrix element, Eq. (80) below.

3.6 Rotated Diatomic Angular Momentum States

Equation (63) shows that the Euler angles are dynamical variables of the diatomic:

$$\begin{aligned} \langle r_1 r_2 \dots r_N r | nJM \rangle \\ = \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \alpha \beta \gamma | nJM \rangle \quad \dots (66) \end{aligned}$$

If analysis of the molecule had begun with the introduction of generalized Lagrangian coordinates, the Euler angles ϕ , θ , and χ would have been introduced first as dynamical variables and only later as parameters of coordinate rotation. This route takes one to the equation:

$$\begin{aligned} \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \phi \theta \chi | nJM \rangle \\ = \sum_{J=-\Omega}^{\Omega} \langle r_1, r_2, \dots, r_{N-1}, \rho \zeta r \phi' \theta' \chi' | nJ\Omega \rangle D_{M\Omega}^{J*}(\alpha\beta\gamma), \quad \dots (67) \end{aligned}$$

where

$$\phi' = \phi - \alpha, \quad \dots (68)$$

$$\theta' = \theta - \beta, \quad \dots (69)$$

$$\chi' = \chi - \gamma. \quad \dots (70)$$

Choosing $\phi = \alpha$, $\theta = \beta$, and $\chi = \gamma$ makes $\phi' = \theta' = \chi' = 0$ thereby removing all angular dependence from $\langle r_1 r_2 \dots r_{N-1} \rho \zeta r | n_{J\Omega} \rangle$ on the right side of Eq. (63).

Multiplication of Eq. (67) by $D_{M\Omega}^J(\alpha\beta\gamma)$ and summation over M yields:

$$\begin{aligned} \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \phi' \theta' \chi' | nJ\Omega \rangle \\ = \sum_{M=-J}^J \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \phi \theta \chi | nJM \rangle D_{M\Omega}^J(\alpha\beta\gamma), \quad \dots (71) \end{aligned}$$

The appearance of $D_{M\Omega}^J(\alpha\beta\gamma)$ on the right side indicates that it originated from application of the inverse of the rotation operator to the left side:

$$\begin{aligned} \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \phi' \theta' \chi' | nJ\Omega \rangle \\ = \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \phi \theta \chi | \mathcal{R}^{-1}(\alpha\beta\gamma) | nJ\Omega \rangle \quad \dots (72) \\ = \langle r_1 r_2 \dots r_{N-1} \rho \zeta r \phi \theta \chi | \mathcal{R}(-\gamma, -\beta, -\alpha) | nJ\Omega \rangle, \quad \dots (73) \end{aligned}$$

where

$$\phi' = \phi + \gamma, \quad \dots (74)$$

$$\theta' = \theta + \beta, \quad \dots (75)$$

$$\chi' = \chi + \alpha. \quad \dots (76)$$

As before, we choose α , β , and γ to remove all angular dependence from the eigenfunction of the right side of Eq. (71).

Placing the observer in the molecular coordinate system is a reversal of motion. Because the order of Euler rotations about different axes is significant (e.g. $\mathcal{R}(\alpha\beta\gamma) \neq \mathcal{R}(\beta\alpha\gamma)$), reversal of motion also requires that the order in which the rotations are taken be reversed, i.e., $\mathcal{R}(\alpha\beta\gamma)^{-1} = \mathcal{R}(-\gamma, -\beta, -\alpha)$. Because the signs of the Euler angles are inverted, one might mistakenly believe that the sign in front of i in Eqs (21–23) would also be inverted thus implying that the anomalous commutators

hold in the molecule-fixed coordinate system, but reversal of motion (also called time reversal) is anti-unitary. The time reversal operator is normally written as the product of a unitary operator and the complex conjugation operator. Thus in reversal of motion, changes in the signs of the Euler angles are canceled by complex conjugation and the sign in front of i in Eqs (21–23) remains unchanged.

3.7 Discussion of Angular Momentum States of the Diatomic Molecule

The significance of Eq. (63) is that it shows the total angular momentum is exactly separable in the diatomic eigenfunction. The separation is independent of the Born-Oppenheimer approximation and is possible for very few simple systems such as the diatomic molecule and hydrogen/hydrogenic atom (see Eq. (64) above).

The summation over Ω in Eq. (63) insures that only one magnetic quantum number, M , is *good*. An element of the D -matrix is a combination of the states $|JM\rangle$ and $|J\Omega\rangle$. No one term in the sum on the right side of Eq. (63) contains a standard angular momentum eigenfunction. The equation $J_{\pm}|J\Omega\rangle = C_{\pm}(J\Omega)|J, \Omega \pm 1\rangle$ indeed holds, but this result is not directly applicable to Hund's case (a) or (b) eigenfunctions. For the diatomic molecule the angular momentum eigenfunction is replaced by a sum over matrix elements of the rotation operator, quantities which are obviously defined in terms of angular momentum but which, nevertheless, are not angular momentum eigenfunctions because J_z and $J_{z'}$ do not commute. Symbols such as $\psi_{JM\Omega}(\alpha\beta\gamma)$ and $\langle\alpha\beta\gamma|JM\Omega\rangle$ (viz. symbols for Hund's case (a) basis states) are best avoided due to difficulties of reconciling these symbols with the formalism and physics of angular momentum.

The α - and γ -dependence of the rotation matrix element is clear,

$$D_{M\Omega}^J(\alpha\beta\gamma) = e^{-iM\alpha} d_{M\Omega}^J(\beta) e^{-i\Omega\gamma}, \quad \dots (77)$$

possibly tempting one to take the matrix element apart and put the γ term with the eigenfunction $\langle r'_1 r'_2 \dots r'_N r | n \rangle$ calling the result the 'electronic-vibrational' eigenfunction. There is historical precedence for separating the total eigenfunction into electronic, vibrational, and rotational parts, but this scheme does not fit the present, thus far exact, formulation. From a practical standpoint,

one who takes the rotation matrix element apart for example to utilize formulae of the kind:

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} D_{m_1\omega_1}^{j_1*}(\alpha\beta\gamma) D_{m_2\omega_2}^{j_2}(\alpha\beta\gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma = \frac{8\pi^2}{2J+1} \delta_{m_1 m_2} \delta_{\omega_1 \omega_2} \delta_{j_1 j_2} \quad \dots (78)$$

and the inverse Clebsch-Gordan series:

$$D_{M\Omega}^J(\alpha\beta\gamma) = \sum_{\substack{m_1 = -j_1 \\ \omega_1 = -j_1}}^{j_1} \sum_{\substack{m_2 = -j_2 \\ \omega_2 = -j_2}}^{j_2} \langle j_1 m_1 j_2 m_2 || JM \rangle \langle j_1 \omega_1 j_2 \omega_2 | J\Omega \rangle D_{m_1\omega_1}^{j_1}(\alpha\beta\gamma) D_{m_2\omega_2}^{j_2}(\alpha\beta\gamma), \quad \dots (79)$$

may find that it is indeed best to not separate the D -matrix.

4. HUND'S CASE (a) AND (b) BASIS FUNCTIONS

The Hund's case (a) eigenfunction is constructed from Eq. (63) by omitting the summation over Ω and re-normalizing the result through use of Eq. (78):

$$\begin{aligned} & \langle r_1, r_2, \dots, r_N, r | nJM\Omega\Sigma \rangle \\ &= \sqrt{\frac{2J+1}{8\pi^2}} \langle r'_1 r'_2 \dots r'_N r | n \rangle \\ & \quad |S\Sigma\rangle D_{M\Omega}^{J*}(\alpha\beta\gamma) \quad \dots (81) \end{aligned}$$

It is noteworthy that the Hund case (a) basis identifies both M and Ω as so-called *good* quantum numbers. The value of a basis may be associated with the ease in accurately constructing the eigenfunction. However, one must realize that Hund's case (a) eigenfunction does not contain standard $|JM\rangle$ or $|J\Omega\rangle$ angular momentum states. Application of the raising and lowering operators to case (a) eigenfunction will reveal nonstandard results.

The Hund case (a) basis cannot rigorously represent a physical state. However, let us investigate its approximate physical significance of a model for a diatomic molecule where nuclear spin effects are not important. For this model, the total angular momentum is the sum of \mathbf{L} the electronic orbital, \mathbf{S} the electronic spin, and \mathbf{R} the nuclear orbital angular momenta.

$$\mathbf{J} = \mathbf{L} + \mathbf{R} + \mathbf{S}, \quad \dots (82)$$

or

$$\mathbf{J} = \mathbf{N} + \mathbf{S}, \quad \dots (83)$$

where \mathbf{N} is the total orbital angular momentum:

$$\mathbf{N} = \mathbf{L} + \mathbf{R}. \quad \dots (84)$$

This last equation, a definition, is further debated: According to the reversed angular momentum method, \mathbf{N} and \mathbf{R} are examples of momenta which are expected to obey Klein's anomalous commutation formulae but \mathbf{L} obeys the standard formulae. The operator which rotates \mathbf{N} when applied to the right side of the above equation must treat \mathbf{L} and \mathbf{R} differently. Construction of such an operator maybe difficult. In comparison, a formalism in which all angular momentum operators obey the same commutator formulae in all coordinate systems is preferred and offers simplicity.

A Clebsch-Gordan expansion of the D -matrix of Eq. (81) results in:

$$\begin{aligned} & \langle r_1, r_2, \dots, r_N, r | nJM\Omega S\Sigma \rangle \\ &= \sqrt{\frac{2J+1}{8\pi^2}} \langle r'_1 r'_2 \dots r'_{N-1} \rho \zeta r | n \rangle | S\Sigma \rangle \times \\ & \sum_{M_N=-N}^N \sum_{M_S=-S}^S \langle N M_N S M_S | JM \rangle \langle N\Lambda S\Sigma | J\Omega \rangle \\ & D_{M_N\Lambda}^{N*}(\alpha\beta\gamma) D_{M_S\Sigma}^{S*}(\alpha\beta\gamma) \quad \dots (85) \end{aligned}$$

Both $\langle N M_N S M_S | JM \rangle$ and $\langle N\Lambda S\Sigma | J\Omega \rangle$ are Clebsch-Gordan coefficients. The quantum numbers M_N and M_S are referenced to laboratory coordinates, Λ and Σ to rotating coordinates. The Clebsch-Gordan coefficients vanish unless $M = M_N + M_S$ and $\Omega = \Lambda + \Sigma$. The two D -matrices in this equation have the same set of Euler angles meaning that N and S are perfectly coupled in accord with the definition of Hund's case (a).

The Hund case (a) basis is a useful physical approximation only when the coupling N and S is strong. Conversely, for weak (or negligibly small) coupling between N and S , construction of another basis set is indicated.

In the absence of electronic and nuclear spin, Eq. (63) reads:

$$\begin{aligned} & \langle r_1 r_2 \dots r_N r | n N M_N \rangle \\ &= \sum_{\Lambda=-N}^N \langle r'_1 r'_2 \dots r'_{N-1} \rho \zeta r | n \rangle D_{M_N\Lambda}^{N*}(\alpha\beta\gamma) \dots (86) \end{aligned}$$

Construction of the Hund case (b) basis begins by omitting the summation over Λ and re-normalizing the result. Subsequently, the spinless equation is multiplied by the electronic spin states $|SM_S\rangle$ and the appropriate Clebsch-Gordan coefficient. Finally the result is summed over all laboratory magnetic quantum numbers:

$$\begin{aligned} & \langle r_1 r_2 \dots r_N r | n J M N \Lambda S \rangle \\ &= \sqrt{\frac{2N+1}{8\pi^2}} \langle r'_1 r'_2 \dots r'_{N-1} \rho \zeta r | n \rangle | S\Sigma \rangle \\ & \sum_{M_S=-S}^S \sum_{M_N=-N}^N \langle N M_N S M_S | JM \rangle D_{M_N\Lambda}^{N*}(\alpha\beta\gamma), \quad \dots (87) \end{aligned}$$

giving Hund's case (b) eigenfunction. States constructed from Clebsch-Gordan coefficients give a diagonal representation of the Hamiltonian only if the two angular momenta that are combined do not interact. Such non-interaction would perfectly match Hund's case (b) (viz. weak or negligibly small electronic spin-orbit interaction).

As one expresses the spin ket in the rotated system:

$$|SM_S\rangle = \sum_{\Sigma=-S}^S |S\Sigma\rangle D_{M_S\Sigma}^{S*}(\alpha_s\beta_s\gamma_s), \quad \dots (88)$$

where α_s , β_s , and γ_s are the Euler angles for rotation of the electronic spin, the following comparison between cases (a) and (b) can be made: For Hund's case (a) the spin Euler angles are equal to the Euler angles describing the rotations of the molecule, but for Hund's case (b) the spin angles are completely independent of α , β , and γ . Consequently, in case (b), $D_{M_N\Lambda}^{N*}(\alpha\beta\gamma)$ and $D_{M_S\Sigma}^{S*}(\alpha_s\beta_s\gamma_s)$ cannot be combined in a Clebsch-Gordan contraction to build the $|JM\rangle$ states as in case (a).

Transformations between cases (a) and (b) are accomplished using:

$$\langle a|b\rangle = \sqrt{\frac{2N+1}{2J+1}} \langle N\Lambda S\Sigma | J\Omega \rangle, \quad \dots (89)$$

$$\langle b|a\rangle = \sqrt{\frac{2J+1}{2N+1}} \langle N\Lambda S\Sigma | J\Omega \rangle, \quad \dots (90)$$

These coefficients can be obtained from Eqs (78), (80), (81), and (87).

5. EFFECTS OF RAISING AND LOWERING OPERATORS ON $D_{M\Omega}^J(\alpha\beta\gamma)$

Operation of the J_+ , J_- , J'_+ , and J'_- on the D -matrices will be explored here. Substitution of Eq. (63) into Eq. (15) gives:

$$\begin{aligned}
 J_{\pm} \sum_{\Omega=-J}^J \langle r'_1 r'_2 \dots r'_{N-1} \rho \zeta r | n \rangle | S \Sigma \rangle D_{M\Omega}^{J*}(\alpha\beta\gamma) \\
 = C_{\pm}(J, M) \sum_{\Omega=-J}^J \langle r'_1 r'_2 \dots r'_{N-1} \rho \zeta r | n \rangle \\
 | S \Sigma \rangle D_{M\pm 1, \Omega}^{J*}(\alpha\beta\gamma) \quad \dots (91)
 \end{aligned}$$

We mentioned above that the eigenfunction $\langle r'_1 r'_2 \dots r'_N r | n \rangle$ has no angular dependence. Therefore, J_{\pm} acts only on the D -matrix elements. A term by term comparison of the left and right sides of Eq. (91) gives:

$$\begin{aligned}
 J_{\pm} D_{M\Omega}^{J*}(\alpha\beta\gamma) \\
 = C_{\pm}(J, M) D_{M\pm 1, \Omega}^{J*}(\alpha\beta\gamma) \quad \dots (92)
 \end{aligned}$$

One recognizes that operation by J_{\pm} gives an expected result when applied to the *complex conjugate* of the D -matrix. The complex conjugate of the D -matrix is given by:

$$D_{M\Omega}^{J*}(\alpha\beta\gamma) = (-)^{M-\Omega} D_{-M, -\Omega}^J(\alpha\beta\gamma), \quad \dots (93)$$

from which one finds:

$$\begin{aligned}
 J_+ D_{M\Omega}^J(\alpha\beta\gamma) \\
 = J_+ (-)^{M-\Omega} D_{-M, -\Omega}^{J*}(\alpha\beta\gamma) \\
 = (-)^{M-\Omega} C_+(J, -M) D_{-M+1, -\Omega}^{J*}(\alpha\beta\gamma) \\
 = -C_-(J, M) D_{M-1, \Omega}^J(\alpha\beta\gamma). \quad \dots (94)
 \end{aligned}$$

In the last step, we used $C_+(J, -M) = C_-(J, M)$ as can be inferred from Eq. (16). This result illustrates that J_+ lowers M -states when applied to the rotation matrix elements.

Note also the minus sign which appears in front of $C_-(J, M)$. Similarly:

$$\begin{aligned}
 J_- D_{M\Omega}^J(\alpha\beta\gamma) \\
 = -C_+(J, M) D_{M+1, \Omega}^J(\alpha\beta\gamma) \quad \dots (95)
 \end{aligned}$$

Now we investigate action of J'_+ and J'_- . Rotation of coordinates is a unitary transformation; therefore, if Eq. (15) holds in the laboratory coordinate system then:

$$\begin{aligned}
 \langle r'_1, r'_2, \dots, r'_k | J'_{\pm} | n J \Omega \rangle \\
 = C_{\pm}(J, \Omega) \langle r'_1, r'_2, \dots, r'_k | n J, \Omega \pm 1 \rangle, \quad \dots (96)
 \end{aligned}$$

must hold in the rotated coordinate system. Substituting Eq. (71) into both sides of Eq. (96) and proceed as before allows us to obtain Eq. (18) and

$$\begin{aligned}
 J'_{\pm} D_{M\Omega}^J(\alpha\beta\gamma) \\
 = C_{\pm}(J, \Omega) D_{M, \Omega \pm 1}^J(\alpha\beta\gamma) \quad \dots (97)
 \end{aligned}$$

Equations (18), (94), (95), and (97) are found by consistently applying standard commutator algebra. In comparison, Van Vleck's reversed angular momentum method would utilize different identities that are difficult to reconcile with our standard formalism. Note the unexpected signs and apparent anomalies in these equations (e.g., in Eq. (95) one sees that J_- raises M and introduces a minus sign). These results lose their mysterious appearance as one recalls that the D -matrix elements cannot be treated as standard angular momentum eigen-functions. Standard angular momentum eigenfunctions show only one but not two magnetic quantum numbers. Expressions like $J_{\pm} D_{M\Omega}^{J*}(\alpha\beta\gamma)$ show several levels of complexity: First, complex conjugation is in effect prompting considerations whether the roles of the raising and lowering operator are reversed. Second, and more importantly, there are two magnetic quantum numbers present. The Appendix shows that evaluation of commutators acting on $D_{M\Omega}^{J*}(\alpha\beta\gamma)$ matrix elements rather than on physical eigenfunctions generates relations that one might very well label "anomalous".

6. THE BORN-OPPENHEIMER APPROXIMATION

Electronic, $\langle r'_1 r'_2 \dots r'_{N-1} \rho \zeta | n \rangle$, and vibrational, $\langle r | v_n \rangle$, basis functions are defined, and Eq. (63) is rewritten to read:

$$\begin{aligned}
 \langle r_1 r_2 \dots r_N r | nJM \rangle &= B(r) \left[\mathbf{J}'^2 + \frac{L_+ L_- + L_- L_+}{2} + L_z'^2 + \mathbf{S}'^2 - \right. \\
 &= \sum_{\Omega=-J}^J \sum_n' \sum_{v_n}' \langle r_1' r_2' \dots r_N' | n \rangle \langle r | v_n \rangle & (J_+ L_- + J_- L_+ + 2J_z L_z') - \\
 &D_{M\Omega}^{J*}(\alpha\beta\gamma), \quad \dots (98) & (J_+ S_- + J_- S_+ + 2J_z S_z') \\
 & & \left. + (L_+ S_- + L_- S_+ + 2L_z S_z') \right]. \quad \dots (100)
 \end{aligned}$$

where a primed summation indicates summation over discrete states and integration over continuum states. The first order Born-Oppenheimer approximation (e.g., see Ref. [26]) consists of omitting the summations over n and v_n . A different electronic eigenfunction is obtained for each value of the internuclear distance. That is, the electronic eigenfunction becomes a parametric function of r , which is denoted by writing the electronic eigenfunction as $\langle r_1' r_2' \dots r_{N-1}' \rho \zeta; r | n \rangle$,

$$\begin{aligned}
 \langle r_1 r_2 \dots r_N r | nJM \rangle &= \sum_{\Omega=-J}^J \langle r_1' r_2' \dots r_{N-1}' \rho \zeta; r | n \rangle \langle r | v_n \rangle \\
 &D_{M\Omega}^{J*}(\alpha\beta\gamma) \quad \dots (99)
 \end{aligned}$$

The physical justification for omitting the summations from Eq. (99) is, of course, the smallness of the electronic mass in comparison to the nuclear mass. In the following the subscript on v_n will be dropped.

7. HUND CASE (a) HAMILTONIAN MATRIX ELEMENTS

Some example matrix elements of the Hamiltonian are calculated here. Standard results will be obtained by application of standard methods. One of the many terms in the Hamiltonian is the kinetic energy of rotation of the nuclei, called the rotational Hamiltonian:

$$\begin{aligned}
 H_{\text{rot}} &= \frac{\hbar}{4\pi c \mu r^2} \mathbf{R}^2 \\
 &= B(r) \mathbf{R}^2 \\
 &= B(r) (\mathbf{J} - \mathbf{L} - \mathbf{S})^2
 \end{aligned}$$

The transformation of the operators from laboratory to molecular coordinates is made because our investigation of the fundamental and geometrical symmetries has shown that the eigenfunction is partially separable in the rotating coordinate system, Eq. (63). A pragmatic comment is that calculation of matrix elements is easier if the operators are expressed in the rotating coordinate system. Reversal of motion is not an issue here. The steps shown above merely take advantage of invariance under proper rotations.

A familiar result from Van Vleck's reversed angular momentum method would be that operation of $J_+ S_-$ on Hund's case (a) eigenfunction lowers both Ω and Σ . One's intuition might be that J_+ should be a raising operator, or if J_+ indeed lowers Ω , why then is S_- not a raising operator? The operator J_+ lowers Ω when applied to the case (a) eigenfunction, Eq. (44), because the operator acts on the complex conjugate of the D -matrix element, not on the angular momentum ket $|J\Omega\rangle$. The operation of S_- is completely standard, it lowers Σ because it acts on the spin ket $|S\Sigma\rangle$. Thus, the contribution of $J_+ S_-$ to the Hamiltonian matrix is $B_v C_-(J, \Omega) C_-(S, \Sigma) \delta(\Omega, \Omega + 1)$. The minus sign carried by $J_+ S_-$ in Eq. (100) is canceled by the minus sign in Eq. (18).

The phase conventions, i.e., sign conventions, which are part of Van Vleck's method produce the same results but for different reasons. Equation (18) is usually not used in Van Vleck's method, leading to occurrence of the opposite sign on the right. Usually a minus sign is introduced for the action of S_{\pm} on the standard ket $|S\Sigma\rangle$. The introduction of this particular sign leads, in turn, to the same result as found with standard methods. In passing we note that Eqs (12) and (13) of Zare et al. [23] carry opposite signs, but these two opposite signs cancel out in the matrix elements of the product $J_+ S_-$.

Lefebvre-Brion and Field [4] use the standard phase convention for the spin kets, their Eq. (2.4.28). The spin-rotation interaction:

$$\begin{aligned}
 H_{SR} &= \gamma(r) \mathbf{N} \cdot \mathbf{S} \\
 &= \gamma(r) (\mathbf{J} - \mathbf{S}) \cdot \mathbf{S} \\
 &= \gamma(r) (\mathbf{J} \cdot \mathbf{S} - \mathbf{S}^2) \\
 &= \gamma(r) \left[\frac{J_+ S_- + J_- S_+}{2} + J_z S_z - S^2 \right], \dots (101)
 \end{aligned}$$

contains terms having the same dependence on J and S as terms in the rotational Hamiltonian above ($\gamma(r)$ is the spin-rotation parameter, not the third Euler angle). Here

$$J_+ S_- \text{ contributes } -\frac{1}{2} \gamma_v C_-(J, \Omega) C_-(S, \Sigma) \delta(\Omega, \Omega + 1).$$

This result agrees with Zare et al. [23] but shows a disparity in sign with Lefebvre-Brion and Field [4]. The latter authors show the opposite sign on the right side of Eq. (18), see their Eqs (1.3.23) and (1.3.25). When combining the opposite sign with sign conventions for the spin kets, it maybe difficult to find correct signs for the spin-rotation matrix elements.

8. DIATOMIC LINE STRENGTHS

The probability of a quantum transition is controlled by the absolute square of the transition moment of the operator responsible for the transition. The line strength is defined by:

$$\begin{aligned}
 S(n'J', n''J'') &= \sum_{M'=-J'}^{J'} \sum_{M''=-J''}^{J''} \left| \langle n'J'M' | T_l^{(k)}(r_1 r_2 \dots r_N r) | n''J''M'' \rangle \right|^2, \dots (102)
 \end{aligned}$$

in which $T_l^{(k)}$ is the l -th component of the irreducible tensor operator of degree k . A single prime denotes the upper state, double primes the lower. As Eq. (63) holds for the diatomic eigenfunction:

$$\begin{aligned}
 T_l^{(k)}(r_1 r_2 \dots r_N r) &= \sum_{\lambda=-k}^k T_{\lambda}^{(k)}(r'_1 r'_2 \dots r'_{N-1} \rho \zeta r) D_{l\lambda}^{k*}(\alpha\beta\gamma), \dots (103)
 \end{aligned}$$

must hold for any diatomic operator. Hund's case (a) transition moments of the components of the operator $\mathbf{T}^{(k)}$ are therefore given by:

$$\begin{aligned}
 \langle n'J'M' | T_l^{(k)}(r_1 r_2 \dots r_N r) | n''J''M'' \rangle &\approx \\
 &= \frac{\sqrt{(2J'+1)(2J''+1)}}{8\pi^2} \\
 &\sum_{\lambda=-k}^k \langle n'v' | T_{\lambda}^{(k)}(r'_1 r'_2 \dots r'_{N-1} \rho \zeta r) \\
 &| n''v'' \rangle \delta(S', S'') \delta(\Sigma', \Sigma'') \times \\
 &\int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} D_{M'\Omega'}^{J'}(\alpha\beta\gamma) D_{l\lambda}^{k*}(\alpha\beta\gamma) D_{M''\Omega''}^{J''*} \\
 &(\alpha\beta\gamma) \sin \beta d\alpha d\beta d\gamma \dots (104)
 \end{aligned}$$

The integral over the Euler angles is the product of two Clebsch-Gordan coefficients:

$$\begin{aligned}
 \langle n'J'M' | T_l^{(k)}(r_1 r_2 \dots r_N r) | n''J''M'' \rangle &\approx \\
 &= \sqrt{\frac{2J''+1}{2J'+1}} \sum_{\lambda=-k}^k \langle n'v' | T_{\lambda}^{(k)}(r'_1 r'_2 \dots r'_{N-1} \rho \zeta r) \\
 &| n''v'' \rangle \langle J''M''kl | J'M' \rangle \langle J''\Omega''k\lambda | J'\Omega' \rangle. \dots (105)
 \end{aligned}$$

Forming the absolute square of the transition moment followed by summation over all M' and M'' gives the diatomic line strength in Hund's case (a) basis,

$$\begin{aligned}
 S(n'v'J', n''v''J'') &= S_{ev}(n'v', n''v'') S(J', J''), \dots (106)
 \end{aligned}$$

where the electronic-vibrational strength is given by:

$$\begin{aligned}
 S_{ev}(n'v', n''v'') &= \left| \langle v' | R_{n'n''}(r) | v'' \rangle \right|^2. \dots (107)
 \end{aligned}$$

The electronic transition moment is:

$$R_{n'n''}(r) = \langle n' | T_{\lambda}^{(k)}(r'_1 r'_2 \dots r'_N; r) | n'' \rangle. \dots (108)$$

The remaining factor, $S(J', J'')$, is the Hund's case (a) Hönl-London or rotational line strength factor:

$$\begin{aligned}
 S(J', J'') &= (2J''+1) \langle J''\Omega''k, \Omega' - \Omega'' | J'\Omega' \rangle^2 \\
 &\delta(S', S'') \delta(\Sigma', \Sigma''). \dots (109)
 \end{aligned}$$

With a Taylor's expansion of the electronic transition moment,

$$R_{n'n''}(r) = a_0 + a_1 r + a_2 r^2 + \dots, \quad \dots (110)$$

and the Franck-Condon factor:

$$q(v', v'') = \langle v' | v'' \rangle^2, \quad \dots (111)$$

and the r -centroids:

$$\bar{r}_j(v', v'') = \frac{\langle v' | r^j | v'' \rangle}{\langle v' | v'' \rangle}, \quad \dots (112)$$

are defined, the electronic-vibrational strength can be written as a product of two factors:

$$S_{\text{ev}}(n'v', n''v'') = |a_0 + a_1 \bar{r}_1(v', v'') + a_2 \bar{r}_2(v', v'') + \dots|^2 q(v', v''). \quad \dots (113)$$

The electronic strength is defined:

$$S_e(n'v', n''v'') = |a_0 + a_1 \bar{r}_1(v', v'') + a_2 \bar{r}_2(v', v'') + \dots|^2. \quad \dots (114)$$

The overall diatomic line strength is:

$$S(n'v'J', n''v''J'') = S_e(n'v', n''v'') q(v', v'') S(J', J''). \quad \dots (115)$$

The diatomic line strength is the product of the electronic strength, $S_e(n'v', n''v'')$, and two unitless strength factors, the Franck-Condon factor, $q(v', v'')$, and the Hönl-London factor, $S(J', J'')$. In molecules with small reduced mass μ and, therefore, large $B(r)$, rotational distortion of the vibrational states gives the Franck-Condon factors and r -centroids J' and J'' dependence.

Equation (115) still holds in the Hund's case (b) basis but the Hönl-London factor is now given in terms of a Wigner $6j$ -symbol rather than a Clebsch-Gordan coefficient:

$$S(J', J'') = (2J' + 1)(2N'' + 1)(2J'' + 1) \langle N'' \Lambda'' k, \Lambda' - \Lambda'' | N' \Lambda' \rangle^2 \left\{ \begin{matrix} S & N & J \\ k & J' & N' \end{matrix} \right\}^2 \delta(S', S''). \quad \dots (116)$$

Calculation of the total line strength requires, obviously, knowledge of the irreducible tensor responsible for the transition. However, the Hönl-London factor depends only on the degree k of the tensor. For $k = 1$, Eqs (109) and (116) give Hönl-London factors for

electric dipole transitions. For $k = 2$, they give the factors for two-photon or Raman transitions, and so forth.

The Hund's cases (a) and (b) eigenfunctions will rarely diagonalize the Hamiltonian to a satisfactory degree of approximation. Since efficient numerical algorithms exist for the diagonalization of symmetric matrices, this is not a serious impediment. Diagonalization of the Hamiltonian gives the term values and the orthogonal matrix U which diagonalized the Hamiltonian. The equation for the line strength must be modified to include the matrices U' and U'' but this is again a minor complication.

Of practical concern is the determination of term combinations that will indeed lead to spectral lines from the upper term values for a fixed J' and lower term values for a fixed J'' . A well established procedure for finding allowed and forbidden lines is based on invoking parity selection rules. An algorithm which correctly gives the parity of states for many different types of states is difficult to devise. However, the parity selection rules can, with no loss of rigor, be replaced by the angular momentum selection rules. A transition for which the Hönl-London factor vanishes is forbidden. One using the parity selection rules must write a new computer program each time he encounters a different type of transition. One using the angular momentum selection rules can write a single program which handles a wide variety of transitions, see Hornkohl et al. [28].

9. APPLICATIONS IN STUDY OF MOLECULAR SPECTRA FOLLOWING LASER-INDUCED OPTICAL BREAKDOWN

Selected diatomic molecular spectra are computed by use of so-called line strength files. For isolated molecular transitions, the Franck-Condon factors are found by solving the radial Schrödinger equation numerically, and the Hönl-London factors are obtained by numerical diagonalization of the rotational and fine-structure Hamiltonian, Hornkohl et al. [28]. For the computation of a diatomic spectrum, typically the temperature and spectral resolution is specified, and in turn, non-linear fitting routines may be used to infer the spectroscopic temperature. For a recent summary on laser-induced breakdown spectroscopy see Miziolek et al. [29], Cremers and Radziemski [30], and Singh and Thakur [31].

Of interest are diatomic molecules such as AlO, C₂, CH, CN, CrF, N₂⁺ 1st Neg, N₂ 1st Pos, N₂ 2nd Pos, NH, NO, OH. Accurate line-strength files are in use for

spectroscopic analysis with the so-called Boltzmann Equilibrium Spectrum Program (BESP), Hornkohl and Parigger [32]. The BESP is used, for example, in the analysis of laser-induced optical breakdown and laser-induced fluorescence.

Figures 1–7 show selected synthetic spectra for OH, AIO, C₂ Swan band overview (pro-gression) and selected sequences $\Delta v = 0, \pm 1$ of the C₂ Swan Band, and CN, respectively.

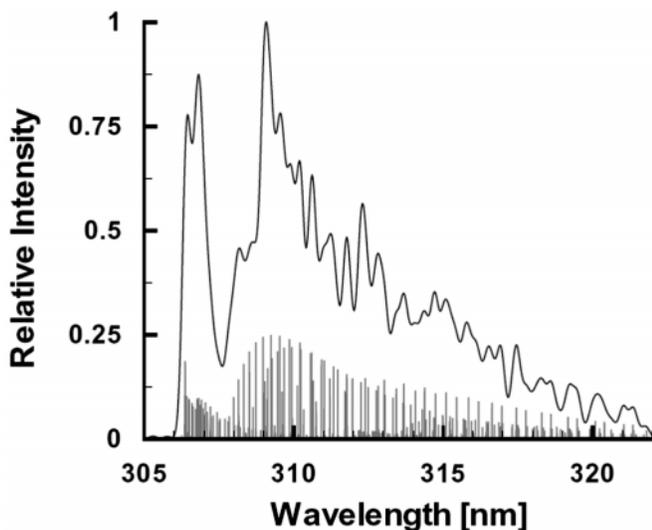


Fig. 1: Computed spectrum of the A²Σ → X²Π uv band of OH, T = 4000 K, for spectral resolutions of $\Delta\tilde{\nu} = 32 \text{ cm}^{-1}$ (top) and $\Delta\tilde{\nu} = 0.2 \text{ cm}^{-1}$ (bottom) of the $\Delta v = 0$ sequence

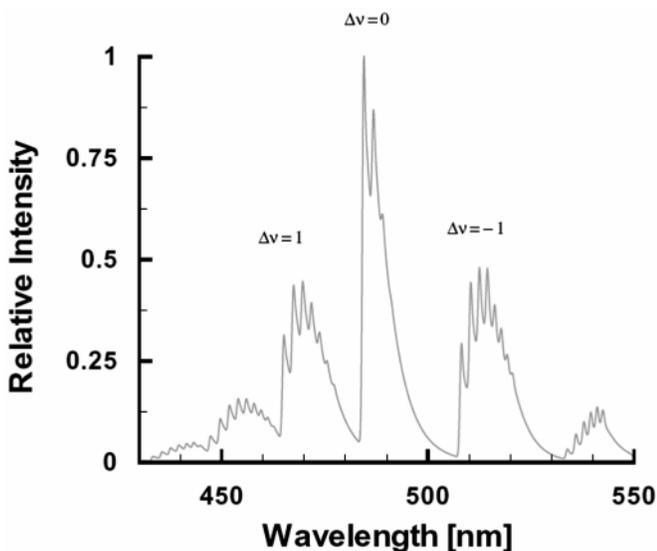


Fig. 2: Computed spectrum of the AIO B²Σ⁺ → X²Σ⁺ band, T = 4000 K, for a spectral resolution of $\Delta\tilde{\nu} = 32 \text{ cm}^{-1}$. Indicated are the $\Delta v = 0, \pm 1$ Sequences of the AIO progression

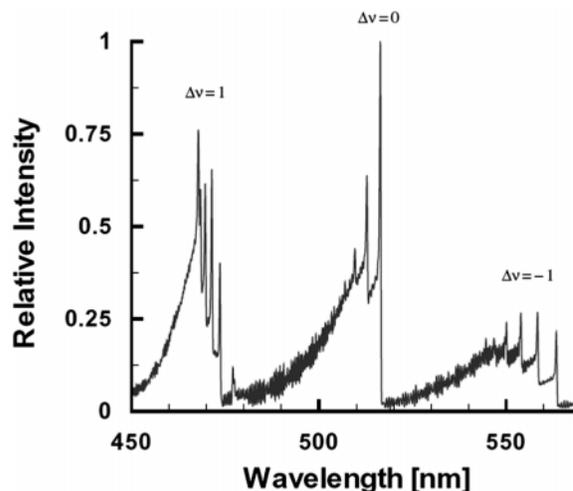


Fig. 3: Computed spectrum of C₂ swan d³Π_g → a³Π_u band progression, T = 8000 K, for a spectral resolution of $\Delta\tilde{\nu} = 12 \text{ cm}^{-1}$. Indicated are the $\Delta v = 0, \pm 1$ sequences of the C₂ progression

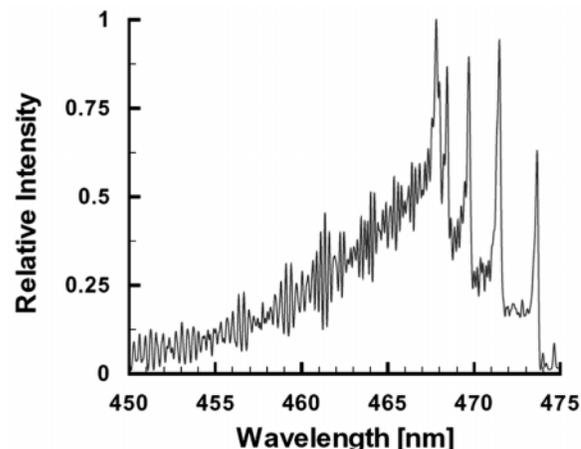


Fig. 4: C₂ swan d³Π_g → a³Π_u band $\Delta v = +1$ sequence, T = 8000 K, $\Delta\tilde{\nu} = 6 \text{ cm}^{-1}$

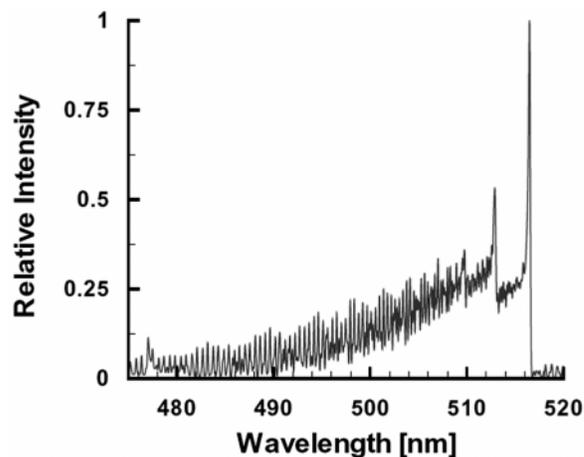


Fig. 5: C₂ swan d³Π_g → a³Π_u band $\Delta v = 0$ sequence, T = 8000 K, $\Delta\tilde{\nu} = 6 \text{ cm}^{-1}$

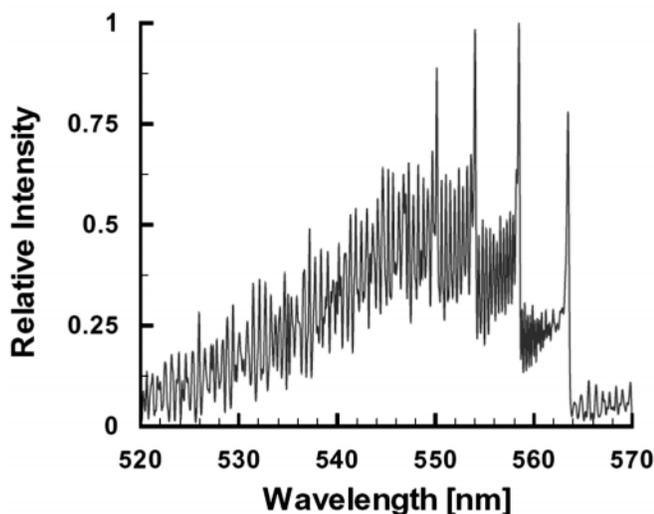


Fig. 6: C_2 Swan $d^3\Pi_g \rightarrow a^3\Pi_u$ band $\Delta v = -1$ sequence, $T = 8000$ K, $\Delta\tilde{\nu} = 6$ cm^{-1}

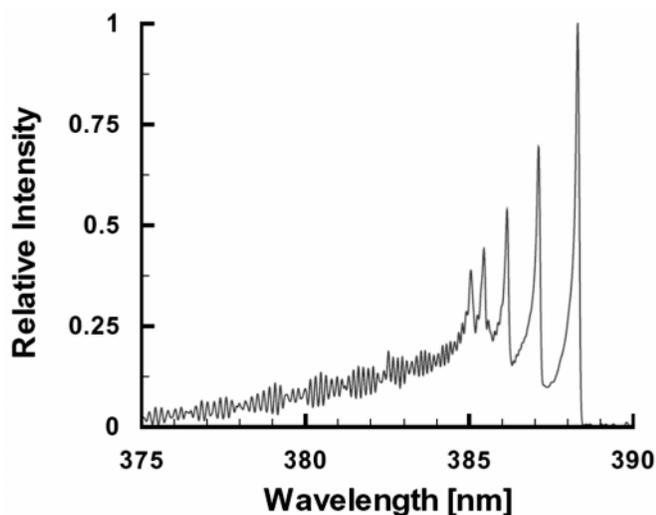


Fig. 7: Computed spectrum of the CN violet $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ band, $T = 8000$ K, for a spectral resolution of $\Delta\tilde{\nu} = 6$ cm^{-1} of the $\Delta v = 0$ sequence

These synthetic spectra have been instrumental in the analysis of laser-induced optical break-down and in general analysis of diatomic molecular spectra, see for example Refs. [33 – 40].

10. CONCLUSIONS

The fully standard methods allow us to compute diatomic spectra. A proper rotation of coordinates preserves the commutation formulae which are customarily taken to be the definition of angular momentum. We compared and contrasted our approach with Klein's anomalous angular momentum commutators and Van Vleck's method. The fully standard method yields results consistent with experimental data. An essential point is

that individual matrix elements of the rotation operator are not standard angular momentum eigenfunctions. It is then clear why the standard formulae for the raising and lowering operators do not apply to Hund's cases *a* and *b* diatomic eigenfunctions. The standard formulae must be replaced by equations which give the effects of the raising and lowering operators on the complex conjugate of *D*-matrix elements. The rigorous treatment of diatomic molecular spectra allows us to accurately compute molecular spectra. Applications include diagnostics of molecular recombination spectra following laser-induced optical breakdown.

APPENDIX A APPLYING ANGULAR MOMENTUM COMMUTATORS TO ROTATION MATRIX ELEMENTS

General relations for commutators are typically obtained by applying the commutator to an abstract ket describing a physical state. Alternatively, in the Schrödinger representation the commutators are obtained by applying differential operators to physical eigenfunctions. In this appendix we demonstrate how two anomalous results may occur. We apply $[J_x, J_y]$ and $[J_y, J_x]$ to the rotation matrix elements $D_{M\Omega}^{J*}(\alpha\beta\gamma)$.

The commutator $[J_x, J_y]$ is evaluated using:

$$\begin{aligned} [J_x, J_y] &= \left[\frac{1}{2}(J'_+ + J'_-), \frac{1}{2i}(J'_+ - J'_-) \right] \\ &= -\frac{i}{2}[J'_-, J'_+] \end{aligned} \quad \dots (A1)$$

and Eq. (18) which for convenience is repeated here

$$\begin{aligned} J'_\pm D_{M\Omega}^{J*}(\alpha\beta\gamma) \\ = -C_\mp(J, \Omega) D_{M, \Omega \mp 1}^{J*}(\alpha\beta\gamma) \end{aligned} \quad \dots (A2)$$

Successive application of the operators in the rotated frame of reference yields the intermediate result:

$$\begin{aligned} -\frac{i}{2}[J'_-, J'_+] D_{M\Omega}^{J*}(\alpha\beta\gamma) \\ = -\frac{i}{2}(C_+(J, \Omega - 1)C_-(J, \Omega) - \\ C_-(J, \Omega + 1)C_+(J, \Omega)) D_{M\Omega}^{J*}(\alpha\beta\gamma) \end{aligned} \quad \dots (A3)$$

which after inserting (compare Eq. (16))

$$C_{\pm}(J, \Omega) = \sqrt{(J \mp \Omega)(J \pm \Omega + 1)}, \quad \dots \text{(A4)}$$

$$[J_y, J_{y'}] D_{M\Omega}^{J*}(\alpha\beta\gamma) = 0. \quad \dots \text{(A8)}$$

leads to:

$$[J_{x'}, J_{y'}] D_{M\Omega}^{J*}(\alpha\beta\gamma) = -i\Omega D_{M\Omega}^{J*}(\alpha\beta\gamma). \quad \dots \text{(A5)}$$

It might be tempting to conclude the anomalous commutator relations, Eq. (4), in the rotated molecular frame from this identity (Eq. (A5)). However, the rotation matrix elements contain two quantum numbers M and Ω , one too many to represent a physical eigenfunction. Similarly, $[J_y, J_{y'}]$ is evaluated using:

$$[J_y, J_{y'}] = \left(\begin{array}{l} -\frac{1}{4} [J_+, J_+] - \frac{1}{4} [J_-, J_-] + \\ \frac{1}{4} [J_+, J_-] + \frac{1}{4} [J_-, J_+] \end{array} \right), \quad \dots \text{(A6)}$$

and applying it to the rotation matrix elements $D_{M\Omega}^{J*}(\alpha\beta\gamma)$. Note $J_{y'}$ acts on Ω (see Eq. (18)) while J_y acts on M (see Eq. (92)). The intermediate step is given here:

$$\begin{aligned} [J_y, J_{y'}] D_{M\Omega}^{J*}(\alpha\beta\gamma) &= +\frac{1}{4} C_-(J, \Omega) J_+ D_{M\Omega-1}^{J*}(\alpha\beta\gamma) + \\ &\frac{1}{4} C_+(J, M) J'_+ D_{M+1\Omega}^{J*}(\alpha\beta\gamma) \\ &+ \frac{1}{4} C_+(J, \Omega) J_- D_{M\Omega+1}^{J*}(\alpha\beta\gamma) + \\ &\frac{1}{4} C_-(J, M) J'_- D_{M-1\Omega}^{J*}(\alpha\beta\gamma) \\ &- \frac{1}{4} C_+(J, \Omega) J_+ D_{M\Omega+1}^{J*}(\alpha\beta\gamma) - \\ &\frac{1}{4} C_+(J, M) J'_- D_{M+1\Omega}^{J*}(\alpha\beta\gamma) \\ &- \frac{1}{4} C_-(J, \Omega) J_- D_{M\Omega-1}^{J*}(\alpha\beta\gamma) - \\ &\frac{1}{4} C_-(J, M) J'_+ D_{M-1\Omega}^{J*}(\alpha\beta\gamma) \quad \dots \text{(A7)} \end{aligned}$$

which reduces to

Again, one might be tempted to falsely conclude that Eq. (A8) is a general commutator relation that also applies to angular momentum states.

REFERENCES

- [1] J.H. Van Vleck, "Rev. Mod. Phys.", **23**, 213, (1951).
- [2] O. Klein, Z. Physik, **58**, 730, (1929).
- [3] J. Brown and A. Carrington, "Rotational Spectroscopy of Diatomic Molecules", Cambridge Univ. Press, Cambridge (2003).
- [4] H. Lefebvre-Brion and R.W. Field, "The Spectra and Dynamics of Diatomic Molecules", Elsevier, Amsterdam (2004).
- [5] P.R. Bunker and P. Jensen, "Fundamentals of Molecular Spectroscopy", IOP Publishing, Bristol 2005.
- [6] J.O. Hornkohl and C. Parigger, "Am. J. Phys.", **64**, 623, (1996).
- [7] A. Messiah, "Quantum Mechanics", **1 and 2**, North Holland, Amsterdam (1962).
- [8] A.S. Davydov, "Quantum Mechanics", Pergamon Press, Oxford (1965).
- [9] H. Goldstein, "Classical Mechanics", 2nd ed., Addison-Wesley, Reading (1981).
- [10] M.E. Rose, "Elementary Theory of Angular Momentum", John Wiley and Sons, New York (1957).
- [11] D.M. Brink and G.R. Satchler, "Angular Momentum", Oxford Univ. Press, Oxford (1968).
- [12] M. Tinkham, "Group Theory and Quantum Mechanics", McGraw-Hill, New York (1964).
- [13] D.A. Varshalovich, A.N. Moskalev, and V.K. Khersonskii, "Quantum Theory of Angular Momentum", World Scientific, Singapore (1988).
- [14] K. Gottfried, "Quantum Mechanics", Addison-Wesley, Reading (1989).
- [15] G. Baym, "Lectures on Quantum Mechanics", Benjamin/Cummings, Reading (1969).
- [16] B.W. Shore and D.H. Menzel, "Principles of Atomic Spectra", Addison-Wesley, Reading (1968).
- [17] B.R. Judd, "Angular Momentum Theory for Diatomic Molecules", Academic Press, New York (1975).
- [18] M. Mizushima, "The Theory of Rotating Diatomic Molecules", John Wiley & Sons, New York (1975).
- [19] K.F. Freed, "J. Chem. Phys.", **45**, 4214, (1966).
- [20] I. Kovacs, "Rotational Structure in the Spectra of Diatomic Molecules", American Elsevier, New York (1969).

- [21] J.T. Hougen, "The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules", N.B.S. Monograph 115, U.S. Government Printing Office, Washington, D.C. (1970).
- [22] A. Carrington, D.H. Levy, and T.A. Miller, "Adv. Chem. Phys." **18**, 149, (1970).
- [23] R.N. Zare, A.L. Schmeltekopf, W.J. Harrop, and D.L. Albritton, "J. Mol. Spectrosc.", **46**, 37, (1973).
- [24] J.M. Brown and B.J. Howard, "Mol. Phys.", **31**, 1517, (1976).
- [25] P.R. Bunker, "J. Mol. Spectrosc.", **28**, 422, (1968).
- [26] B.H. Bransden and C.J. Joachain, "Physics of Atoms and Molecules", 2nd edition, Pearson Education Limited, London (2003).
- [27] G. Herzberg, "Molecular Spectra and Molecular Structure", *I. Spectra of Diatomic Molecules*, Van Nostrand, Princeton, (1950), pp. 213.
- [28] J.O. Hornkohl, C.G. Parigger, and L. Nemes, "Appl. Opt.", **44**, 3686, (2005).
- [29] A.W. Miziolek, V. Palleschi, and I. Schechter, eds. "Laser-Induced Breakdown Spectroscopy (LIBS), Fundamentals and Applications", Cambridge University Press, New York, NY (2006).
- [30] D.E. Cremers and L.J. Radziemski, "Handbook of Laser-Induced Breakdown Spectroscopy", Cambridge University Press, New York, NY, (2006).
- [31] J.P. Singh and S.N. Thakur, eds. "Laser Induced Breakdown Spectroscopy", Elsevier Science, New York, NY (2007).
- [32] J.O. Hornkohl and C.G. Parigger, "Boltzmann Equilibrium Spectrum Program (BESP)", *The University of Tennessee Space Institute*, Tullahoma, Tenn, USA, 2002, <http://view.utsi.edu/besp/>.
- [33] C.G. Parigger, J.O. Hornkohl, and L. Nemes, "Int. J. Spectroscopy", 2010, 593820, (2010).
- [34] J.O. Hornkohl, L. Nemes, and C.G. Parigger, "Spectroscopy, Dynamics and Molecular Theory of Carbon Plasmas and Vapors, in Advances in the Understanding of the Most Complex High-Temperature Elemental System", L. Nemes and S. Irle, Eds., World Scientific, 2009.
- [35] C.G. Parigger, "Laser-induced Breakdown in Gases: Experiments and Simulation, in Laser Induced Breakdown Spectroscopy", A.W. Miziolek, V. Palleschi, and I. Schechter, Eds., Chapter 4, Cambridge University Press, New York, NY (2006).
- [36] L. Nemes, A.M. Keszler, J.O. Hornkohl, and C.G. Parigger, "Appl. Opt.", **44**, 3661, (2005).
- [37] C.G. Parigger, G. Guan, and J.O. Hornkohl, "Appl. Opt." **42**, 5986, (2003).
- [38] I.G. Dors, C. Parigger, and J.W. L. Lewis, "Opt. Lett.", **23**, 1778, (1998).
- [39] C. Parigger, D.H. Plemmons, J.O. Hornkohl, and J.W.L. Lewis, "J. Quant. Spectrosc. Radiat. Transfer", **52**, 707, (1994).
- [40] J.O. Hornkohl, C. Parigger, and J.W.L. Lewis, "J. Quant. Spectrosc. Radiat. Transfer", **46**, 405, (1991).