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5.80 Small-Molecule Spectroscopy and Dynamics
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Lecture # 14 Supplement

ROTATION AND ANGULAR MOMENTA

The matrix elements for the rotational Hamiltonian matrix will be derived. The matrix elements of several angular momentum operators will be listed, not derived, and several important commutation rules will be stated.

I. Nomenclature

Following is a list of quantum numbers used to label the rotational energy levels of diatomic molecules in the presence of spin and orbital angular momenta:

		Projection on Internuclear Axis
Total angular momentum	J	$J_z = \Omega = \Lambda + \Sigma$
Orbital angular momentum	L	$L_z = \Lambda$
Spin	S	$S_z = \Sigma$
End-over-end rotation	R	none, $R_z = 0$
$\tilde{J} - \tilde{S}$	N	$N_z = L_z$
Projection of J on lab-fixed axis	M	—

$$J \equiv R + L + S \quad (1)$$

Electronic states are usually designated as follows: The component of the orbital angular momentum along the internuclear axis, Λ , is represented by a capital Greek letter

$$\begin{array}{cccccc} \Lambda = 0 & 1 & 2 & 3 & 4 & \\ & \Sigma & \Pi & \Delta & \Phi & \Gamma \end{array}$$

There is a left superscript corresponding to the spin-multiplicity of the state. The spin-multiplicity is $2S + 1$, where S is the total electron spin. There is a right subscript, Ω , which corresponds to the projection of J on the internuclear axis. So an electronic state is designated $^{2S+1}\Lambda_{\Omega}$. For example $^3\Delta_3$ means $S = 1$, $\Lambda = 2$, $\Omega = 3$.

Often there is a letter in front of this symbol which tells us which such state is meant. Transitions between states are usually specified as follows, regardless of whether the transition is emission or absorption:

- A. The upper state is listed first.
- B. The upper state quantum numbers are listed with a single prime, the lower state with double prime (and very rarely with no prime).
- C. Rotational transitions are specified as $P(J)$, $Q(J)$, $R(J)$ (sometimes N , O , S , T also) where the letter indicates the change in the pattern-forming rotational quantum number, J in case (a) and N in case (b). $|\Delta J| \leq 1$. For simplicity the pattern-forming quantum number will be designated by J here. The J in parentheses is always J'' , the J of the lower level. The letter used has the meaning
- $$J' = \begin{array}{ccccccc} & N & O & P & Q & R & S & T \\ & J'' - 3 & J'' - 2 & J'' - 1 & J'' & J'' + 1 & J'' + 2 & J'' + 3. \end{array}$$
- D. Often two letters are used to specify a rotational transition: ${}^P Q(J)$. The lower letter tells you the change in J , the upper the change in N .
- E. The letter used to identify the electronic state obeys some rules too. A capital X implies the ground state. The excited states are usually labeled alphabetically in order of increase in energy. Capital letters are used for excited states of the same multiplicity (same value of spin S) as the ground state. Small letters are used for states of other multiplicities.
- F. There are other symbols which will be discussed later such as g and u , s and a , $+$ and $-$, e and f .

II. The Rotational Hamiltonian

The rotational Hamiltonian is deceptively simple in appearance

$$\mathbf{H} = B\mathbf{R}^2. \quad (2)$$

There are two complications. The first is that B is actually $B(r)$, thus it has off-diagonal matrix elements between the vibrational eigenfunctions which correspond to the molecular potential curve $V(r)$. This problem will be treated by second order perturbation theory in a later handout. Second, the matrix elements of \mathbf{R}^2 are exceptionally nontrivial. Our first task will be to re-express the \mathbf{R}^2 operator in terms of operators whose matrix elements are easily derived.

$$\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S} \quad (3)$$

Note that \mathbf{R} has no z -component because it is associated with end-over-end molecular rotation. Another way of looking at this is that there can be no rotational angular momentum about the internuclear axis because the nuclei are point masses and the moment of inertia for such rotation is zero. Thus

$$\mathbf{R}^2 = \mathbf{R}_x^2 + \mathbf{R}_y^2 \quad (4)$$

Let us define ladder-type operators of the form

$$\begin{aligned}\mathbf{R}_+ &= \mathbf{R}_x + i\mathbf{R}_y \\ \mathbf{R}_- &= \mathbf{R}_x - i\mathbf{R}_y\end{aligned}\quad (5)$$

Thus

$$\mathbf{R}^2 = \frac{1}{2}(\mathbf{R}_+\mathbf{R}_- + \mathbf{R}_-\mathbf{R}_+).\quad (6)$$

Equation (6) is not more complicated than it needs to be because angular momentum operators have the obnoxious property of not commuting — that means that often

$$\mathbf{A} \cdot \mathbf{B} \neq \mathbf{B} \cdot \mathbf{A}.\quad (7)$$

A commutator is defined $[\mathbf{A}, \mathbf{B}] = \mathbf{A} \cdot \mathbf{B} - \mathbf{B} \cdot \mathbf{A}$. We will need to know the following commutators:

$$[\mathbf{J}_\pm, \mathbf{J}_\mp] = \pm i\hbar\mathbf{J}_z\quad (8)$$

$$[\mathbf{J}_\pm, \mathbf{V}_\mp] = \pm i\hbar\mathbf{V}_z \quad \text{where } \mathbf{V} = \mathbf{L}, \mathbf{S}\quad (9)$$

$$[\mathbf{V}_\pm, \mathbf{V}_\mp] = \pm i\hbar\mathbf{V}_z\quad (10)$$

$$[\mathbf{L}_\pm, \mathbf{S}_\mp] = 0\quad (11)$$

Returning to our analysis of \mathbf{R}^2 , we know

$$\mathbf{R}_\pm = \mathbf{J}_\pm - \mathbf{L}_\pm - \mathbf{S}_\pm\quad (12)$$

$$\mathbf{R}_+\mathbf{R}_- = \mathbf{J}_+\mathbf{J}_- + \mathbf{L}_+\mathbf{L}_- + \mathbf{S}_+\mathbf{S}_- - (\mathbf{J}_+\mathbf{L}_- + \mathbf{L}_+\mathbf{J}_-) - (\mathbf{J}_+\mathbf{S}_- + \mathbf{S}_+\mathbf{J}_-) + (\mathbf{L}_+\mathbf{S}_- + \mathbf{S}_+\mathbf{L}_-)\quad (13)$$

Thus

$$\begin{aligned}\frac{1}{2}(\mathbf{R}_+\mathbf{R}_- + \mathbf{R}_-\mathbf{R}_+) &= \frac{1}{2}(\mathbf{J}_+\mathbf{J}_- + \mathbf{J}_-\mathbf{J}_+) + \frac{1}{2}(\mathbf{L}_+\mathbf{L}_- + \mathbf{L}_-\mathbf{L}_+) + \frac{1}{2}(\mathbf{S}_+\mathbf{S}_- + \mathbf{S}_-\mathbf{S}_+) \\ &\quad - \frac{1}{2}(\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+ + \mathbf{L}_+\mathbf{J}_- + \mathbf{L}_-\mathbf{J}_+) \\ &\quad - \frac{1}{2}(\mathbf{J}_+\mathbf{S}_- + \mathbf{J}_-\mathbf{S}_+ + \mathbf{S}_+\mathbf{J}_- + \mathbf{S}_-\mathbf{J}_+) \\ &\quad + \frac{1}{2}(\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+ + \mathbf{S}_+\mathbf{L}_- + \mathbf{S}_-\mathbf{L}_+)\end{aligned}\quad (14)$$

But

$$\frac{1}{2}(\mathbf{J}_+\mathbf{J}_- + \mathbf{J}_-\mathbf{J}_+) = \mathbf{J}_x^2 + \mathbf{J}_y^2 = \mathbf{J}^2 - \mathbf{J}_z^2\quad (15)$$

and similarly for the $\mathbf{L}_+\mathbf{L}_-$ and $\mathbf{S}_+\mathbf{S}_-$ terms. Next

$$\frac{1}{2}(\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+ + \mathbf{L}_+\mathbf{J}_- + \mathbf{L}_-\mathbf{J}_+) = (2\mathbf{J}_+\mathbf{L}_- + [\mathbf{L}_-, \mathbf{J}_+] + 2\mathbf{J}_-\mathbf{L}_+ + [\mathbf{L}_+, \mathbf{J}_-])\quad (16)$$

but since

$$[\mathbf{L}_-, \mathbf{J}_+] = -[\mathbf{L}_+, \mathbf{J}_-]$$

thus

$$\frac{1}{2}(\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+ + \mathbf{L}_+\mathbf{J}_- + \mathbf{L}_-\mathbf{J}_+) = (\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+). \quad (17)$$

A similar result is obtained for the \mathbf{J}, \mathbf{S} cross terms. For the \mathbf{L}, \mathbf{S} cross terms $[\mathbf{L}_\pm, \mathbf{S}_\mp] = 0$ so we get the same simplification but for a different reason. Collecting terms

$$\mathbf{R}^2 = (\mathbf{J}^2 - \mathbf{J}_z^2) + (\mathbf{S}^2 - \mathbf{S}_z^2) + (\mathbf{L}^2 - \mathbf{L}_z^2) - (\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+) - (\mathbf{J}_+\mathbf{S}_- + \mathbf{J}_-\mathbf{S}_+) + (\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+) \quad (18)$$

This operator algebra has been rigorous and no choice of basis set has yet been implied.

III. Matrix Elements

We are now ready to pick a basis set and evaluate the $B\mathbf{R}^2$ matrix elements. A convenient set of quantum numbers is n, Λ, S, Σ where n tells us which electronic state of quantum numbers Λ, S, Σ we mean (i.e., which potential curve). We also designate v to specify the exact vibrational eigenfunction that belongs to the potential curve indexed by n, Λ, S, Σ . Finally we specify Ω, \mathbf{J}, M . We will see that Ω is not a good quantum number but we preserve it as a useful index in specifying the spin-components of a state. M will not concern us because in the absence of applied magnetic or electric fields, M is always a good quantum number. Also, M does not appear in the rotational Hamiltonian or any of its field free matrix elements. Our basis functions are product functions

$$|v\rangle |n\Lambda S\Sigma\rangle |\Omega\mathbf{J}M\rangle.$$

We will need the following matrix elements

$$\langle (\Omega \mp 1)\mathbf{J}'M' | \mathbf{J}_\pm | \Omega\mathbf{J}M \rangle = \delta_{J'J} \delta_{M'M} \hbar [J \mp \Omega + 1] (J \pm \Omega)^{1/2} \quad (19)$$

$$\langle \Omega'J'M' | \mathbf{J}_z | \Omega\mathbf{J}M \rangle = \hbar \Omega \delta_{\Omega'\Omega} \delta_{J'J} \delta_{M'M} \quad (19a)$$

$$\langle n'\Lambda'S'(\Sigma \pm 1) | \mathbf{S}_\pm | n\Lambda S\Sigma \rangle = \delta_{\Lambda'\Lambda} \delta_{S'S} \hbar [(S \mp \Sigma)(S \pm \Sigma + 1)]^{1/2} \quad (20)$$

$$\langle n'\Lambda'S'\Sigma' | \mathbf{S}_z | n\Lambda S\Sigma \rangle = \delta_{\Lambda'\Lambda} \delta_{S'S} \delta_{\Sigma'\Sigma} \hbar \Sigma \quad (20a)$$

$$\langle n'(\Lambda \pm 1)S'\Sigma' | \mathbf{L}_\pm | n\Lambda S\Sigma \rangle = \delta_{S'S} \delta_{\Sigma'\Sigma} \hbar [(L \mp \Lambda)(L \pm \Lambda + 1)]^{1/2} \quad (21)$$

$$\langle n'\Lambda'S'\Sigma' | \mathbf{L}_z | n\Lambda S\Sigma \rangle = \delta_{S'S} \delta_{\Sigma'\Sigma} \delta_{\Lambda'\Lambda} \hbar \Lambda \quad (21a)$$

The matrix element for \mathbf{L}_\pm in equation (21) is a fake because it is usually not possible to know or specify L for a diatomic molecule. The Λ selection rule is left unchanged by this ambiguity, but the matrix element of (21) is usually left as an unspecified constant.

$$\langle \Omega'J'M' | \mathbf{J}^2 | \Omega\mathbf{J}M \rangle = \delta_{J'J} \delta_{\Omega'\Omega} \delta_{M'M} \hbar^2 J(J+1) \quad (22)$$

$$\langle n'\Lambda'S'\Sigma' | \mathbf{S}^2 | n\Lambda S\Sigma \rangle = \delta_{\Lambda'\Lambda} \delta_{S'S} \delta_{\Sigma'\Sigma} \hbar^2 S(S+1) \quad (23)$$

$$\langle n'\Lambda'S'\Sigma' | \mathbf{L}^2 | n\Lambda S\Sigma \rangle = \delta_{\Lambda'\Lambda} \delta_{S'S} \delta_{\Sigma'\Sigma} \quad (\text{unknown constant}) \quad (24)$$

The unknown constant of matrix element (24) is unknown due to our inability to specify L for a diatomic molecule.

It is now possible to write the matrix elements of $B\mathbf{R}^2$

$$\begin{aligned} & \langle v' | \langle n' \Lambda' S' \Sigma' | \langle \Omega' J' M' | B\mathbf{R}^2 | \Omega JM \rangle | n \Lambda S \Sigma \rangle | v \rangle \\ & = \hbar^2 \langle v' | B(r) | v \rangle \{ [J(J+1) - \Omega^2] + [S(S+1) - \Sigma^2] + [L_{\perp}^2] + \text{off-diagonal elements} \} \end{aligned} \quad (25)$$

Remember that \mathbf{L}_{\perp}^2 is some sort of unknown constant. The $\mathbf{J}_{\pm}\mathbf{L}_{\mp}$, $\mathbf{J}_{\pm}\mathbf{S}_{\mp}$, and $\mathbf{L}_{\pm}\mathbf{S}_{\mp}$ matrix elements are what make life difficult, because they are responsible for all of the non-diagonal matrix elements.

$\mathbf{J}_{+}\mathbf{L}_{-}$ decreases Ω and Λ by 1

$\mathbf{J}_{+}\mathbf{S}_{-}$ decreases Ω and Σ by 1

$\mathbf{L}_{+}\mathbf{S}_{-}$ increases Λ by 1, decreases Σ by 1, and of course Ω is left unchanged.

The $\mathbf{J}_{\pm}\mathbf{S}_{\mp}$ matrix elements are easily shown to be

$$\begin{aligned} & \langle (\Omega \mp 1) J' M' | \langle n' \Lambda' S' (\Sigma \mp 1) | \mathbf{J}_{\pm} \mathbf{S}_{\mp} | n \Lambda S \Sigma \rangle | \Omega JM \rangle \\ & = \hbar^2 \delta_{\Lambda' \Lambda} \delta_{S' S} \delta_{J' J} \delta_{M' M} [(S \pm \Sigma)(S \mp \Sigma + 1)(J \mp \Omega + 1)(J \pm \Omega)]^{1/2} \end{aligned} \quad (26)$$

It is now possible to write down the elements of the $B\mathbf{R}^2$ matrix for any electronic state and also for “perturbations” between electronic states. The terms responsible for such perturbations are the $\mathbf{J}_{\pm}\mathbf{L}_{\mp}$ and $\mathbf{L}_{\pm}\mathbf{S}_{\mp}$ matrix elements.

IV. Other Important Interactions

So far we have not considered a very important part of the Hamiltonian operator, the spin-orbit interaction. It is appropriate to consider the spin-orbit and other magnetic dipole-magnetic dipole interactions such as spin-spin and spin-rotation interactions simultaneously with the rotational part of the Hamiltonian because the energies involved are all of comparable magnitude. In the interest of simplicity I will not derive the correct forms of $\mathbf{H}_{\text{spin-orbit}}$, $\mathbf{H}_{\text{spin-spin}}$, and $\mathbf{H}_{\text{spin-rotation}}$, but will present a phenomenological form of these terms which has matrix elements nearly identical with the correct forms.

$$\mathbf{H}_{\text{spin-orbit}} = A\mathbf{L} \cdot \mathbf{S} \quad (27)$$

where A has the magic property of being able to change S by ± 1 . $A\mathbf{L} \cdot \mathbf{S}$ cannot have matrix elements off diagonal in J , M , or Ω .

$$\mathbf{L} \cdot \mathbf{S} = \mathbf{L}_z \mathbf{S}_z + \frac{1}{2}(\mathbf{L}_+ \mathbf{S}_- + \mathbf{L}_- \mathbf{S}_+) \quad (28)$$

$$\mathbf{H}_{\text{spin-rotation}} = \gamma \mathbf{R} \cdot \mathbf{S} \quad (29)$$

$$= \gamma(\mathbf{J} - \mathbf{L} - \mathbf{S}) \cdot \mathbf{S} \quad (30)$$

This is a small term and will usually be too small to observe.

$$\mathbf{H}_{\text{spin-spin}} = \frac{2}{3}\gamma(3\mathbf{S}_z^2 - \mathbf{S}^2) + \frac{1}{2}\alpha(\mathbf{S}_+^2 + \mathbf{S}_-^2) \quad (31)$$

The spin-spin term is intermediate in size between spin-orbit and spin-rotation and is usually observable. It is of great importance in determining the spin-splitting in $^2\Sigma$, $^3\Sigma$, $^4\Sigma$ states and in the Λ doubling of $^3\Pi$ states.