

Asymmetric Tops

(7.)

$$I_A \neq I_B \neq I_C$$

Rotational
Constants

$$A = \frac{h}{8\pi^2 I_A}$$

$$B = \frac{h}{8\pi^2 I_B}$$

$$C = \frac{h}{8\pi^2 I_C}$$

$$K = \frac{2B - A - C}{A - C} \text{ is Ray's asymmetry parameter}$$

$$K = -1$$

prolate

→

$$K = +1$$

oblate

$$J_{K, K_C} = J_{K, K_{+1}}$$

↑ ↑
not good quantum numbers.

For symmetric top $K = 0, \pm 1, \dots, \pm J$. Now, the asymmetry in the molecule allows us to distinguish the \pm projections of J . K_A (or K_{-1}) and K_C (or K_{+1}) are the projections of J in the limit of the molecule being prolate ($K = -1$) or oblate ($K = +1$). The real projections of J on the "prolate" or "oblate" axes in the molecule precess w/ time (not good quantum numbers).

Asymmetric Top Selection Rules

(8)

Depends on orientation of $\vec{\mu}$.

Note if $\vec{\mu}$ lies along multiple principle axes, then both sets of selection rules apply.

Electric Dipole

Selection Rules

$$\underline{\mu_A} \neq 0$$

$$\Delta J = 0, \pm 1 \quad \underline{\Delta K_a = 0, \pm 2, \dots} \quad \Delta K_c = \pm 1, \pm 3$$

$$\underline{\mu_B} \neq 0$$

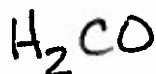
$$\Delta J = 0, \pm 1 \quad \underline{\Delta K_a = \pm 1, \pm 3, \dots} \quad \underline{\Delta K_c = \pm 1, \pm 3}$$

$$\underline{\mu_C} \neq 0$$

$$\Delta J = 0, \pm 1 \quad \Delta K_a = \pm 1, \pm 3, \dots \quad \underline{\Delta K_c = 0, \pm 2, \dots}$$

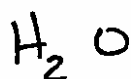
EXAMPLES :

(1)



$\mu_a = 2.33 \text{ D}$ so $\Delta J = 0, \pm 1$ w/
 $\Delta K_a = 0$ $\Delta K_c = \pm 1$
are prominent transitions

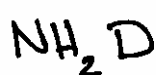
(2)



$\mu_b = 1.85 \text{ D}$ so $\Delta K_a = \pm 1$ $\Delta K_c = \pm 1$
both changing are the
prominent transitions

NOTE: A famous H_2O maser transition
 $J_{K_a K_c} = 6_{1,4} \rightarrow 5_{2,3}$ @ 22 GHz is
an example of $\Delta K_c = \pm 3$.

(3)



$$\mu_a = -0.18 \text{ D (weak!)}$$

$$\Delta K_a = 0 \quad \Delta K_c = \pm 1$$

are weak transitions

$$\mu_c = 1.46 \text{ D (strong) transitions}$$

so

$$\text{because } A_{\text{E.D.}} \sim \mu^2$$

$$\Delta K_a = \pm 1 \quad \Delta K_c = 0$$

are prominent
transitions

Ro - Vibrational Transitions

(7)

For a harmonic oscillator potential, the solutions to Schrödinger's Equation is

$$\psi \sim H_n(r) \cdot e^{-r^2/2}$$

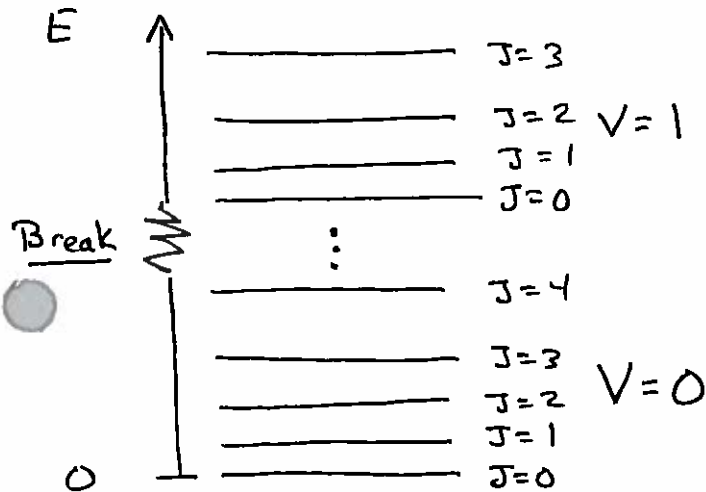
Hermite
polynomials

$$E = h\nu_0(v + \frac{1}{2})$$

Vibrational quantum number

$$\omega_0 = \sqrt{\frac{k}{\mu}} \leftarrow \begin{array}{l} \text{spring constant} \\ \text{reduced mass} \end{array} = 2\pi\nu_0$$

fundamental frequency



For $V=1-0$ $J_u \rightarrow J_l$

ΔJ

+2

+1

0

-1

-2

Notation

O(J_l)

P(J_l)

Q(J_l)

R(J_l)

S(J_l)

electric quadrupole

"dipole"

"P branch"

"quadrupole or dipole"

"Q branch"

"dipole"

"R branch"

etc.

electric quadrupole

Because real molecular potential is anharmonic

$\Delta V \geq 1$ allowed. $\Delta V \geq 2$ are usually weaker though ("overtones")

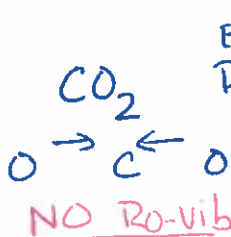
Examples: CO Electric Dipole $\Rightarrow \Delta J = \pm 1 \Rightarrow R(J_l)$ and $P(J_l)$ branches

$\Delta J = 0$ NOT allowed NO Q branch

However - in solid state, no rotations, so

Q branch observed as band.

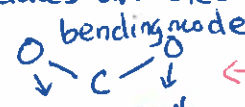
H₂ Electric Quadrupole $\Rightarrow \Delta J = 0, \pm 2 \Rightarrow O, Q,$ and S branches



Electric Dipole but
Depends on whether vibration induces an electric dipole
asymmetric stretch

O \rightarrow C \leftarrow O

Yes $\Delta J = \pm 1$
branches



Yes $\Delta J = 0$ allowed
Q, R branch allowed

When μ_e change is \perp to mol. axis, $\Delta J = 0$ allowed.

A NOTE ABOUT BANDHEADS

Ro-vibrational transition: $V_u \rightarrow V_e$ $J_u \rightarrow J_e$

$$\nu_{\text{rovib}} = \nu_0 + B_{v_u} J_u(J_u+1) - B_{v_e} J_e(J_e+1)$$

\uparrow fundamental freq. of $v_u \rightarrow v_e$
 \uparrow rotational constants for v_u and v_e J ladders.

Define $\alpha = B_{v_e} - B_{v_u}$ — the difference in the rotational constants.

R branch $\Rightarrow J_u = J_e + 1$

$$\begin{aligned} \nu_R &= \nu_0 + B_{v_u} (J_e+1)^2 + B_{v_u} (J_e+1) - B_{v_e} J_e^2 - B_{v_e} J_e \\ &= \nu_0 + (B_{v_u} - B_{v_e}) J_e^2 + (3B_{v_u} - B_{v_e}) J_e + 2B_{v_u} \\ &= \nu_0 + 2B_{v_u} + (3B_{v_u} - B_{v_e}) J_e - \alpha J_e^2 \end{aligned}$$

Notice signs are different. So at high J_e , $-\alpha J_e^2$ will eventually dominate and ν_R will "head back" towards ν_0 .

P branch $\Rightarrow J_u = J_e - 1$

$$\begin{aligned} \nu_P &= \nu_0 + B_{v_u} (J_e-1)^2 + B_{v_u} (J_e-1) - B_{v_e} J_e^2 - B_{v_e} J_e \\ &= \nu_0 - (B_{v_u} - B_{v_e}) J_e - \alpha J_e^2 \end{aligned}$$

Same sign! So P branch doesn't "reverse" in freq.

Bandhead formed by R branch lines piling up (typically $J_e \sim 50$)

Hyperfine Splitting

10

Nuclei of atoms also have spin :

$$\vec{I} \equiv \text{spin of nucleus}$$

Define hyperfine quantum number

F such that :

$$\vec{F} = \vec{J} + \vec{I}$$

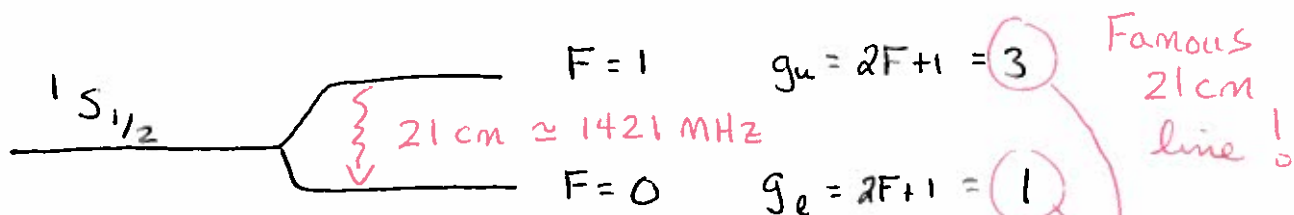
$$\Rightarrow F = J+I, J+I-1, \dots, |J-I|$$

^1H	$I = 1/2$
^2D	$I = 1$
^3He	$I = 1/2$
^4He	$I = 0$
^{12}C	$I = 0$
^{13}C	$I = 1/2$
^{14}N	$I = 1$
^{16}O	$I = 0$
^{17}O	$I = 5/2$
^{18}O	$I = 0$
etc.	

Example : Hydrogen ^1H $I = 1/2$

Grand Electronic State $^1S_{1/2} \Rightarrow J = 1/2$

$$\begin{aligned} \text{so } F &= J+I, \dots, |J-I| \\ &= \frac{1}{2} + \frac{1}{2}, \left| \frac{1}{2} - \frac{1}{2} \right| \\ &= 1, 0 \end{aligned}$$



Selection rules : $\Delta F = 0, \pm 1$ but $0 \nrightarrow 0$

What are these states?

There are 4 ways to combine spins of nucleus & e^- :

$$\begin{aligned} &|\uparrow\uparrow\rangle \\ &|\downarrow\downarrow\rangle \\ &\frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle \\ &\frac{1}{\sqrt{2}}|\uparrow\uparrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\downarrow\rangle \end{aligned}$$

These three states are symmetric and correspond to upper state $= g_u = 3$!

This state is antisymmetric and corresponds to lower state $g_l = 1$

- Nuclear spin ($I \neq 0$) can couple with rotation of molecule:

$$\vec{F} = \vec{J} + \vec{I}$$

$$F = J+I, J+I-1, \dots, |J-I|$$

If $I \geq \frac{1}{2}$ nucleus has magnetic dipole moment

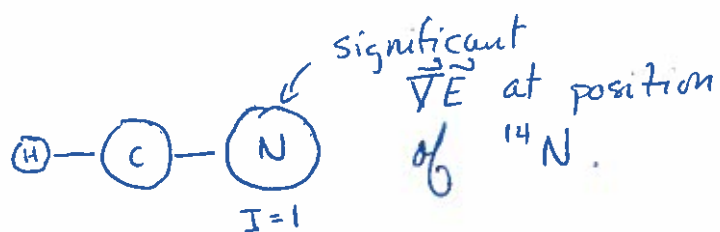
If $I \geq 1$ nucleus has electric quadrupole moment

Electric Dipole selection rules:

$$\Delta F = 0, \pm 1 \quad \text{with } 0 \nrightarrow 0$$

- In atoms, magnetic dipole hyperfine interactions dominate; but, in molecules with $I \geq 1$, electric quadrupole interactions dominate! why? A nuclear electric quadrupole moment couples with $\vec{\nabla} \vec{E}$ at the position of the nucleus.

In atoms, this coupling is small since the nucleus is located at the center of charge. In molecules, nuclei are generally located away from the center of charge and experience larger $\vec{\nabla} \vec{E}$.



well by the interaction between the atomic electron and its radiation field [177]. The calculation is very difficult to carry out accurately, but the calculated shift for hydrogen agrees within about 0.5 Mc with the observed shift [876].

Probably the simplest atom from the theoretical point of view is positronium. It consists of a positron and electron only, so that there is no complication from the short-range forces associated with heavy nucleons. This atom is not stable, decaying in about 10^{-12} sec with the annihilation of the particles and emission of either two or three γ rays. Consequently, it is not easy to study experimentally, and was discovered only recently by Deutsch [568c]. Two γ rays are emitted in opposite directions from states with $J = 0$. States with $J = 1$ must emit three photons to conserve angular momentum, and hence have a longer lifetime. If transitions could be induced by a radio-frequency field from the $J = 1$ to the $J = 0$ states, triplet positronium would be converted to singlet, and the transition detected by the increase in double quantum annihilation. For this direct experiment, a frequency near 2×10^4 Mc would be needed.

However, lower frequencies can be used to measure the fine structure of positronium with the aid of the Zeeman effect. In a magnetic field the $J = 1$ state is split into $M = 0$ and $M = \pm 1$ components. The $M = 0$ state acquires some singlet character, so that double quantum annihilation can occur from it. Weinstein, Deutsch, and Brown [977a] have used the annihilation radiation to detect microwave induced transitions from the $J = 1, M = \pm 1$ to the $M = 0$ levels. Since this Zeeman splitting depends in part on the ratio of magnetic field to the singlet-triplet separation, this measurement determined the fine structure splitting between the $J = 0$ and 1 states as $(2.0338 \pm 0.0004) \times 10^4$ Mc. The calculated value of 2.0337×10^4 Mc [712a] is in excellent agreement.

A few other fine-structure splittings in atoms can probably be studied by microwave techniques. However, in many cases the fine structure is so large that transition frequencies do not lie in the microwave region, or in other cases the lifetimes of both states are so small that application of microwave techniques is difficult.

5-7. Hyperfine Structure. Atomic nuclei have radii near 10^{-13} cm, and hence are very small compared with the size of electron orbits, which are approximately 10^{-8} cm. Nuclei are also some 10^4 times heavier than electrons. To a good approximation electronic energies can therefore be obtained by considering nuclei to be positive point charges of infinite mass. However, effects on electronic energy levels due to the finite size and mass of nuclei, although small, often appear on careful observation of atomic spectra. They are called hyperfine structure because they produce a very small splitting of atomic lines, usually much smaller than the fine structure.

If the nucleus is to be considered other than a point charge, it must be recognized that the nucleus involves a charge distribution and that this charge distribution may be in motion, producing magnetic fields and giving the nucleus an angular momentum. As for an atom or any other quantum-mechanical system, the angular momentum of the nucleus must be $I\hbar/2\pi$, where I is an integer or half integer and is usually called the nuclear spin.

A number of types of hyperfine interactions between nuclei and electrons are independent of the relative orientation of nuclear spin I and electronic angular momentum J . These include the small shifts due to the finite nuclear mass, variation of the electron potential from a coulomb potential when electrons are within the nuclear radius, and isotropic (i.e., independent of nuclear orientation) polarization of the nucleus by electron fields. These effects slightly change each electronic energy level but can usually be detected only by examining their variation between two or more isotopes, and hence are called "isotope effects." Thus a given chemical element may produce a number of slightly different superimposed spectra, each associated with a particular isotope of the element. Since the "isotope effects" do not represent small splittings of the energy levels of any one atomic system, but rather small differences between the spectra of different systems, they are not generally observed by microwave spectroscopy.

On the other hand, hyperfine interactions which vary with nuclear orientation give small splittings of electronic energy levels and are often observed with microwave or radio-frequency techniques. These effects may be either electric or magnetic in origin. Although the magnetic effects are usually most prominent in atoms, electric effects predominate in molecules. The electric interactions will be discussed first.

Hyperfine Structure Due to Electric Charge Distribution in the Nucleus. Motion of the center of mass of the nucleus is unchanged in considering possible nuclear orientations; hence it is the natural origin in considering a nucleus of finite size. Let V_e be the electrostatic potential produced at the nuclear center of mass by all electronic charges in the atom, and $\partial V_e/\partial z$ represent its derivative evaluated at the same point. The electrostatic energy of a charge $\rho(x, y, z) \Delta x \Delta y \Delta z$, where ρ represents the nuclear charge density, is $\Delta W = \rho \Delta x \Delta y \Delta z V(x, y, z)$.

Expanding V as a series and writing the volume element $\Delta x \Delta y \Delta z = \Delta r$

$$\begin{aligned} \Delta W = \rho \Delta r \left[V_0 + x \frac{\partial V_0}{\partial x} + y \frac{\partial V_0}{\partial y} + z \frac{\partial V_0}{\partial z} + \frac{1}{2} x^2 \frac{\partial^2 V_0}{\partial x^2} + \frac{1}{2} y^2 \frac{\partial^2 V_0}{\partial y^2} \right. \\ \left. + \frac{1}{2} z^2 \frac{\partial^2 V_0}{\partial z^2} + xy \frac{\partial^2 V_0}{\partial x \partial y} + yz \frac{\partial^2 V_0}{\partial y \partial z} + zx \frac{\partial^2 V_0}{\partial z \partial x} \right. \\ \left. + \dots + \frac{x^2 y^2 z^2}{n! m! p!} \frac{\partial^{n+m+p} V_0}{\partial x^n \partial y^m \partial z^p} + \dots \right] \quad (5-24) \end{aligned}$$

Integrating over the entire nuclear volume,

$$W = \int \rho(x, y, z) \left[V_0 + x \frac{\partial V_0}{\partial x} + y \frac{\partial V_0}{\partial y} + z \frac{\partial V_0}{\partial z} + \frac{1}{2} x^2 \frac{\partial^2 V_0}{\partial x^2} + \frac{1}{2} y^2 \frac{\partial^2 V_0}{\partial y^2} + \frac{1}{2} z^2 \frac{\partial^2 V_0}{\partial z^2} + xy \frac{\partial^2 V_0}{\partial x \partial y} + yz \frac{\partial^2 V_0}{\partial y \partial z} + xz \frac{\partial^2 V_0}{\partial z \partial x} + \dots \right] dv \quad (5-25)$$

The first term may be easily integrated to give ZeV_0 , where Z is the atomic number of the nucleus and Ze its total charge. This is the term which is independent of nuclear size or shape. The second term may be written

$$\frac{\partial V_0}{\partial x} \int \rho(x, y, z) x \, dv$$

where the integral is the nuclear dipole moment in the x direction. If this nuclear dipole is not produced by an external field, such as that of the electrons, but is a property only of the nucleus, it can be shown to be zero except in very rare cases. Suppose the wave function and hence the charge distribution for a nucleus is known and the dipole moment in the x direction, $\int \rho x \, dx \, dy \, dz$, has the value μ_x . If the positive directions of the nuclear coordinates x, y , and z are now reversed, a new wave function can be found and a new charge density which is just the same function of the new coordinates x', y', z' as it was of the old coordinates x, y, z . This is possible because, for all known forces within the nucleus, the Hamiltonian or wave equation turns out to depend only on even powers of the coordinates and hence remains unchanged when the signs of all coordinates are reversed. The charge density at x will be replaced by a similar charge density at x' or $-x$. However, the direction of the angular momentum does not change on reversing all coordinates. In the new coordinate system, the dipole moment $\mu_{x'}$ has the same value as before but is oppositely directed, that is, $\mu_{x'} = -\mu_x$. Other nuclear properties, however, including the nuclear angular momentum, will have remained unchanged. We must conclude, therefore, that if the nucleus has a dipole moment in one direction with respect to its angular momentum, there must be a degenerate nuclear state, or one of the same energy, with an oppositely directed dipole. Normally, such identical or degenerate states of the nucleus are not encountered, and hence the nucleus has no inherent dipole moment.* If a nucleus has angular momentum I , there are

* A similar proof may be applied to any system, showing that no dipole moments may exist in nature without degeneracy. What is ordinarily referred to as the permanent dipole moment of a molecule in fact does not give a molecule an average dipole moment in one direction unless there is degeneracy or an external field. The dipole moment of a large macroscopic collection of charges may be regarded as existing only because of the very close spacing, and hence effective degeneracy, of the rotational energy levels of such a large system.

$2I + 1$ different possible states having the same energy, corresponding to the different values of M_I , the projection of I on a fixed direction. It might be thought that this is a degeneracy which allows a dipole moment. However, since the angular momentum operator is similar to the Hamiltonian in that it does not change sign when all coordinates are reversed, an argument similar to that above shows that no dipole moment can exist unless the system has two states of the same energy and the same value of M_I . It can thus be shown that all terms of (5-25) involving odd powers of the coordinates will normally be zero. However, terms such as $\int \frac{1}{2} \rho x^2 \, dv$ and $\int \rho xy \, dv$ are not necessarily zero because they do not change sign with reversal of direction of all coordinates. These terms are associated with the quadrupole moment of the nucleus.

Before reexpressing these terms in a more convenient form, it is interesting to note their approximate magnitude. The potential V produced by the electron is e/r , where r is the distance between electron and nucleus. Hence $\partial^2 V / \partial x^2$ is roughly e/r^3 . The integral $\int \frac{1}{2} \rho x^2 \, dv$ is of the order $\int \rho r^2 \, dv = Ze r_n^2$, where r_n is the nuclear radius. Hence the term $\partial^2 V / \partial x^2 \int \frac{1}{2} \rho x^2 \, dv \approx Ze^2 r_n^2 / r^3$. This might be compared with the first term in our expansion, $ZeV = Ze^2 / r$, giving the electrostatic energy for a point nucleus. The ratio of the two is r_n^2 / r^2 , or 10^{-4} if r_n is 10^{-12} cm and an average value of 10^{-8} cm is taken for r . The usual electrostatic energy is of the order 10^5 cm $^{-1}$, so the energy associated with the small correction terms of this type is expected to be 0.001 cm $^{-1}$, or 30 Mc. Still higher-order terms in the expansion (5-24) which are nonzero involve fourth powers of the coordinates [that is, $x^4 (\partial^4 V / \partial x^4)$, etc.] They are associated with the nuclear hexadecapole (16-pole) and are expected to be still smaller than the quadrupole terms by a factor of roughly 10^4 . In most cases this makes them only a few cycles per second, and too small for present experimental accuracy to detect.

Part of the energy due to terms of (5-25) containing second derivatives of the potential does not vary with nuclear orientation. To eliminate this part we subtract

$$\int \frac{1}{2} \rho (x^2 + y^2 + z^2) \left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} \right) dv \text{ or } \nabla^2 V \int \frac{1}{2} \rho r^2 \, dv$$

If electrons do not penetrate the nucleus, then $\nabla^2 V$ is zero everywhere ρ is not zero, and this energy integral vanishes. If the electrons do penetrate the nucleus, then this energy represents a deviation from a Coulomb field within the nuclear radius, and is an important part of the atomic isotope shift.

The Electric Quadrupole Moment. Eliminating then the parts of (5-25) which are independent of nuclear orientation and the dipole terms, which have been shown to vanish, the remaining terms are attributable to a

nuclear electric quadrupole and may be written

$$W_Q = \frac{1}{2} \int \rho \left[(3x^2 - r^2) \frac{\partial^2 V}{\partial x^2} + (3y^2 - r^2) \frac{\partial^2 V}{\partial y^2} + (3z^2 - r^2) \frac{\partial^2 V}{\partial z^2} + 6xy \frac{\partial^2 V}{\partial x \partial y} + 6yz \frac{\partial^2 V}{\partial y \partial z} + 6xz \frac{\partial^2 V}{\partial z \partial x} \right] dv \quad (5-26)$$

or

$$W_Q = -\frac{1}{2} Q : \nabla E \quad (5-27)$$

which is the inner product between the quadrupole moment dyadic

$$Q = \int (3rr - r^2 I) \rho \, dx \, dy \, dz \quad (5-28)$$

and the gradient of the electric field due to the electrons.

The properties of dyadics may be found in [105] or [63]. A dyadic AB is formed from the two vectors $A = A_i \mathbf{e}_i + A_j \mathbf{e}_j + A_k \mathbf{e}_k = \sum_i A_{i\alpha} \mathbf{e}_i \mathbf{e}_\alpha$.

$B = B_j \mathbf{e}_j + B_k \mathbf{e}_k = \sum_j B_{j\beta} \mathbf{e}_j \mathbf{e}_\beta$, where \mathbf{e}_α represents one of the three unit vectors i, j , or k . The dyadic has nine components and may be written $\sum_{i\alpha} A_{i\alpha} B_{j\beta} \mathbf{e}_i \mathbf{e}_\alpha \mathbf{e}_j \mathbf{e}_\beta$. The unit dyadic I is $ii + jj + kk$, and is said to be diagonal because no "cross terms" of the type ij or jk occur. The inner product of two dyadics $AB:CD$ is the scalar quantity $\sum_{i\alpha} A_{i\alpha} B_{j\beta} C_{j\beta} D_{i\alpha}$, which is analogous to the scalar product of two vectors.

By a proper choice of axes any symmetric dyadic such as the quadrupole moment dyadic may be diagonalized. This eliminates all terms except those multiplying ii, jj , or kk .

The charges in the nucleus are rotating very rapidly about the direction of the nuclear spin. If an average is made over a time long enough for the nuclear particles to rotate many times, but so short that the electrons or charges outside the nucleus have not appreciably changed position, the electric field gradient may be considered constant and the nuclear charge distribution cylindrical. Using a new coordinate system with z_n in the direction of the nuclear spin, all nondiagonal terms of Q become zero, and the diagonal terms are simply related;

$$\int \rho (3x_n^2 - r^2) \, dv = \int \rho (3y_n^2 - r^2) \, dv = -\frac{1}{2} \int \rho (3z_n^2 - r^2) \, dv \quad (5-29)$$

The entire quadrupole moment dyadic may hence be expressed in terms of one constant, called "the" nuclear quadrupole moment

$$Q = \frac{1}{e} \int \rho (3x_n^2 - r^2) \, dx \, dy \, dz \quad (5-30)$$

where e is the charge of one proton. From (5-30) it can be seen that a nucleus whose charge distribution is spherical has zero quadrupole

moment, for then the average value of $3x_n^2$ is just equal to the average value of $r^2 = x_n^2 + y_n^2 + z_n^2$. The quadrupole moment may be considered then a measure of the deviation of the nuclear charge from spherical shape. If the charge distribution is somewhat elongated along the nuclear axis z_n , then Q is positive; if it is flattened along the nuclear axis, Q is negative. From (5-28) the quadrupole energy becomes

$$W_Q = \frac{e}{6} Q \left[\frac{\partial^2 V}{\partial z_n^2} - \frac{1}{2} \left(\frac{\partial^2 V}{\partial x_n^2} + \frac{\partial^2 V}{\partial y_n^2} \right) \right] \quad (5-31)$$

If the potential V is due entirely to charges outside the nucleus, then

$$\frac{\partial^2 V}{\partial x_n^2} + \frac{\partial^2 V}{\partial y_n^2} = -\frac{\partial^2 V}{\partial z_n^2}$$

from Laplace's equation, and

$$W_Q = \frac{e}{4} Q \frac{\partial^2 V}{\partial z_n^2} \quad (5-32)$$

The potential V is produced by electrons which are in rapid motion, so rapid that the nuclear axis z_n may be considered stationary during the time that the electrons traverse their entire orbits, or take up all possible positions. Hence, (5-31) may be averaged over all possible electron positions

$$W_Q = \frac{e}{6} Q \left[\frac{\partial^2 V}{\partial z_n^2} - \frac{1}{2} \left(\frac{\partial^2 V}{\partial x_n^2} + \frac{\partial^2 V}{\partial y_n^2} \right) \right]_{av} \quad (5-33)$$

or, using Laplace's equation again

$$W_Q = \frac{e}{4} Q \left(\frac{\partial^2 V}{\partial z_n^2} \right)_{av} \quad (5-34)$$

If the average electron charge density is spherical, then

$$\frac{\partial^2 V}{\partial x_n^2} = \frac{\partial^2 V}{\partial y_n^2} = \frac{\partial^2 V}{\partial z_n^2} \quad \text{and} \quad W_Q = 0$$

Since only s electrons, which have spherically symmetric distributions, have large probabilities of being found within the nucleus, it is customary to set

$$W_Q = \frac{e}{4} Q \left(\frac{\partial^2 V'}{\partial z_n^2} \right)_{av} \quad (5-35)$$

where V' is the potential due only to the electronic distribution outside a small sphere surrounding the nucleus. This gives a small error, because p or d electrons, which are not spherically distributed, have a finite, though small, probability of being inside the nucleus. The density of a nonspherically distributed p electron must, however, be zero at the center of the nucleus, and its average density within the

Multiple Coupling Nuclei

(2)

Example: N_2H^+

$N-N-H^+$
Linear molecule

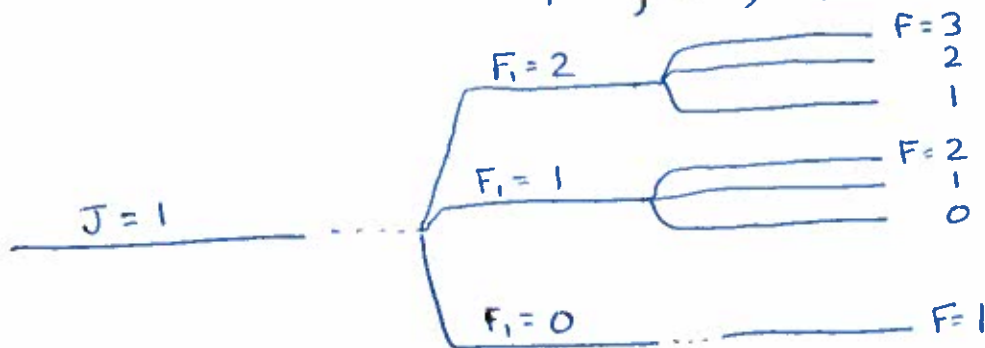
$I(^{14}N_{outer}) = 1$ largest $\vec{\nabla E}$ $eQq \sim -5.7 \text{ MHz}$
 $I(^{14}N_{inner}) = 1$ smaller $\vec{\nabla E}$ $eQq \sim -1.3 \text{ MHz}$
 $I(^1H) = 1/2$ Magnetic dipole weak $C_I \sim 20 \text{ kHz}$

Coupling Scheme: (1) $\vec{F}_1 = \vec{I}_1 + \vec{J}$ $I_1 = \text{outer nitrogen}$
 (2) $\vec{F} = \vec{I}_2 + \vec{F}_1$ $I_2 = \text{inner nitrogen}$
 (ignore weak 1H splitting)

For $J=1-0$ $F_1 = 1+1, \dots, |1-1| = 2, 1, 0$



$F = F_1 + 1, \dots, |F_1 - 1|$



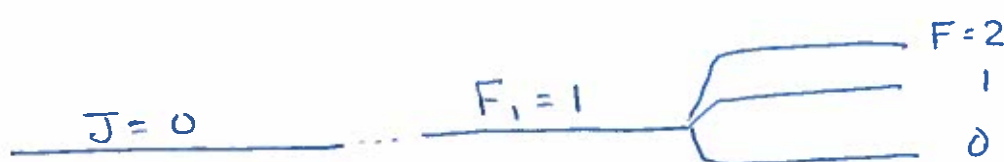
Selection Rules

$$\Delta F_1 = 0, \pm 1$$

$$\Delta F = 0, \pm 1$$

$$0 \nrightarrow 0$$

(+)



} These levels are degenerate

$\Rightarrow 7$ transitions from $J=1-0$.

Summary of Einstein Coefficients

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Electric Dipole
Transitions (E1):

$$A_{ul} = \frac{64\pi^4}{3hc^3} \nu^3 |\mu_{el}|^2$$

Strong ν dependence

Electric Dipole moment matrix
element for $u \rightarrow l \sim \mu_e^2$

Magnetic Dipole
Transitions (M1):

$$A_{ul} = \frac{64\pi^4}{3hc^3} \nu^3 |\mu_{ml}|^2$$

NOTE "Dipole" similarity
in equations

Magnetic Dipole moment matrix
element for $u \rightarrow l \sim \mu_B^2$
Bohr magneton

Electric Quadrupole
Transitions (E2):

$$A_{ul} = \frac{32\pi^6}{5hc^5} \nu^5 |Q_{el}|^2$$

any combination!

Electric Quadrupole moment matrix
element for $u \rightarrow l$

The matrix elements above are sometimes
written in terms of the "Strength", S_{ul} , of
the transition

$$|\mu_{el}|^2 = \frac{S_{ul}}{g_u}$$

$$|Q_{el}|^2 = \frac{S_{ul}}{g_u}$$

These depend on
quantum numbers
and are unique for
each transition.