14. Introduction to nuclear spin and electron spin

Fuller treatment can be found in a standard statistical mechanics reference. I use Davidson *Statistical Mechanics*, which is now very old, but still excellent. Also, Bernath, Sections 7.2 and 9.4.

Definitions

Nuclear spin I = integral: Bosons; they obey Bose-Einstein statistics
Nuclear spin I = half-integral: Fermions; they obey Fermi-Dirac statistics

The total wave function Φ must be either symmetric or antisymmetric with respect to the interchange of the coordinates of the two identical (in type and molecular location) nuclei, for bosons (integral nuclear spin, I) or fermions (half-integral nuclear spin), respectively. This is a consequence of the *Pauli exclusion principle*, which states that two fermions may not simultaneously occupy the same quantum state. Bosons may, leading to some interesting physical consequences (neutron stars, Bose-Einstein condensates – BECs). Half-integral spin values were discovered, accidentally, in 1922 by *Stern and Gerlach* during magnetic deflection studies of a beam of (nuclear spin ½) silver atoms.

Nucleus	Spin (I)
H	½
D (=^{2}H)	1
^{14}N	1
^{12}C	0
^{16}O	0
^{35}Cl	3/2
^{37}Cl	3/2

Bosons: $P_{AB}\Phi = +\Phi$

Fermions: $P_{AB}\Phi = -\Phi$,

Where P_{AB} is the permutation operator and Φ is the wave function, which is the product of an electronic, a vibrational, a rotational, and a nuclear spin wave function:

$$\Phi = \Phi_{elect}\Phi_{vib}\Phi_{rot}\Phi_{spin}.$$

Φ_{elect} is symmetric with respect to the permutation for the electronic ground state of H_2 (the more usual case); Φ_{vib} is symmetric (always), and Φ_{rot} are symmetric with respect to permutation of A and B for even J and asymmetric for odd J.

For H_2, where the nuclei (protons) A and B have spins of I = 1/2 (and are thus fermions), the two possible spin wave functions for each proton may be called α and β, where α (A) is the state where proton A has angular momentum +1/2 (in units of $\hbar$) along the axis of quantization (the internuclear axis), and β (A) has angular momentum -1/2 along the axis. Possible nuclear spin wave functions for the molecule are:

$\phi(A)\phi(B)$
$\phi(A)\phi(B)$
$[\phi(A)\phi(B) + \phi(A)\phi(B)]/\sqrt{2}$
$[\phi(A)\phi(B) - \phi(A)\phi(B)]/\sqrt{2}$

The first three are symmetric with respect to permutation of *A* and *B* and the last one asymmetric with respect to permutation of *A* and *B*. To make $P_{AB}\phi = -\phi$, required for fermions, asymmetric nuclear spin wave functions (1-fold degenerate) may only go with symmetric rotational wave functions (even *J*). Conversely, symmetric nuclear spin wave functions (3-fold degenerate) may only go with asymmetric rotational wave functions (odd *J*).

The states of higher spin degeneracy are called *ortho* states, and those of lower spin degeneracy are called *para* states. Thus for H_2, the nuclear spin degeneracies are:

$g_N = 1$ for even *J* (para) g_N
$= 3$ for odd *J* (ortho).

For homonuclear diatomics in general, both bosons and fermions, the ortho/para ratio is $(I+1)/I$. When $P_{AB}\phi_{elect} = +\phi_{elect}$ (the more usual case), this is the ratio of even *J* to odd *J* spin degeneracies for bosons and of odd *J* to even *J* spin degeneracies for fermions. Thus $^{14}N_2$ ($I = 1$) has $g_N = 2$, *J* even and $g_N = 1$, *J* odd.

When $P_{AB}\phi_{elect} = -\phi_{elect}$, $(I+1)/I$ is the ratio of odd *J* to even *J* spin degeneracies for bosons and of even *J* to odd *J* spin degeneracies for fermions. Thus $^{16}O_2$ ($I = 0$), which has a $^3\Sigma_g$ ground state, has *only* odd rotational states ($^{16}O^{17}O$ and $^{16}O^{18}O$ have both).

Thus, there are ortho and para forms of H_2 and of H_2O, and of other molecules as well. This affects the rotational parts of the spectrum very significantly. The nuclear spin degeneracies must be included in the Boltzmann factors and partition functions:
$b_J = g_N(2J+1)e^{-c E_{2J}/T}$

$$Q_{rot} = \sum_{J=0} b_J .$$

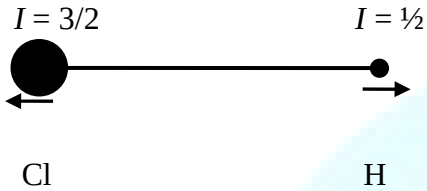
Polyatomics have a straightforward continuation of these permutation principles (*e.g.*, for CO_2, H_2O, O_3, NH_3), but we will not develop them here.

In general, ortho and para states of molecules behave as independent species, unconnected to one another by electromagnetically-allowed transitions. If an equilibrium

mixture changes temperature, equilibrium may only be re-established by other, chemical, means, where dissociation and reformation is permitted.

Molecules in general: *Hyperfine* structure, due to nuclear spins □ 1/2 give (small) additional corrections to the energy levels. This includes "dipolar" contributions due to the interaction of the nuclear spin magnetic moments with internal magnetic fields. Hyperfine structure also includes contributions from nuclear *quadrupole* moments: Nuclear spins □ 1 have nuclear quadrupole moments, *Q*, giving rise to somewhat larger (but still small) energy corrections through *Q E*:□ .

Nuclear spins *always* add to the total angular momentum.



I like *Townes and Schawlow* for discussion of these effects: Chapter 8 for magnetic hyperfine and Chapter 6 for nuclear electric quadrupole.

15. Electronic orbital angular momentum, electronic spin angular momentum, electronic transitions

See *Bernath*, Chapter 9, *Townes and Schawlow* Chapter 7.

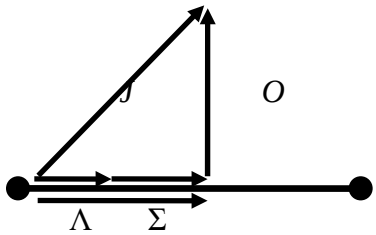
For a diatomic molecule, the electronic state is given by $^{2S\square 1}\square$, *e.g.*, $^{2}\square$, $^{3}\square$, $^{1}\square$, etc. □ is the quantized *orbital* angular momentum projected onto the intermolecular axis. □ = 0 □ □ state, □ = 1 □ □ state, □ = 2 □ □ state, etc. No half-integral orbital angular momentum values are allowed. *L* is the total electron orbital angular momentum. *S* is the electron spin angular momentum (half-integral spin angular momentum values are allowed; the electron has spin ½). 2*S* + 1 is the *multiplicity*. There may be additional complexities (due to additional symmetries), *e.g.*, the O_2 ground state is $^{3}\square^{\square}_{g}$, where *g* stands for *gerade* (German for *even*, as opposed to *ungerade*). A *gerade* state is even with respect to *inversion*. A state may only (and must be) *g* or *u* only if it is a state of a homonuclear diatomic molecule. The superscript "-" refers to reflection in a plane containing both nuclei. This symmetry only applies to molecules in Σ states, because they are non-degenerate.

How do angular momenta couple? In diatomic molecules, they couple according to

Hund's cases. Angular momenta must be positive quantities. Angular momenta A and B (A □ B) couple to give resulting totals A - $|B|$ to A + $|B|$, in integer steps (e.g., 1 + 1/2 = 1/2 or 3/2). Here are the two most common Hund's cases (there are others):

Hund's case (a)

□



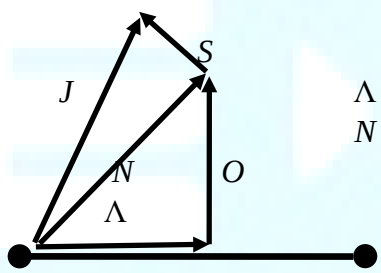
$\Lambda + \Sigma =$
□ $+ O =$
J

e.g., $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ states

□

Σ is the axial projection of the spin angular momentum (exists only for $\Lambda > 0$).

Hund's case (b)



$\Lambda + O = N$
$N + S = J$

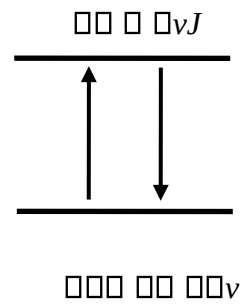
N.B., there is no perfect coupling except when symmetry requires it; otherwise only total angular momentum is an exact quantum number. Also, for a given molecule in a given electronic state, the closest Hund's case may change as rotational state changes as angular momenta uncouple and recouple as strengths of interactions change.

Where are angular momentum coupling and perturbations in the spectra due to them important? In free radicals: OH, O_2 (!), NO, HO_2, ClO, …. In OH (B = 18.87 cm^{-1}), the *spin-orbit* interaction is so strong that the first transitions are at 61 cm^{-1} rather than at 38 cm^{-1} (except for fine structure "maser" transitions, as seen in astrophysical OH masers). Also, the OH spectrum looks totally unlike that of an evenly-spaced diatomic spectrum.

Ultraviolet/visible (electronic) spectroscopy

For electronic transitions

$|$□$_{u}$□$_{l}|^2$□ $q_{v\,v}$□ □□ $|\,R_e|^2\,S_{J}$□□ /(2J□□1), and $|$□$_{l}$□$_{u}|^2$□ $q_{v\,v}$□ □□ $|\,R_e|^2\,S_{J}$□□ /(2J□□□1), where S_{J}□□ is a *rotational line strength* term (*Bernath*) □ *Hönl-London factor*. ≡ ≡ ≡ ≡



$S_{J\square\square}$ is like earlier rotational terms, but now involving □□,□□□.

Remember $|\square_{J\square\,\square J\,1}|^2\square\ \square_0^2(J\ \square 1)/(2J\ \square 1)$ and

$|\square_{J\square\,\square J\,1}|^2\square\ \square_0^2(J\ \square 1)/(2J\ \square\ 3)$ for simple rotational spectra.

$J\ \square 1$ is the Hönl-London factor in this simple case
J

$q_{v\,v\square\,\square\square}$ is the *Franck-Condon Factor* or *vibrational overlap*: $|\ \square\ \square\ \square^{\square}{}_{v\square v\square\square}d\square|^2$ **(show vertical transition here)**

R_e is the electronic transition dipole moment: $R_e\square\ \square\ \square\square_{el}\square_e\square\square\square_{el}d\square$. See *Bernath*

chapters 9 and 10 for copious details.

$$S\ (\text{cm})\ \square\ 8\square_3\square(e_{\square c\,E_{2\,l}/T}\square e_{\square c\,E_{2\,u}/T})\ g_l\,|\square_{l\square u}|_2$$

Then,

$$\frac{3hc\quad Q\ T(\ )\qquad\qquad\square\ 8\square_3}{\square(e_{\square c\,E_{2\,l}/T}\square\ e_{\square c\,E_{2\,u}/T})\ q_{v\,v}|_2\ S_{J\square\square}.}$$

$$\frac{R}{\square\ \square\square\quad e|}$$

$$3hc\qquad Q\ T()$$

Sum rule: $\square S_{J\square\square}\ \square\ 2J\square\square\square 1$
$J\square$

"Sums of the line strengths of all transitions to or from a given rotational level are proportional to the statistical weight of that level." Herzberg, *Spectra of Diatomic Molecules*, pp. 208-209.

Finally, what we mostly do with electronic spectra is to use cross sections ( ),□ □ in cm^2, often with temperature dependence and occasionally with pressure dependence, to calculate spectra.