5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #17: Hund's Cases: $^2\Pi$, $^2\Sigma^{\pm}$ Examples

4 ways to think about Hund's Cases:

1. Pattern forming quantum numbers. A search for $^1\Sigma^+$-like rotational level pattern

   $BJ(J+1)$ cases a and c

   $BN(N+1)$ case b

   Repeated $^1\Sigma$-like patterns as in $^3\Pi$ state.

*** 2. $\mathbf{H}^{eff}$ and Perturbation Theory. When is $\mathbf{H}'_{12} \gg \Delta E^o_{12}$ and vice versa?

3. Vector precession models. How do the various angular momenta project into the body and laboratory? What gets averaged out and what does not as vectors precess? Are various angular momenta components expected to be conserved?

4. Basis set transformations (like $|JMLS\rangle \leftrightarrow |LM_L\rangle|SM_S\rangle$ for atoms) 3j, 6j, 9j transformation coefficients. Alternate form of $\hat{\mathbf{H}}$ example: $\hat{\mathbf{H}}^{ROT} = B(R)[\hat{N} - \hat{L}]^2$.

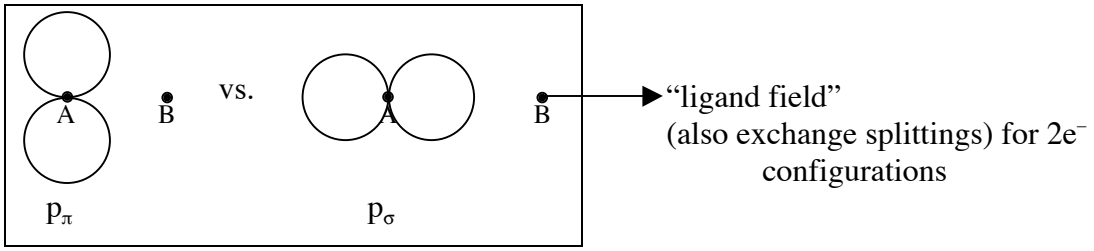
We are going to look at the $^2\Pi$, $^2\Sigma^+$ matrix and use perturbation theory to identify and describe each of the Hund's limiting cases.

Exclude γ $y = J + 1/2$ Treat $^2\Pi$, $^2\Sigma^+$ together because they could form "p-complex".

$\begin{pmatrix} e \\ f \end{pmatrix}$	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$^2\Sigma^+$
$^2\Pi_{3/2}$	$E_\Pi + A_\Pi/2 + B_\Pi(y^2 - 2)$	$-B_\Pi(y^2-1)^{1/2}$	$-\beta(y^2-1)^{1/2}$
$^2\Pi_{1/2}$	sym	$E_\Pi - A_\Pi/2 + B_\Pi y^2$	$\alpha + \beta(1 \mp y)$
$^2\Sigma^+$	sym	sym	$E_\Sigma + B_\Sigma(y^2 \mp y)$

Crucial Energy Denominators:

$$\begin{cases} \Delta E^o_\Pi = \Pi_{3/2} - \Pi_{1/2} = A_\Pi - 2B_\Pi & \text{(spin-orbit)} \\ \Delta E^o_{\Pi-\Sigma} = E_\Pi - E_\Sigma \end{cases}$$



Crucial Coupling Terms

$-B\hat{J}_{\pm}\hat{S}_{\mp} \Rightarrow -B_{\Pi}\left(y^2-1\right)^{1/2}$ (spin-uncoupling)

$-B\hat{J}_{\pm}\hat{L}_{\mp} \Rightarrow -\beta\left(y^2-1\right)^{1/2}$ (ℓ-uncoupling)

$\hat{\mathbf{H}}^{SO} \Rightarrow \alpha$ (spin-orbit)

Case (a) Strong spin-orbit, stronger non-spherical field

$$\Delta E_{\Pi\Sigma} \gg A,\alpha \gg By, \beta y$$

Ω, Λ, S good $|n\Lambda S\Sigma\rangle$ $|\Omega JM\rangle$
patterns $BJ(J+1)$ one for each Ω, separated in energy by $A\Lambda$

Case (b) Weak spin-orbit, strong field

$$\Delta E_{\Pi\Sigma} \gg By, \beta y \gg A,\alpha$$

Λ,S good, Σ,Ω bad $|n\Lambda SNJM\rangle$
patterns $BN(N+1)$ - with fine structure splittings

Case (c) Strongest spin-orbit, moderate field

$$A,\alpha \gg \Delta E_{\Pi\Sigma} \gg By, \beta y$$

Ω good, N, S, Λ, Σ bad $|n\Omega JM\rangle$ (J_a and Ω_a atom-in-molecule quantum numbers)

isolated $BJ(J+1)$ patterns
[A,α can also be large with respect to $\Delta G(1/2)$. Relativistic adiabatic potential curves]

Case (d) weak spin-orbit, weak field

$$By, \beta y \gg A,\alpha \approx \Delta E_{\Pi\Sigma}$$

ℓ, S, R good, Λ, Σ, N, Ω bad $|n\ell SRM\rangle$
$BR(R+1)$

Case (e) Strong spin-orbit, weak field

$$A,\alpha \gg By, \beta y \gg \Delta E_{\Pi\Sigma}$$

Now let us examine $^2\Pi$, $^2\Sigma^+$ blocks separately near the case (a) limit.

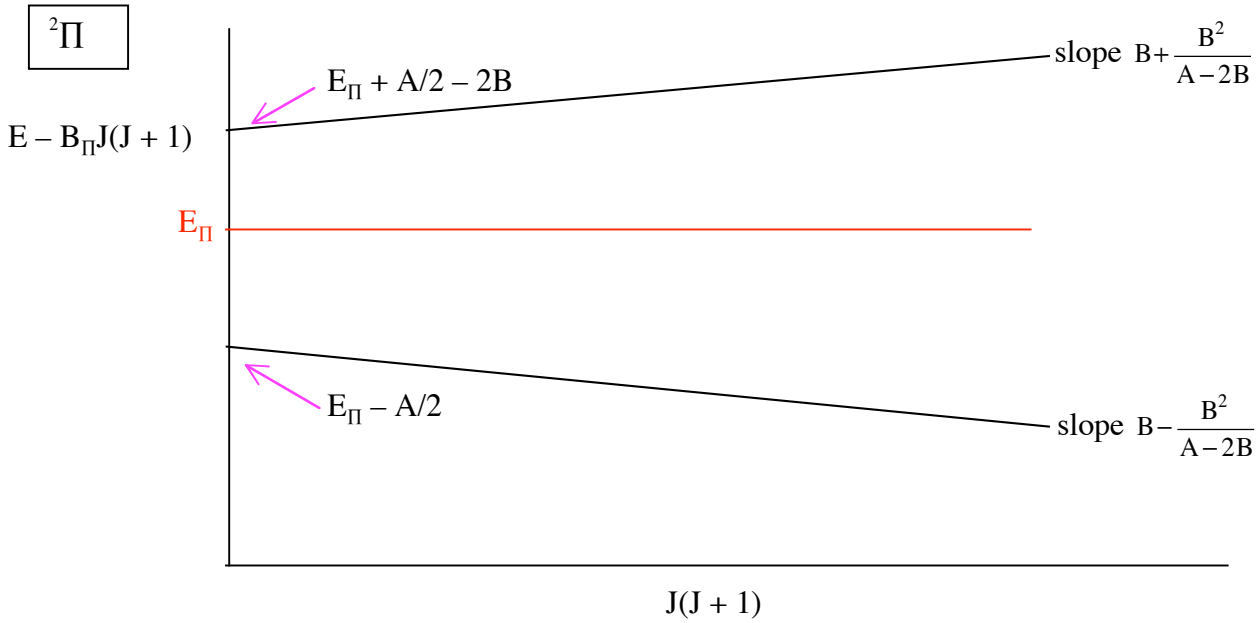
$$\Delta E^{o}_{\Pi_{3/2}\,\Pi_{1/2}} = A_\Pi - 2B_\Pi \gg \mathbf{H}'_{3/2,1/2} = B_\Pi\left(y^2-1\right)^{1/2} \approx B_\Pi J$$

In this case we have two independent sub-states:

$$E^{\Pi}_{vJ\Omega} = E^{o}_{v\Omega} + B_{v_\Pi} J(J+1) + \underbrace{\frac{B^2\left(y^2-1\right)}{E^{o}_{v\Omega} - E^{o}_{v\Omega'}}}_{\text{2nd order correction. Acts like correction to BJ(J + 1).}}$$

($J(J+1)$ above the numerator)

$$B^{eff}_{3/2} = B_\Pi + \frac{B^2_\Pi}{A-2B}$$



$^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ appear to be two completely separate substates with identical ΔG and similar B_v values. $^1\Sigma^+$-like quantum number is J.

At high-J, $H'_{12} > \Delta E°$ therefore must diagonalize $2 \times 2 \rightarrow$ case b. LATER

<u>Vector Coupling picture</u>

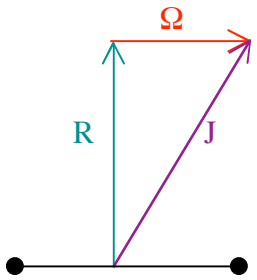
L precesses about z (unit vector $\hat{k}$) to define Λ (all of L does not get averaged to zero)

Λ provides a unique body-fixed direction for S to couple to! S can't see $\hat{k}$ without Λ to mark it!

S precesses about z to define Σ.

$\Lambda + \Sigma = \Omega$ (because $R \perp \hat{k}$ hence it makes no contribution to projection of J on z-axis)

$$\Omega\hat{k} + \hat{R} = \hat{J}$$



R, $\Omega\hat{k}$ have non-zero projections on J and precess about $\vec{J}$.

Since J projects into laboratory, the precession of Ω,R about J carries information about Ω,R into laboratory.

At high J, $BJ_{\pm}S_{\mp}$ causes S to couple to a direction other than body $\hat{k}$. S begins to precess about J rather than $\hat{k}$ and $\sum$ is no longer defined (transition to case (b)). J has well defined projnection in laboratory. Therefore S also has well defined lab projection. S has decoupled from body frame. M_J and M_S. Zeman effect explained by vector model.

Case (b) limit

$A - 2B = 0$ (or $|A - 2B| \ll BJ$)

S can't find z-axis because coupling mechanism ($\mathbf{H}^{SO}$) is turned off.

Look at $^2\Pi$ matrix for A = 2B

$$\begin{matrix} {}^2\Pi_{3/2} \\ {}^2\Pi_{1/2} \end{matrix}\begin{pmatrix} E+B\left(y^2-1\right) & -B\left(y^2-1\right)^{1/2} \\ \text{sym} & E+B\left(y^2-1\right) \end{pmatrix}$$ (trivial to diagonalize)

Let $(y^2 - 1)^{1/2} = z$.

$$\mathbf{H}_{\Pi}^{\text{eff}} = \begin{pmatrix} E+Bz^2+Bz & 0 \\ 0 & E+Bz^2-Bz \end{pmatrix}$$
$$= \begin{pmatrix} E+Bz(z+1) & 0 \\ 0 & E+Bz(z-1) \end{pmatrix}$$

What is z? It is the new **pattern forming quantum number**. Note that two states follow Bm(m + 1) where m's change in steps of 1.

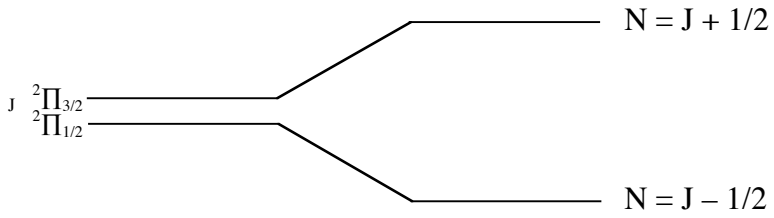
y = J + 1/2 (integer if J is half-integer)
$z = (y^2 - 1)^{1/2} = (J^2 + J + 1/4 - 1)^{1/2} \approx J + 1/2$ at high J.

Let's look at the diagonal $\mathbf{H}^{\text{eff}}$ in this case b limit:

$$= \begin{pmatrix} E + BN(N+1) & 0 \\ 0 & E + BN'(N'+1) \end{pmatrix}$$

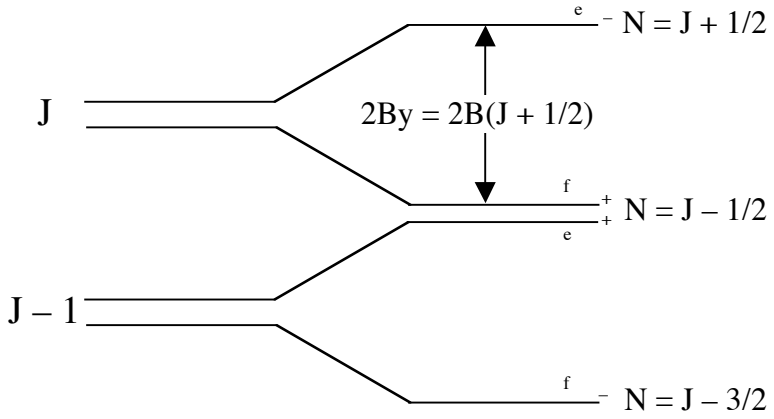
N = J + 1/2

N′ = J – 1/2



This is the same pattern that always is found in $^2\Sigma^+$ state.

$$^2\Sigma^+\begin{pmatrix} e \\ f \end{pmatrix} \longrightarrow E_\Sigma + By(y \mp 1)$$



Get pairs of eigenvalues for each J separated by 2By. This is the rotational level separation for BN(N + 1).

Get each N split slightly into two J's (fine structure).

case (b) $^2\Pi\begin{pmatrix} e \\ f \end{pmatrix}$ E + BN(N + 1)

$^2\Sigma^+\begin{pmatrix} e \\ f \end{pmatrix}$ E + BN(N + 1)

Near degenerate pairs have same N, different J, same parity, opposite e/f (e always above or always below f). $^2\Pi$ looks like a $^2\Sigma^+$ plus a $^2\Sigma^-$ state.

L precesses about z to form Λ (usually $\Lambda = 0$).

S does not see Λ (therefore projections of S are quantized in lab, not body).

$\Lambda\hat{k} + \vec{R} = \vec{N}, \qquad \vec{S} + \vec{N} = \vec{J}$

S and N couple weakly by magnetic dipoles, therefore S is easily uncoupled from anything that carries any information about body. Zeeman effect.

Case (c) Super-Strong $\mathbf{H}^{SO}$ $(\Delta\Omega = 0)$

α,A large with respect to ΔG, $\Delta E_{\Pi\Sigma}$, $\Delta E_{S,S\pm1}$

each Ω acts as a separate electronic state (distinct shapes of potential curves, especially when $A \gtrsim D^e$ and both Ω's try to dissociate to same separated atom asymptote).

Ω,J defined
S,Σ,Λ not defined, lose a lot of information

Often have a hidden quantum number $L + S = J_a$ atomic total angular momentum
J_a precesses about z to define Ω
$\Omega\hat{k} + \vec{R} = J \qquad \mathbf{H}^{ROT} = B(J - J_a)^2$

Consider a p-complex in case (c) and let $E_\Pi \equiv E_\Sigma \equiv E$

$\langle p\Pi|L_+|p\Sigma\rangle = 2^{1/2}, \qquad \alpha = 2^{1/2}A/2 = 2^{-1/2}A$, and $\beta = 2^{1/2}B$

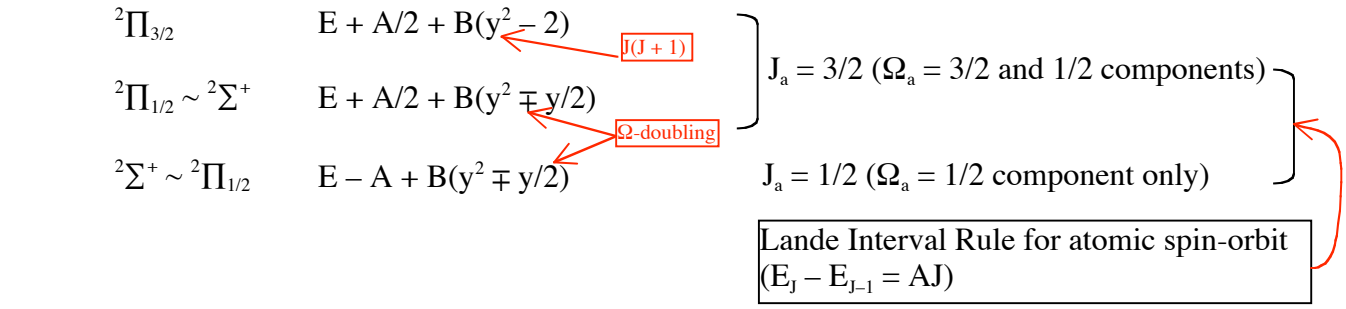
$\binom{e}{f}$	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$^2\Sigma^+$
$^2\Pi_{3/2}$	$E + A/2 + B(y^2 - 2)$	$-B(y^2 - 1)^{1/2}$	$-2^{1/2}B(y^2 - 1)^{1/2}$
$^2\Pi_{1/2}$		$E - A/2 + By^2$	$2^{-1/2}A + 2^{1/2}B(1 \mp y)$
$^2\Sigma^+$			$E + B(y^2 \mp y)$

When $A \gg Bx$, must diagonalize 2×2 $\Omega = 1/2$ sub-matrix. First subtract out center of gravity.

$$E - A/4 + By^2 \mp B(y/2) + \begin{pmatrix} -A/4 \pm By/2 & 2^{-1/2}A \\ \text{sym} & A/4 \mp By/2 \end{pmatrix} \begin{pmatrix} e \\ f \end{pmatrix}$$

solve secular equation, eigenvalues are $\approx \pm$ 3/4A when $A \gg Bx \approx By2$ (thus $A \gg By$)

Get atom-like energy level patterns



(large A prevents Ω = 1/2 and Ω = 3/2 mixing). (Large spin-orbit destroys Λ.)

Case (d)

Consider a p-complex again, now in case (d) and let A = 0 $\beta = 2^{1/2}B$ $E_\Pi = E_\Sigma = E$

$\binom{e}{f}$	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$^2\Sigma^+$
$^2\Pi_{3/2}$	$E + B(y^2 - 2)$	$-B(y^2 - 1)^{1/2}$	$-2^{1/2}B(y^2 - 1)^{1/2}$
$^2\Pi_{1/2}$		$E + By^2$	$2^{1/2}B(1 \mp y)$
$^2\Sigma^+$			$E + By(y \mp 1)$

Simplify by first transforming $^2\Pi$ block to case (b).

$\psi_\pm = 2^{-1/2}\left[|3/2\rangle \pm |1/2\rangle\right]$ (± is NOT parity)

ΔJ = 0 matrix elements:

$$\left\langle \psi_{\pm} \left| \widehat{\mathbf{H}} \right| \psi_{\pm} \right\rangle = E + B\left(y^2 - 1\right) \mp B\left(y^2 - 1\right)^{1/2}$$

$$= E + Bz(z \mp 1) \qquad z \equiv \left(y^2 - 1\right)^{1/2} \approx y$$

$$\left\langle \psi_{\pm} \left| \widehat{\mathbf{H}} \right| \psi_{\mp} \right\rangle = -B$$

$$\left\langle \psi_{\pm} \left| \widehat{\mathbf{H}} \right| \Sigma_e^+ \right\rangle = -B\left[\left(y^2 - 1\right)^{1/2} \pm (y - 1)\right] \approx -B(y \pm y) \qquad \text{(zero for } -\text{)}$$

$$\left\langle \psi_{\pm} \left| \widehat{\mathbf{H}} \right| \Sigma_f^+ \right\rangle \approx -B(y \mp y) \qquad \text{(zero for } +\text{)}$$

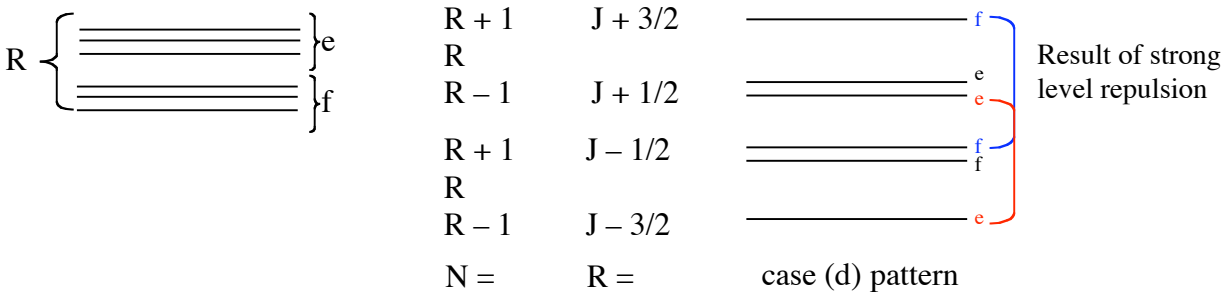
$$+^{e}\begin{pmatrix} E + Bz(z-1) & -B & -2By \\ -B & E + Bz(z+1) & 0 \\ & & E + By(y-1) \end{pmatrix}$$

$$-\Sigma$$

$$+^{f}\begin{pmatrix} E + Bz(z-1) & -B & 0 \\ -B & E + Bz(z+1) & -2By \\ & & E + By(y+1) \end{pmatrix}$$

$$-\Sigma$$

Get groupings of same-R levels as follows.



(same R levels)
[total parity is $(-1)^{R+1}$]

Can you draw correlation diagram?

case(c) case(b) case(d)

For Rydberg states

$N = N^+ + \ell_R$ (N^+ is same as R)

N is good quantum number (because spin-orbit is negligibly small) but N^+ is pattern-forming. We can determine N from "stacked plots", viewing same energy region from different, known-N intermediate levels. How do we determine N^+ (and ℓ_R) from patterns in the spectrum?

$N = N^+ + \ell_R$ (ℓ_R is projection of ℓ on $R \equiv N^+$ here)

$$E(N^+) = BN^+(N^+ + 1) = B\left[(N - \ell_R)(N - \ell_R + 1)\right]$$

$$= B\left[N(N+1) - 2N\ell_R + \ell_R^2 - \ell_R\right]$$

Know N from spectroscopic selection rules. Know B from ion-core B-value.

Plot $E - BN(N + 1)$ vs. N. Get straight line plot of slope $-2B\ell_R$. Knowing N and ℓ_R, know N^+.