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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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Lecture #18: Perturbations

Last time: pattern forming rotational quantum numbers give
 * $^1\Sigma^+$ -like pattern
 * natural grouping of several nearly identical patterns
 * coupling terms that give systematic departure from one limiting case
 e.g. S-uncoupling in Λ -S multiplet
 ℓ -uncoupling in Rydberg complex (“pure precession”)

Today: “Accidental” departures from regular pattern
 * level spacings
 * intensities
 due to accidental degeneracy between zero-order states.

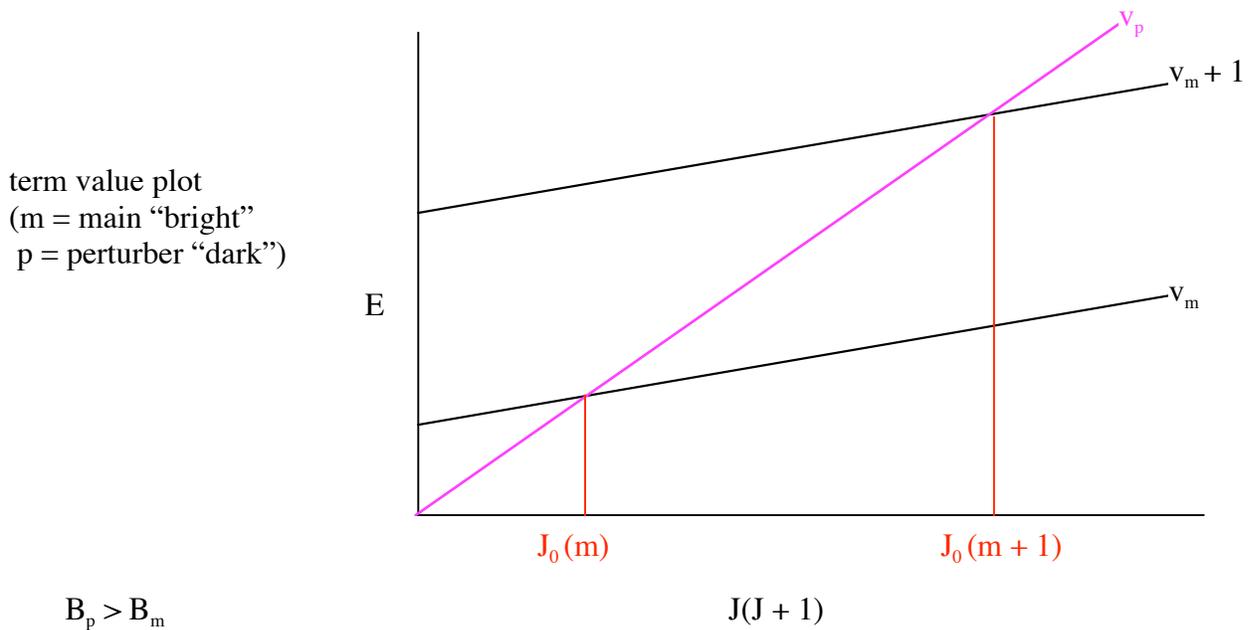
Avoided crossings on term value plots
 Disruption of spectrum - lines out of order, extra lines
 Railroad tie diagrams for perturbations - importance of e and f rather than + and - labels
 2×2 degenerate perturbation theory secular equation.

trace invariance

intensities

Suppose there are 2 electronic states near each other. If they have different ω_e and B_e values, there will be many intersections of the rotational term value plots.

Always $[\hat{H}, \mathbf{J}^2] = 0$ J is a rigorous quantum number. No $\Delta J \neq 0$ matrix elements of \hat{H} .



What happens to spectrum for levels near curve crossings?

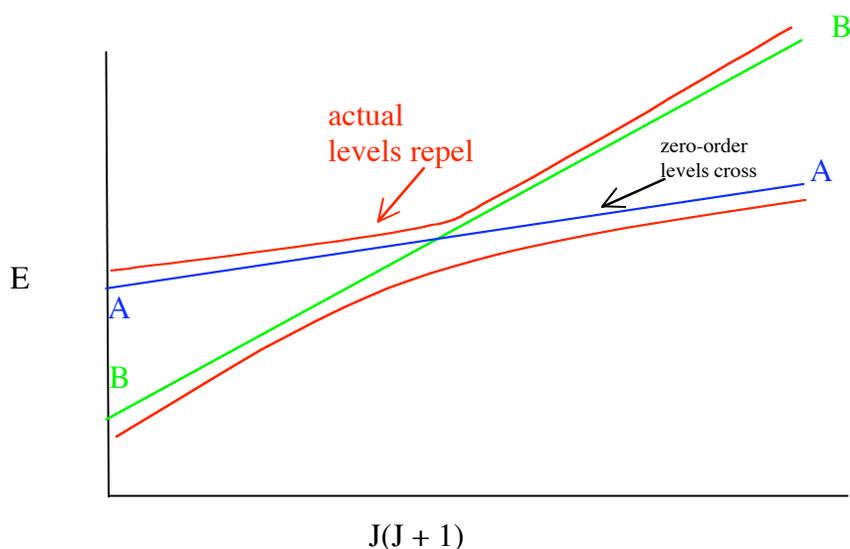
Born-Oppenheimer breakdown effects:

- * avoided crossing
- * level repulsion
- * mixing
- * extra lines
- * intensity borrowing
- * a perturbation
- * interference effects-subtle (anomalous R:P intensity ratios)

Spectra get complicated and difficult to assign because patterns get disrupted.

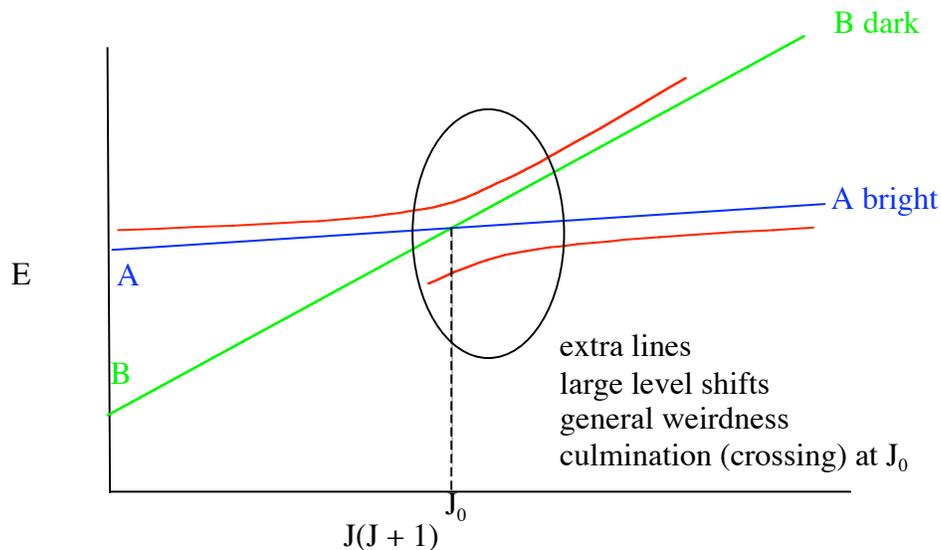
What do we expect?

Avoided Crossing (not of potential curves but of term value plots).



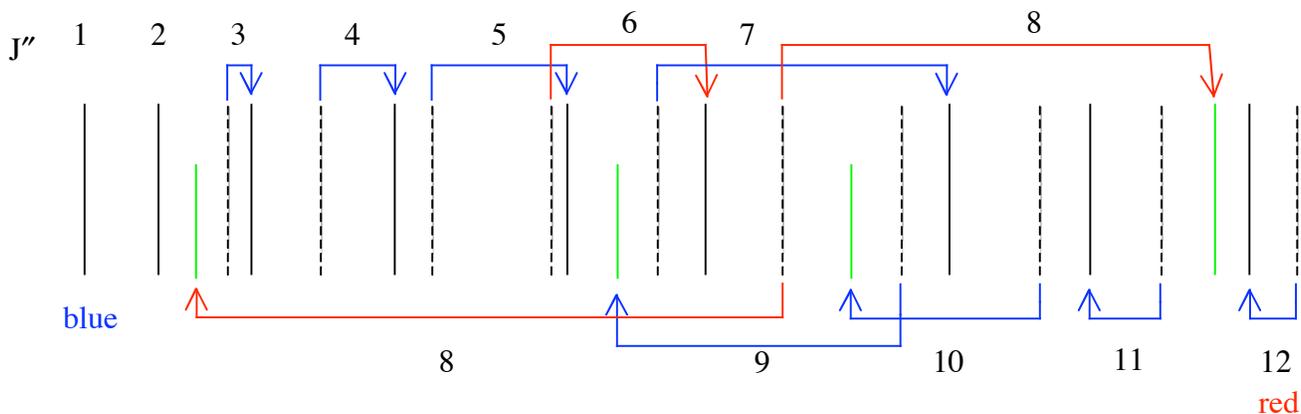
If you follow a continuous series of levels, you go smoothly from A-like at low-J to B-like at high-J.

What typically happens in observable spectrum is that only one of 2 zero order states is “bright” - i.e. has an allowed transition from the initial state. Say A is bright. Would then see two incomplete and unconnected series of A-like levels. (“Bright” vs. “Dark” is experiment-specific.)



Levels get shifted from expected location by amount that can be large with respect to spacings between consecutive lines in a branch.

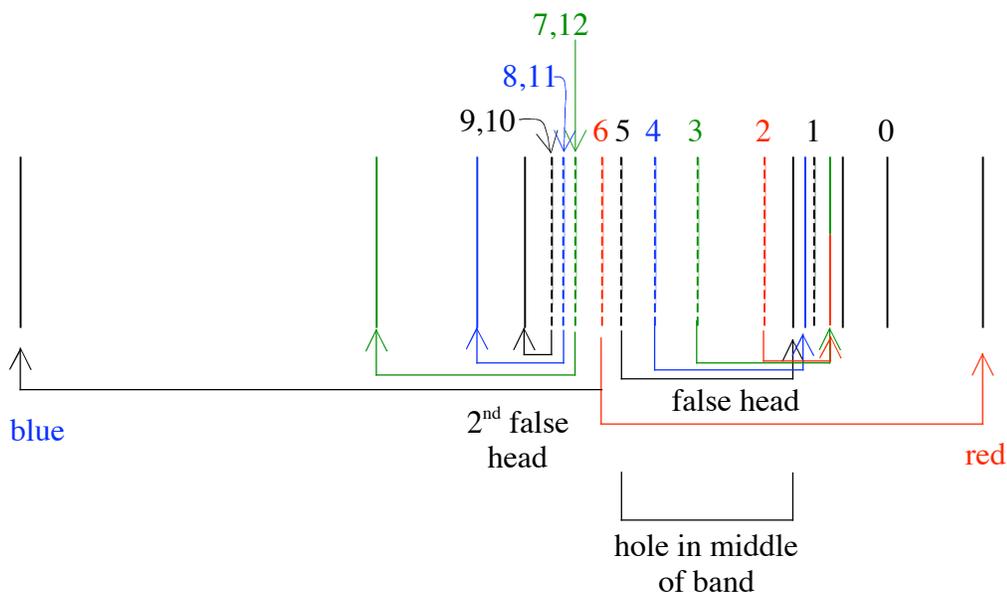
E.g. P branch - perturbation in upper state. Dotted lines are predicted (not perturbed) and solid lines are observed (perturbed). (Above diagram is for dark state with larger B-value than bright-state. Diagram below is for dark state with smaller B-value than bright state. Sorry!)



If perturbation is in upper state by a perturber with smaller B-value than the bright state, bright levels are here shown being pushed to lower energy below the $J' = J_0 = 7$ level of the maximum shift.

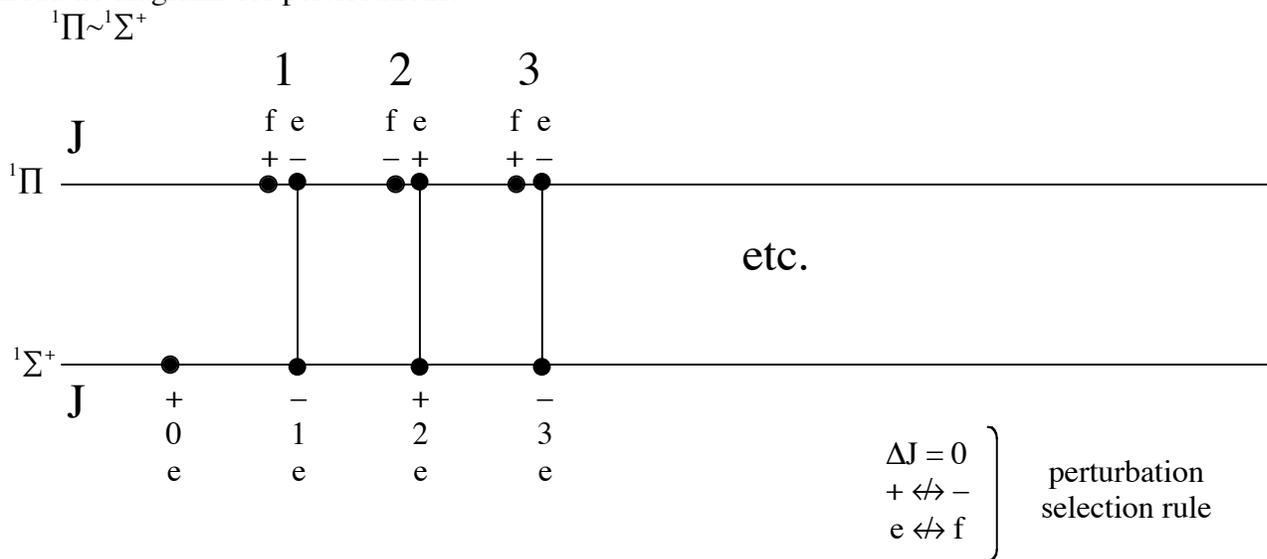
- * branch out of order
- * two P(8) lines!
- * two series of term values
- * level shifts reverse sign on opposite sides of the “culmination” at $J' = 7$

What happens in R branch (head forming)?



Use 2×2 degenerate perturbation theory to compute level shift and relative intensity of main and extra lines (later).

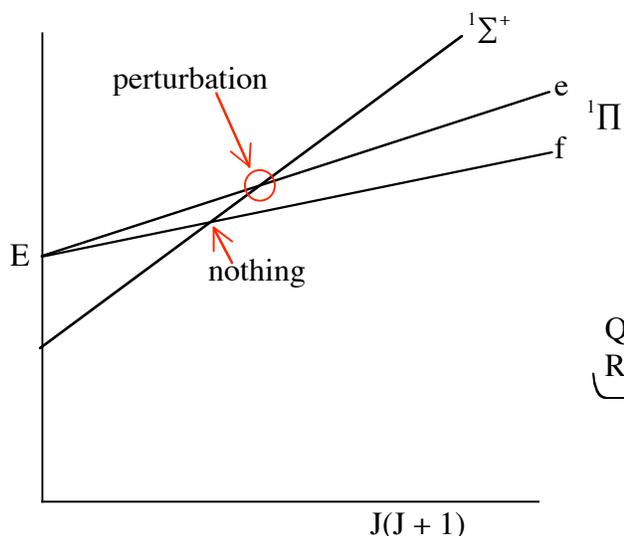
Railroad tie diagrams for perturbations.



Note how e/f works:

- * e always above f (or vice versa) in ${}^1\Pi$
- * all ${}^1\Sigma^+$ levels are e
- * ${}^1\Pi \sim {}^1\Sigma^+$ perturbations only affect ${}^1\Pi_e$ levels.

* NOT SHOWN, for $\dots {}^1\Pi - {}^1\Sigma^+$ transitions, all R,P branches sample e levels and all Q lines sample f levels. Perturbations would not occur in Q branch, only appear in R, P branches!



$$B_e^\Pi - B_f^\Pi \equiv q_\Pi$$

↙ Λ-doubling constant

Upper state combination defects

$$Q(J) - P(J) = B_f J(J+1) - B_e J(J-1) \quad (\text{called QP})$$

$$R(J) - Q(J) = B_e (J+1)(J+2) - B_f (J+1) \quad (\text{called RP})$$

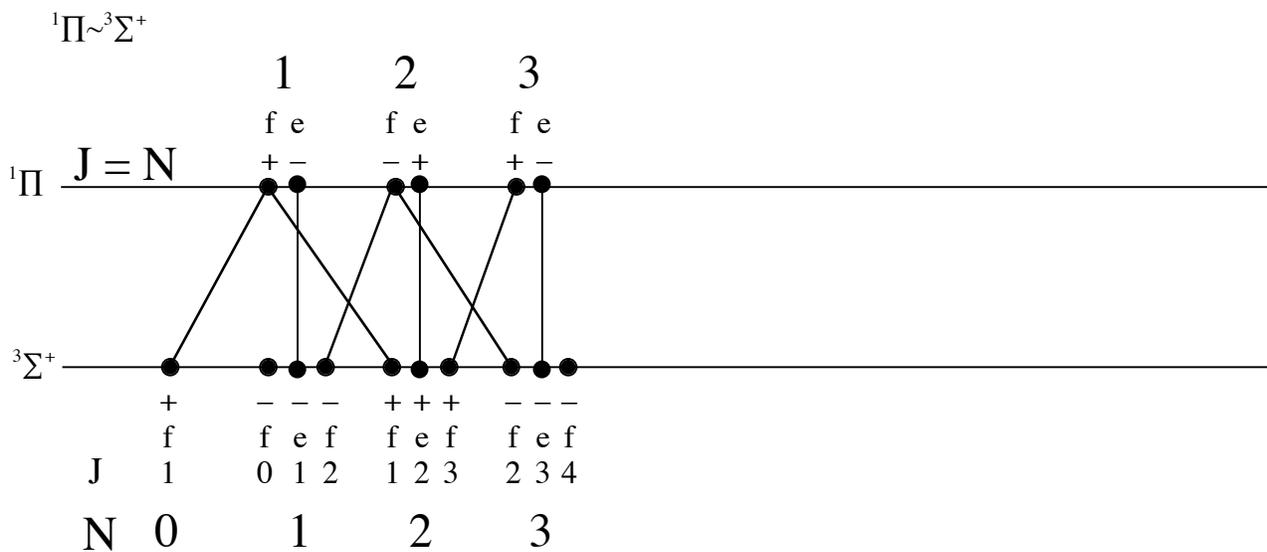
same lower-state J''

$$QP = 2JB_e - J(J+1)q$$

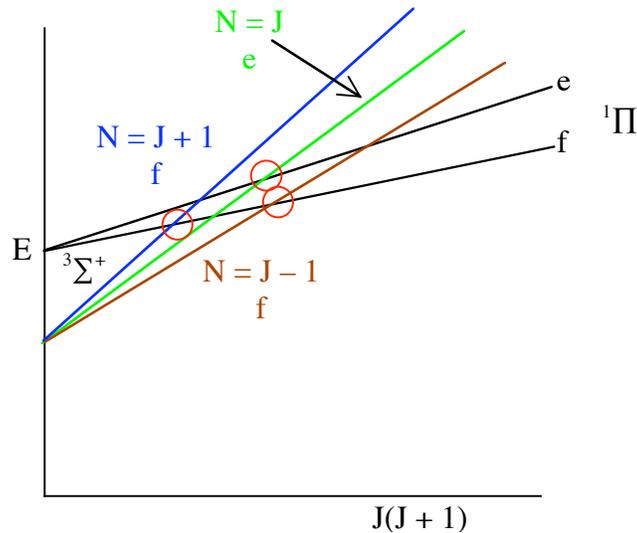
$$QP/2J = B_e - [(J+1)/2]q$$

$$RQ = 2(J+1)B_e + J(J+1)q$$

$$RQ/2(J+1) = B_e + (J/2)q$$



Every $^1\Pi_f$ level perturbed (twice) by $N = J \pm 1$ $^3\Sigma^+$ levels.
 Every $^1\Pi_e$ level perturbed (once) by only $N = J$ $^3\Sigma^+$ levels.



How do we model these perturbation effects?

$$E_{Av_A J}^o = T_A^o + G_A^o(v_A) + F_{A,v_A}^o(J) = T_{Av_A}^o + B_{Av_A}^o J(J+1)$$

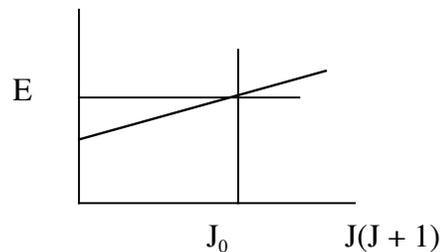
$$E_{Bv_B J}^o = T_{Bv_B}^o + B_{v_B}^o J(J+1)$$

(o's mean zero-order or “deperturbed” quantities)

Let $E_{Bv_B, J_0}^o - E_{Av_A, J_0}^o \equiv 0$ (definition of non-integer J_0 of level crossing)

$$\mathbf{H} = \begin{vmatrix} E_{Av_A J}^o & \mathbf{H}_{Av_A J; Bv_B J} \\ \text{sym} & E_{Bv_B J}^o \end{vmatrix}$$

$$= \begin{vmatrix} \bar{E}_J & 0 \\ 0 & \bar{E}_J \end{vmatrix} + \begin{vmatrix} d_J & V_J \\ V_J & -d_J \end{vmatrix}$$



$$\bar{E}_J \equiv \frac{E_{Av_A J}^{\circ} + E_{Bv_B J}^{\circ}}{2} = \bar{T}^{\circ} + \bar{B}^{\circ} J(J+1)$$

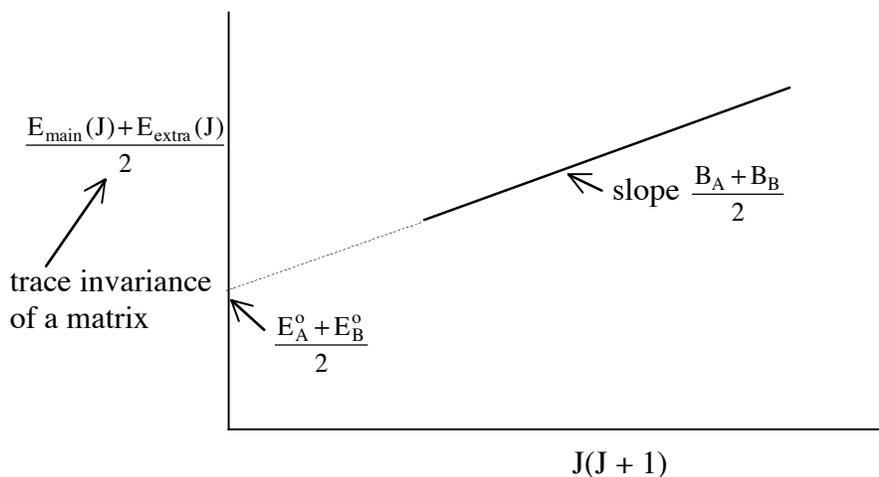
$$d_J \equiv [\Delta T^{\circ} + \Delta B^{\circ} J(J+1)]/2$$

$$V_J = V_0 + J V_1 + \dots$$

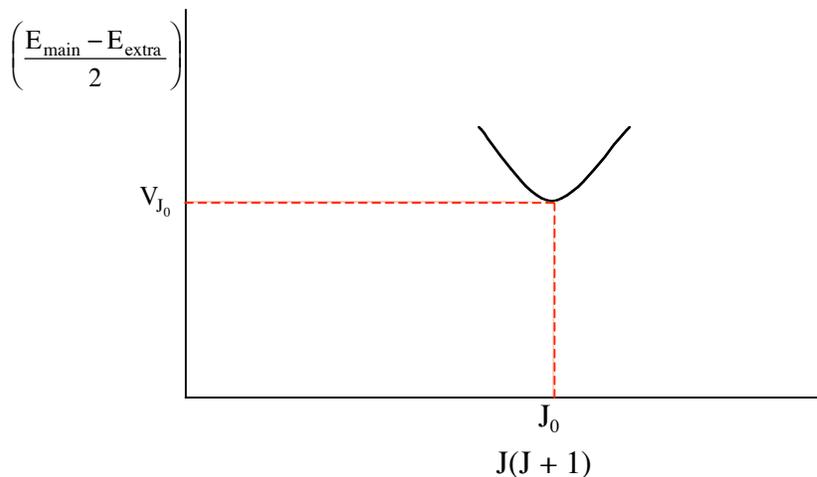
← Homogeneous perturbations ($\Delta\Omega = 0$)
← Heterogeneous perturbations ($\Delta\Omega = \pm 1$)

Eigenvalues of 2×2 (observed levels): $E_{J\pm} = \bar{E}_J \pm [d_J^2 + V_J^2]^{1/2}$.

Some useful tricks:

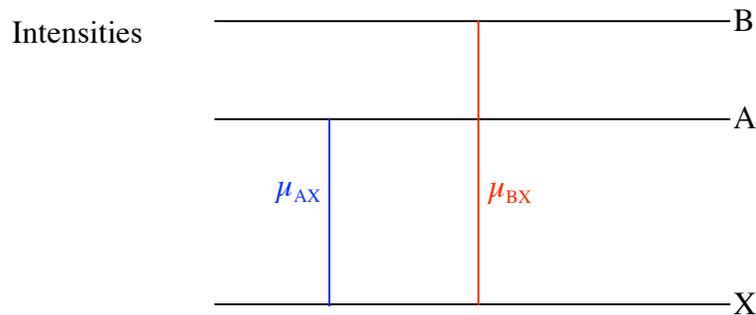


Usually know E_A° , B_A° , so can derive $E_B^{\circ} + B_B^{\circ}$ from slope and intercept of above plot.



Because $\left(\frac{E_{\text{main}} - E_{\text{extra}}}{2}\right) = [d_J^2 + V_J^2]^{1/2}$ where, at J_0 , $d_{J_0} \equiv 0$

Get V_{J_0} from minimum separation of main and extra lines.



Assume B is “dark”. $\mu_{BX} = 0$

Mixed levels:

$$|J + \rangle = \overset{\text{higher of 2}}{(1 - \alpha_J^2)^{1/2}} |B v_B J \rangle + \alpha_J |A v_A J \rangle$$

$$|J - \rangle = \overset{\text{lower of 2}}{-\alpha_J} |B v_B J \rangle + (1 - \alpha_J^2)^{1/2} |A v_A J \rangle$$

$$I_+ \propto \left| \langle + | \mu | X \rangle \right|^2 = \underbrace{(1 - \alpha_J^2) \mu_{BX}^2 + \alpha_J^2 \mu_{AX}^2}_{\text{always positive}} + \underbrace{2\alpha_J (1 - \alpha_J^2)^{1/2} \mu_{AX} \mu_{BX}}_{\text{either positive or negative}}$$

Similar equation for I_-
If only state A is bright.

$$\frac{I_-}{I_+} = \frac{1 - \alpha_J^2}{\alpha_J^2} \quad \begin{array}{l} \text{extra} \\ \text{main} \end{array}$$

From eigenvectors of 2×2

$$\alpha_J^2 = \frac{1}{2} \left[1 - \frac{d_J}{(d_J^2 + V_J^2)^{1/2}} \right] \approx \left(\frac{V_J}{\underbrace{2d_J}_{\Delta E^\circ(J)}} \right)^2$$

If $2d_J \gg V_J$ can use
non-degenerate
perturbation theory.

If $|\mu_{AX}| \approx |\mu_{BX}|$ get amazing interference effects

$$I_+ \propto \left| \langle + | \mu | X \rangle \right|^2 = \underbrace{(1 - \alpha_J^2) \mu_{BX}^2 + \alpha_J^2 \mu_{AX}^2}_{\text{always positive}} + \underbrace{2\alpha_J (1 - \alpha_J^2)^{1/2} \mu_{AX} \mu_{BX}}_{\text{can be positive or negative}}$$

Here, direction cosine factors are included in μ_{AB} and μ_{BX} . For perturbation between states with \parallel and \perp type transitions from the X state, direction cosines for R and P of \perp have opposite signs, but R and P of \parallel have same signs. Get R, P intensity anomaly.