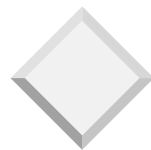


Ligand Field Theory Notes

Read:

- Highbanks, *Antisymmetry* (Handout).
- Carter, *Molecular Symmetry...*, Sections 7.4-6.
- Cotton, *Chemical Applications...*, Chapter 9.
- Harris & Bertolucci, *Symmetry and Spectroscopy...*, Chapter 5, pp. 316-30, pp. 395-419.

1



States and Configurations

- ★ Each of the electronic states of an atom or a molecule are usually described as being built up from one (or perhaps more than one) configuration.
- ★ The physical origin of energy differences between atomic states for a single configuration is e⁻e⁻ repulsion.
- ★ Hund's Rules are based on the systematics of differential e⁻e⁻ repulsion.

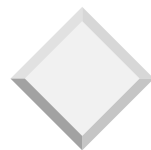
2



Hund's Rules for Atomic Ground States

- ★ For states of an atom or a molecule built up from one configuration.
- ★ 1st rule: Ground state has maximum spin multiplicity (largest value of S).
- ★ 2nd rule: For a given value of S , state with maximum L is most stable.
- ★ 3rd rule: For a given S and L , the min. J state most stable if shell is $< 1/2$ -filled & max. J most stable if shell is $> 1/2$ -filled.

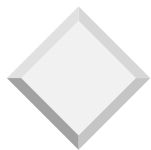
3



Examples

- ★ States for a Ti²⁺ ion with a [Ar]3d² configuration?
- ★ States for a Cr³⁺ ion with a [Ar]3d³ configuration?

4



Splitting of Atomic States in Chemical Environments

★ How do atomic states split in non-spherical chemical environments? Before addressing this question, we need a general formula for the character for a rotation operation by angle α when operated on a state with angular momentum L :

$$\chi(C_\alpha) = \frac{\sin(L+1/2)\alpha}{\sin\alpha/2}$$

5

Mathematical Origin of Formula

$$C_\alpha e^{im\varphi} \rightarrow e^{im(\varphi-\alpha)} = e^{i(-m)\alpha} e^{im\varphi}$$

$$C_\alpha \begin{bmatrix} e^{iL\varphi} \\ e^{i(L-1)\varphi} \\ \vdots \\ e^0 \\ \vdots \\ e^{i(1-L)\varphi} \\ e^{i(-L)\varphi} \end{bmatrix} = \begin{bmatrix} e^{i(-L)\alpha} e^{iL\varphi} \\ e^{i(1-L)\alpha} e^{i(L-1)\varphi} \\ \vdots \\ e^0 \\ \vdots \\ e^{i(L-1)\alpha} e^{i(1-L)\varphi} \\ e^{iL\alpha} e^{i(-L)\varphi} \end{bmatrix} = \begin{bmatrix} e^{i(-L)\alpha} & & & & & & \\ & e^{i(1-L)\alpha} & & & & & \\ & & \ddots & & & & \\ & & & 0 & & & \\ & & & & e^0 & & \\ & & & & & \ddots & \\ & & & & & & e^{i(L-1)\alpha} \\ & & & & & & & e^{iL\alpha} \end{bmatrix} \begin{bmatrix} e^{iL\varphi} \\ e^{i(L-1)\varphi} \\ \vdots \\ e^0 \\ \vdots \\ e^{i(1-L)\varphi} \\ e^{i(-L)\varphi} \end{bmatrix}$$

$$\chi(C_\alpha) = e^{i(-L)\alpha} + e^{i(1-L)\alpha} + \dots + e^0 + \dots + e^{i(L-1)\alpha} + e^{iL\alpha} = \frac{z^{-(L+1/2)} - z^{L+1/2}}{z^{-1/2} - z^{1/2}} \quad (z = e^{i\alpha})$$

[do clever factoring and use geometric series: $\sum_0^\infty z^n = 1/(1-z)$ with $z = e^{i\alpha}$]

$$\chi(C_\alpha) = \frac{\sin(L+1/2)\alpha}{\sin\alpha/2}$$

A more complete analysis shows that is a result of angular momentum commutation relations.

6

2 proofs of Formula

Trigonometric Proof

$$S = e^{i(-L)\alpha} + e^{i(1-L)\alpha} + \dots + e^0 + \dots + e^{i(L-1)\alpha} + e^{iL\alpha} = 1 + 2\cos\alpha + \dots + 2\cos L\alpha$$

$$= \frac{\sin\frac{\alpha}{2} + 2\cos\alpha\sin\frac{\alpha}{2} + \dots + 2\cos L\alpha\sin\frac{\alpha}{2}}{\sin\frac{\alpha}{2}}$$

Now, repeatedly use the formula $2\cos A\sin B = \sin(A+B) - \sin(A-B)$ to get

$$S = \frac{1}{\sin\frac{\alpha}{2}} \left[\sin\frac{\alpha}{2} + \left(\sin\frac{3\alpha}{2} - \sin\frac{\alpha}{2} \right) + \left(\sin\frac{5\alpha}{2} - \sin\frac{3\alpha}{2} \right) + \dots + \left(\sin\frac{(2L+1)\alpha}{2} - \sin\frac{(2L-1)\alpha}{2} \right) \right]$$

$$= \frac{\sin(L+1/2)\alpha}{\sin\alpha/2}$$

Complex numbers Proof, using geometric series

$$\chi(C_\alpha) = e^{i(-L)\alpha} + e^{i(1-L)\alpha} + \dots + e^0 + \dots + e^{i(L-1)\alpha} + e^{iL\alpha} = e^{i(-L)\alpha} (1 + e^\alpha + \dots + e^{i2L\alpha})$$

$$= e^{i(-L)\alpha} (1 + e^{i\alpha} + \dots + e^{i2L\alpha} + e^{i(2L+1)\alpha} + \dots) - e^{i(L+1)\alpha} (1 + e^{i\alpha} + \dots + e^{i2L\alpha} + e^{i(2L+1)\alpha} + \dots)$$

$$= \frac{(e^{i(L+1)\alpha} - e^{i(-L)\alpha})}{e^{i\alpha} - 1} \times \frac{e^{-i\alpha/2}}{e^{-i\alpha/2}} = \frac{(e^{i(L+1/2)\alpha} - e^{-i(L+1/2)\alpha})}{e^{i\alpha/2} - e^{-i\alpha/2}} = \frac{\sin(L+1/2)\alpha}{\sin\alpha/2}$$

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Formulas for All Operations

Carter, p. 205

$$\chi(E) = 2J + 1$$

$$\chi(C_\alpha) = \frac{\sin[(J+1/2)\alpha]}{\sin(\alpha/2)}$$

$$\chi(i) = \pm(2J+1)$$

$$\chi(S_\alpha) = \pm \frac{\sin[(J+1/2)(\alpha+\pi)]}{\sin[(\alpha+\pi)/2]}$$

$$\chi(\sigma) = \pm \sin[(J+1/2)\pi]$$

- + signs apply for a *gerade atomic state* and - signs apply for an *ungerade atomic state*, whether the point group under consideration has inversion symmetry or not. Examples: a 3P state derived from either p^2 configuration ($u \times u$) or a d^2 configuration ($g \times g$) give g states. However, a 2D state derived from a p^3 configuration ($u \times u \times u$) gives a u state, while a 2D state derived from a d^3 configuration ($g \times g \times g$) gives a g state.
- The symbol J refers to the angular momentum quantum number of the state under consideration. In the Russell-Saunders scheme, J can be replaced by L when considering a spatial wave function.

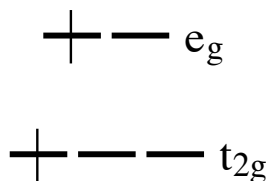
8



States from Molecular Configurations; the d^2 case

Electronic configurations for which there is no possibility of violating the Pauli principle are easy to handle:

For example, the $(t_{2g})^1(e_g)^1$ configuration



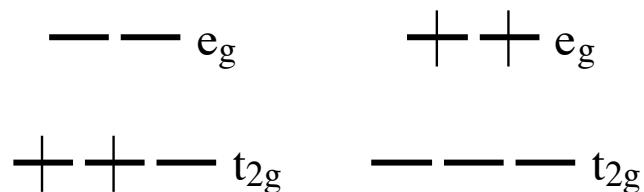
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States from Molecular Configurations; the d^2 case

Configurations for which Pauli principle violations can occur must be handled carefully:

The t_{2g}^2 or e_g^2 configuration



10

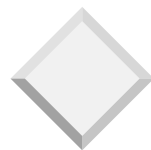
Antisymmetric Wavefunctions (Pauli Principle)

⇒ **Read:** *Antisymmetry* handout; Harris & Bertolucci, *Symmetry and Spectroscopy...*, Chapter 5, pp. 316-30.

⇒ Wavefunctions describing 'Fermions' (e.g., electrons) must be antisymmetric with respect to interchange of any two particles (electrons) labels.

$$\Psi(1,2,\dots,i,\dots,j,\dots,N) = -\Psi(1,2,\dots,j,\dots,i,\dots,N)$$

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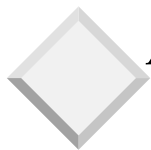


Singlets and Triplets

★ If two electrons occupy two different orbitals, one can form either a singlet or triplet state. Including spin functions, these have the form:

$$\begin{array}{l} \left. \begin{array}{l} S=1; 2S+1=3 \\ {}^3\Psi = \frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)) \end{array} \right\} \begin{array}{l} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{array} \right\} \begin{array}{l} M_S \\ 1 \\ 0 \\ -1 \end{array} \\ \left. \begin{array}{l} S=0 \\ {}^1\Psi = \frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)) \end{array} \right\} \begin{array}{l} \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \\ 0 \end{array} \end{array}$$

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Antisymmetric Wavefunctions (Pauli Principle)

★ Singlets:

$${}^1\Psi = \frac{1}{\sqrt{2}} \overbrace{(\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2))}^{\text{Symmetric}} \times \overbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}^{\text{Antisymmetric}} \quad M_S = 0$$

★ Triplets:

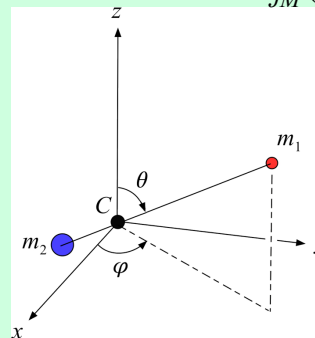
$${}^3\Psi = \frac{1}{\sqrt{2}} \overbrace{(\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))}^{\text{Antisymmetric}} \times \left\{ \begin{array}{l} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{array} \right\} \quad \begin{array}{l} 1 \\ 0 \\ -1 \end{array}$$

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Digression: Ortho- and Parahydrogen

Rotational wavefunctions, $Y_{JM}(\theta, \varphi)$
Permuting nuclei is equivalent to inversion

$$Y_{JM}(\theta, \varphi) \rightarrow (-1)^J Y_{JM}(\theta, \varphi)$$



Note: The $Y_{JM}(\theta, \varphi)$ functions are the same as the $Y_{l, m_l}(\theta, \varphi)$ functions familiar to you as the atomic orbitals with quantum nos. l and m_l .

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Digression: Ortho- and Parahydrogen

The rotational and nuclear spin wavefunctions are affected by permutation of the two protons. Since protons are fermions, the product of the two wavefunctions must be antisymmetric. There are two possibilities.

Rotational wavefunctions, $Y_{JM}(\theta, \varphi)$
Permuting nuclei is equivalent to inversion
 $Y_{JM}(\theta, \varphi) \rightarrow (-1)^J Y_{JM}(\theta, \varphi)$

$$\Psi_{\text{ortho}} = \overbrace{Y_{JM}(\theta, \varphi)}^{\text{Antisymmetric}} \times \overbrace{\left\{ \begin{array}{l} \alpha_1^N \alpha_2^N \\ \frac{1}{\sqrt{2}}(\alpha_1^N \beta_2^N + \beta_1^N \alpha_2^N) \\ \beta_1^N \beta_2^N \end{array} \right\}}^{\text{Symmetric}} \quad J = 1, 3, 5, \dots$$

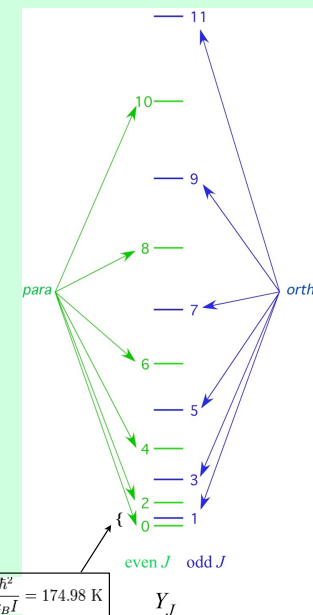
$$\Psi_{\text{para}} = \overbrace{Y_{JM}(\theta, \varphi)}^{\text{Symmetric}} \times \overbrace{\left\{ \begin{array}{l} \alpha_1^N \alpha_2^N \\ \frac{1}{\sqrt{2}}(\alpha_1^N \beta_2^N - \beta_1^N \alpha_2^N) \\ \beta_1^N \beta_2^N \end{array} \right\}}^{\text{Antisymmetric}} \quad J = 0, 2, 4, \dots$$

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Digression: Ortho- and Para-H₂

In *para*-H₂ only rotational levels with even J are allowed, In *ortho*-H₂ only rotational levels with odd J are allowed. The *ortho*-H₂ wavefunctions have 3-fold spin degeneracy, the *para*-H₂ wavefunctions have no spin degeneracy.

At low T, *ortho*-H₂ has residual rotational energy and entropy (molecules can fall to $J = 1$ level, not into $J = 0$ level). Heat capacities of the two forms are quite different!



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Some Statistical Thermodynamic Relations

$$E_J = \frac{J(J+1)\hbar^2}{2I}; g_J = 2J+1$$

$$Z = \sum_J g_J e^{-E_J/k_B T}; \text{ partition fct. (sum over states)}$$

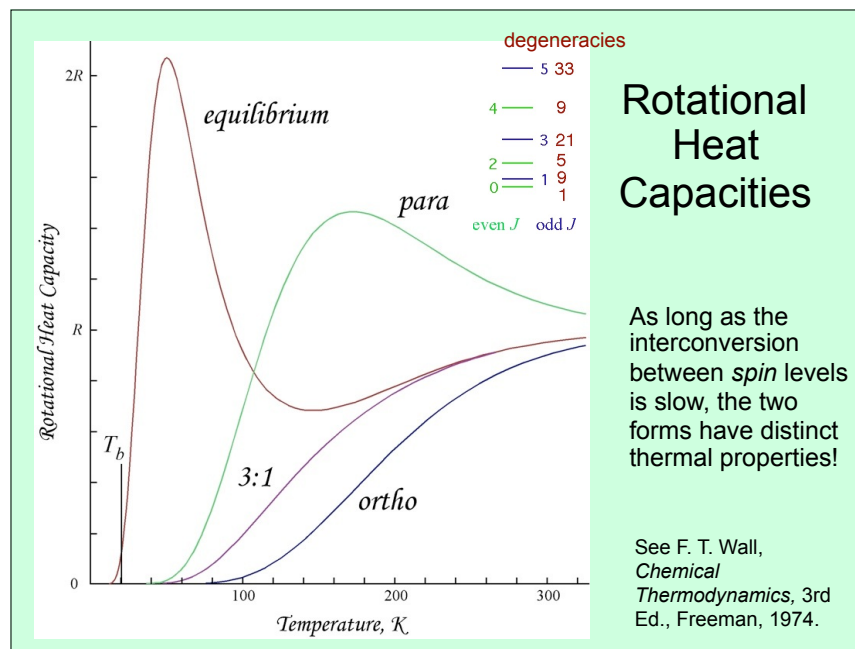
$$Z_{\text{para}} = \sum_{\text{even } J} g_J e^{-E_J/k_B T} = \sum_{\text{even } J} (2J+1) e^{-J(J+1)\hbar^2/2Ik_B T}$$

$$Z_{\text{ortho}} = 3 \sum_{\text{odd } J} g_J e^{-E_J/k_B T} = 3 \sum_{\text{odd } J} (2J+1) e^{-J(J+1)\hbar^2/2Ik_B T}$$

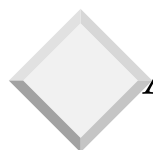
$$Z_{\text{equil}} = \sum_{J=0}^{\infty} (2 - (-1)^J)(2J+1) e^{-J(J+1)\hbar^2/2Ik_B T}$$

$$U_{\text{rot}} = RT^2 \left(\frac{\partial \ln Z}{\partial T} \right); C_{\text{rot}} = \left(\frac{\partial U_{\text{rot}}}{\partial T} \right)$$

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Antisymmetric Direct Product

If two electrons occupy degenerate orbitals, one can form either a singlet or triplet state. The irreducible representation of the triplet state can be determined by finding the antisymmetric direct product*:

$$\chi^-(R) = \frac{1}{2}(\chi^2(R) - \chi(R^2))$$

*See *Antisymmetry* handout for proof.

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Aside: Some Extra Details

The hydrogen atom is a physical problem with much higher symmetry than molecules; the potential energy exerted by the nucleus has spherical symmetry. The role of symmetry is enormous! Nevertheless, that isn't exploited in elementary treatments because the group theory is more demanding. (With great power comes greater difficulty!)

We won't go there in this course, but here are a few suggestive slides...

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Aside: SO(3): The Full Rotation Group*

SO(3)	E	...	∞C_α	...	Normalized Basis Functions (Spherical Harmonics)
$\Gamma_{l=0}$	1	...	1	...	$\frac{1}{\sqrt{4\pi}}$ (s orbitals)
$\Gamma_{l=1}$	3	...	$\frac{\sin(3/2)\alpha}{\sin\alpha/2}$...	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta, \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\varphi}$ (p orbitals)
$\Gamma_{l=2}$	5	...	$\frac{\sin(5/2)\alpha}{\sin\alpha/2}$...	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta-1), \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta e^{\pm i\varphi}, \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\varphi}$ (d orbitals)
...
Γ_l	$2l+1$...	$\frac{\sin(l+1/2)\alpha}{\sin\alpha/2}$...	$Y_{lm}(\theta, \varphi), m = -l, -l+1, \dots, l-1, l$
...

- The *Spherical Harmonics* for each l form a basis for $(2l+1)$ -degenerate irreducible representation, $\Gamma_{l=n}$. From a group theoretical point of view, that's why the hydrogen-atom's p, d, f, \dots orbitals are degenerate (within each set).
- SO(3) is an infinite-order group; in fact, each rotation C_α belongs to an infinite-order class. Consequently, there are an infinite number of irreducible representations, and the order of the I.R.'s grows without bound.

*Special Orthogonal Group of Order 3

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Aside: SO(3) used to get term symbols

Group theory can be used to get atomic terms;

$$\chi(C_\alpha) = \frac{\sin(L+1/2)\alpha}{\sin\alpha/2}$$

Example, what are the terms for a d^2 ion ($\ell = 2$)?

$$\chi^2(C_\alpha) = \frac{\sin^2 5\alpha/2}{\sin^2 \alpha/2} \quad ; \quad \chi(C_\alpha^2) = \frac{\sin 5\alpha}{\sin \alpha}$$

$$\text{Since } \frac{\sin^2 5\alpha/2}{\sin^2 \alpha/2} = 1 + \frac{\sin 3\alpha/2}{\sin \alpha/2} + \frac{\sin 5\alpha/2}{\sin \alpha/2} + \frac{\sin 7\alpha/2}{\sin \alpha/2} + \frac{\sin 9\alpha/2}{\sin \alpha/2},$$

then $\Gamma_d \otimes \Gamma_d = \Gamma_s \oplus \Gamma_p \oplus \Gamma_D \oplus \Gamma_F \oplus \Gamma_G$.

$$\text{But } \frac{\sin 5\alpha}{\sin \alpha} = 1 - \frac{\sin 3\alpha/2}{\sin \alpha/2} + \frac{\sin 5\alpha/2}{\sin \alpha/2} - \frac{\sin 7\alpha/2}{\sin \alpha/2} + \frac{\sin 9\alpha/2}{\sin \alpha/2},$$

$$\text{So } [\Gamma_d \otimes \Gamma_d]^- = \Gamma_p \oplus \Gamma_F \quad \text{and} \quad [\Gamma_d \otimes \Gamma_d]^+ = \Gamma_s \oplus \Gamma_D \oplus \Gamma_G$$

Atomic terms are therefore $^3P, ^3F, ^1S, ^1D$, and 1G

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Aside, continued: In this case, the group theoretic approach isn't necessarily easier! The trigonometric proofs aren't simple...

$$\text{To prove, } \frac{\sin^2(n+\frac{1}{2})\alpha}{\sin\alpha/2} = \sin\alpha/2 + \sin 3\alpha/2 + \dots + \sin(2n+\frac{1}{2})\alpha = S$$

We'll need the formulae:

$$\sin x = \frac{e^{ix} - e^{-ix}}{2i} \quad ; \quad \cos x = \frac{e^{ix} + e^{-ix}}{2} \quad ; \quad \sin^2 \frac{x}{2} = \frac{1 - \cos x}{2} \quad ; \quad \sum_{l=0}^{\infty} x^l = \frac{1}{1-x}$$

Letting $e^{i\alpha} = u$ and using the formula for $\sin x$, we can write the sum S as

$$S = \frac{u^{1/2} - u^{-1/2}}{2i} + \frac{u^{3/2} - u^{-3/2}}{2i} + \dots + \frac{u^{2n+1/2} - u^{-(2n+1/2)}}{2i}$$

$$\text{Gathering terms and factoring, } S = \frac{1}{2i} \left[u^{1/2} \sum_{l=0}^{2n} u^l - u^{-1/2} \sum_{l=0}^{2n} (u^{-1})^l \right]$$

Each term can be summed using geometric series,

$$u^{\pm 1/2} \sum_{l=0}^{2n} u^{\pm l} = u^{\pm 1/2} \left(\sum_{l=0}^{\infty} u^{\pm l} - u^{\pm(2n+1)} \sum_{l=0}^{\infty} u^{\pm l} \right) = (1 - u^{\pm(2n+1)}) \frac{u^{\pm 1/2}}{1 - u^{\pm 1}} = \frac{\mp(1 - u^{\pm(2n+1)})}{u^{1/2} - u^{-1/2}}$$

$$\text{Substituting and rearranging, } S = \frac{1}{2i} \left[\frac{-(1 - u^{2n+1}) - (1 - u^{-(2n+1)})}{u^{1/2} - u^{-1/2}} \right]$$

$$S = \frac{1}{4} \left[\frac{2 - (u^{2n+1} + u^{-(2n+1)})}{(1/2i)(u^{1/2} - u^{-1/2})} \right] = \frac{(1 - \cos(2n+1)\alpha)/2}{\sin\alpha/2} = \frac{\sin^2(n+\frac{1}{2})\alpha}{\sin\alpha/2}$$

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Aside, continued...

$$\text{To prove: } \frac{\sin 5\alpha}{\sin \alpha} = 1 - \frac{\sin 3\alpha/2}{\sin \alpha/2} + \frac{\sin 5\alpha/2}{\sin \alpha/2} - \frac{\sin 7\alpha/2}{\sin \alpha/2} + \frac{\sin 9\alpha/2}{\sin \alpha/2} = S$$

$$\frac{\sin 9\alpha/2}{\sin \alpha/2} = e^{-4i\alpha} + e^{-3i\alpha} + e^{-2i\alpha} + e^{-i\alpha} + 1 + e^{i\alpha} + e^{2i\alpha} + e^{3i\alpha} + e^{4i\alpha}$$

$$-\frac{\sin 7\alpha/2}{\sin \alpha/2} = -e^{-3i\alpha} - e^{-2i\alpha} - e^{-i\alpha} - 1 - e^{i\alpha} - e^{2i\alpha} - e^{3i\alpha}$$

$$\frac{\sin 5\alpha/2}{\sin \alpha/2} = e^{-2i\alpha} + e^{-i\alpha} + 1 + e^{i\alpha} + e^{2i\alpha}$$

$$-\frac{\sin 3\alpha/2}{\sin \alpha/2} = -e^{-i\alpha} - 1 - e^{i\alpha}$$

$$\text{Summing, } S = e^{-4i\alpha} + e^{-2i\alpha} + 1 + e^{2i\alpha} + e^{4i\alpha}$$

If we use the formula for $\frac{\sin 5\beta/2}{\sin \beta/2}$ and replace $\beta/2$ with α , we obtain the desired result!

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Slater Determinants

- Determinants have the antisymmetry property "built-in":

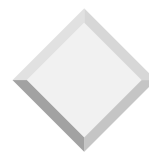
$$\Psi(1,2,\dots,i,\dots,j,\dots,N) = \phi(i) = \varphi(i)[\text{spinfuction}(i)]$$

Different Spin Orbitals in Columns

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_p(1) & \dots & \phi_q(1) & \dots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_p(2) & \dots & \phi_q(2) & \dots & \phi_z(2) \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ \phi_a(i) & \phi_b(i) & \dots & \phi_p(i) & \dots & \phi_q(i) & \dots & \phi_z(i) \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ \phi_a(j) & \phi_b(j) & \dots & \phi_p(j) & \dots & \phi_q(j) & \dots & \phi_z(j) \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ \phi_a(N) & \phi_b(N) & \dots & \phi_p(N) & \dots & \phi_q(N) & \dots & \phi_z(N) \end{vmatrix}$$

Different electrons in rows

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Slater Determinant - N atom

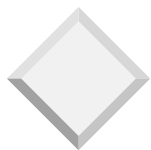
$$\frac{1}{\sqrt{7!}} \begin{vmatrix} 1s(1) & \overline{1s(1)} & 2s(1) & \overline{2s(1)} & 2p_x(1) & 2p_y(1) & 2p_z(1) \\ 1s(2) & \overline{1s(2)} & 2s(2) & \overline{2s(2)} & 2p_x(2) & 2p_y(2) & 2p_z(2) \\ 1s(3) & \overline{1s(3)} & 2s(3) & \overline{2s(3)} & 2p_x(3) & 2p_y(3) & 2p_z(3) \\ 1s(4) & \overline{1s(4)} & 2s(4) & \overline{2s(4)} & 2p_x(4) & 2p_y(4) & 2p_z(4) \\ 1s(5) & \overline{1s(5)} & 2s(5) & \overline{2s(5)} & 2p_x(5) & 2p_y(5) & 2p_z(5) \\ 1s(6) & \overline{1s(6)} & 2s(6) & \overline{2s(6)} & 2p_x(6) & 2p_y(6) & 2p_z(6) \\ 1s(7) & \overline{1s(7)} & 2s(7) & \overline{2s(7)} & 2p_x(7) & 2p_y(7) & 2p_z(7) \end{vmatrix}$$

$2p$ \uparrow \uparrow \uparrow
 $2s$ $\uparrow\downarrow$
 $1s$ $\uparrow\downarrow$

which is written as

$$\begin{vmatrix} 1s & \overline{1s} & 2s & \overline{2s} & 2p_x & 2p_y & 2p_z \end{vmatrix}$$

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Slater Determinants-Properties

notation: $\phi(i) = \varphi(i)[\alpha(i) \text{ or } \beta(i)]$ $i = \text{electron label}$

- Swap any two columns (or rows) and the determinant switches sign:

$$|\phi_A \dots \phi_p \dots \phi_q \dots| = -|\phi_A \dots \phi_q \dots \phi_p \dots|$$

\therefore if any two columns (rows) are identical, the determinant vanishes!

- Columns (rows) can be factored:

$$|\phi_A \dots \phi_p + \phi_q \dots \phi_R \dots| = |\phi_A \dots \phi_p \dots \phi_R \dots| + |\phi_A \dots \phi_q \dots \phi_R \dots|$$

- Any constant (including -1) can be factored out:

$$|\phi_A \dots c\phi_p \dots \phi_R \dots| = c|\phi_A \dots \phi_p \dots \phi_R \dots|$$

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Example: Show that the form of the singlet and triplet wavefunctions I gave in "expanded out" form can be expressed as determinants.:

$${}^1\Psi = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)) \left\{ \frac{1}{\sqrt{2}} (\alpha_1\beta_2 - \beta_1\alpha_2) \right\} \begin{matrix} M_S \\ 0 \end{matrix}$$

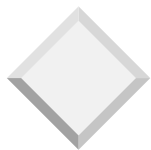
$${}^3\Psi = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)) \left\{ \begin{matrix} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}} (\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{matrix} \right\} \begin{matrix} 1 \\ 0 \\ -1 \end{matrix}$$

Start with four determinants

$$|\phi_a\phi_b|, |\overline{\phi_a}\overline{\phi_b}|, |\phi_a\overline{\phi_b}|, \text{ and } |\overline{\phi_a}\phi_b|$$

expand them out (using the notation and normalizing factors discussed in above), and show that you can recover the "expanded out" forms from the compact determinants. Hint: you will need to take combinations of determinants for both of the $M_S = 0$ cases.

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Exercise: Answers

$$|\phi_a \phi_b\rangle = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\alpha_1 & \varphi_b(1)\alpha_1 \\ \varphi_a(2)\alpha_2 & \varphi_b(2)\alpha_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (\varphi_a(1)\alpha_1 \cdot \varphi_b(2)\alpha_2 - \varphi_b(1)\alpha_1 \cdot \varphi_a(2)\alpha_2)$$

$${}^3\Psi = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))\alpha_1\alpha_2 \quad (M_S = 1)$$

$$|\overline{\phi_a \phi_b}\rangle = \frac{1}{\sqrt{2!}} \begin{vmatrix} \overline{\phi_a(1)} & \overline{\phi_b(1)} \\ \overline{\phi_a(2)} & \overline{\phi_b(2)} \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\beta_1 & \varphi_b(1)\beta_1 \\ \varphi_a(2)\beta_2 & \varphi_b(2)\beta_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (\varphi_a(1)\beta_1 \cdot \varphi_b(2)\beta_2 - \varphi_b(1)\beta_1 \cdot \varphi_a(2)\beta_2)$$

$${}^3\Psi = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))\beta_1\beta_2 \quad (M_S = -1)$$

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$$|\overline{\phi_a \phi_b}\rangle = \frac{1}{\sqrt{2!}} \begin{vmatrix} \overline{\phi_a(1)} & \phi_b(1) \\ \overline{\phi_a(2)} & \phi_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\beta_1 & \varphi_b(1)\alpha_1 \\ \varphi_a(2)\beta_2 & \varphi_b(2)\alpha_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (\varphi_a(1)\beta_1 \cdot \varphi_b(2)\alpha_2 - \varphi_b(1)\alpha_1 \cdot \varphi_a(2)\beta_2)$$

$$= \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) \cdot \beta_1\alpha_2 - \varphi_b(1)\varphi_a(2) \cdot \alpha_1\beta_2)$$

$$|\phi_a \overline{\phi_b}\rangle = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_a(1) & \overline{\phi_b(1)} \\ \phi_a(2) & \overline{\phi_b(2)} \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\alpha_1 & \varphi_b(1)\beta_1 \\ \varphi_a(2)\alpha_2 & \varphi_b(2)\beta_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) \cdot \alpha_1\beta_2 - \varphi_b(1)\varphi_a(2) \cdot \beta_1\alpha_2)$$

$$\left(\frac{1}{\sqrt{2}}\right) (|\overline{\phi_a \phi_b}\rangle + |\phi_a \overline{\phi_b}\rangle) =$$

$${}^3\Psi = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)) \frac{1}{\sqrt{2}} (\alpha_1\beta_2 + \beta_1\alpha_2) \quad (M_S = 0)$$

$$\left(\frac{1}{\sqrt{2}}\right) (|\phi_a \overline{\phi_b}\rangle - |\overline{\phi_a \phi_b}\rangle) =$$

$${}^1\Psi = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)) \frac{1}{\sqrt{2}} (\alpha_1\beta_2 - \beta_1\alpha_2) \quad (M_S = 0)$$

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Summary:

Key Features of Slater Determinants

- Antisymmetry
 - If one swaps any two rows or any two columns, the determinant changes sign.
- Pauli Principle
 - If any two columns are identical, the determinant must be zero \Leftrightarrow no two electrons can have the same quantum numbers.
 - Adding (or subtracting) one column to (from) another column doesn't change Ψ .
- Orthonormality
 - Slater determinants are normalized and determinants built from different orthogonal basis orbitals are orthogonal to each other.
- Symmetry operations on determinants act upon all the *spatial parts* of the orbitals that make up the determinants.

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Irreducible Reps and Determinants

- ♦ Closed shells always belong to the totally symmetric representation
 - ♦ Example: show that the Slater determinant for a chloride ion belongs to the a_1 rep. in $4mm$ (C_{4v}) symmetry.
- ♦ To determine the state symmetries for open shell molecules, work out orbitals and use properties of determinants.
 - ♦ Example: What states arise from the ground configuration of cyclobutadiene (D_{4h})?

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D_{4h}	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		$x^2 - y^2$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

D_4	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	z, R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

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Cyclobutadiene

Example - Answers

$${}^3A_{2g} \begin{cases} |e_a e_b| & 1 \\ \frac{1}{\sqrt{2}} (|\bar{e}_a e_b| + |e_a \bar{e}_b|) & 0 \\ |\bar{e}_a \bar{e}_b| & -1 \end{cases}$$

$$M_S$$

$${}^1B_{1g} : \frac{1}{\sqrt{2}} (|\bar{e}_a e_b| - |e_a \bar{e}_b|) \quad 0$$

$${}^1A_{1g} : \frac{1}{\sqrt{2}} (|e_a \bar{e}_a| + |e_b \bar{e}_b|) \quad 0$$

$${}^1B_{2g} : \frac{1}{\sqrt{2}} (|e_a \bar{e}_a| - |e_b \bar{e}_b|) \quad 0$$

$$M_S$$

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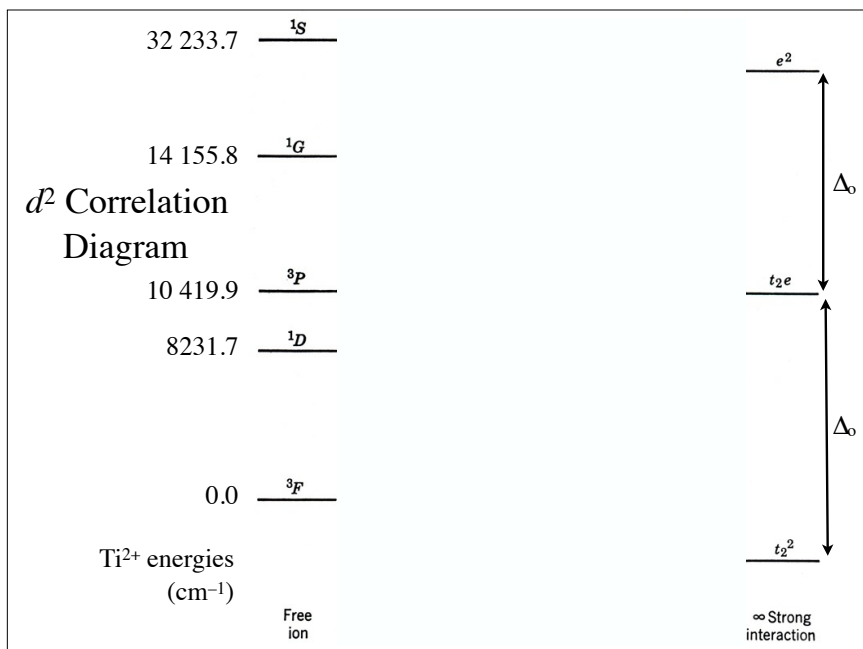
A Worked Example: t_{2g}^2 in O_h

- ★ How many microstates (determinants)?
- ★ What states arise from this configuration?
- ★ Find one wavefunction for each state.
- ★ Use qualitative reasoning to deduce the relative energies of the states (not strictly an exercise in group theory).

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O	E	$8C_3$	$3C_2$ ($= C_4^2$)	$6C_4$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	$(R_x, R_y, R_z); (x, y, z)$	
T_2	3	0	-1	-1	1		(xy, xz, yz)

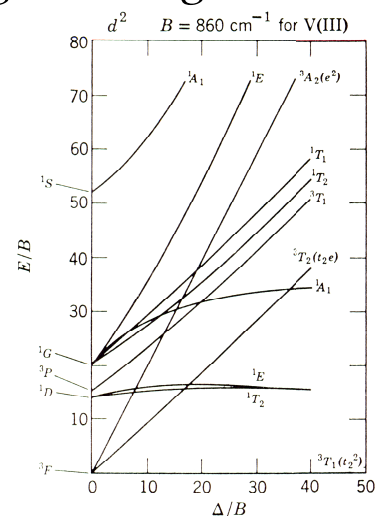
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d^2 Tanabe-Sugano Diagram

- Semiquantitative correlation diagram connecting states of free ion and molecule
- All energies are taken relative to the ground state.
- In strong-field limit, curves group into families according to slopes, each of which is correlated with a config.
- States of like symmetry never cross.



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Three Equivalent Electrons

If three electrons occupy orbitals that are at least 3-fold degenerate, one can form either a doublet or quartet states. The characters of the reducible representations of the states are given by:

$$\chi^{S=3/2}(R) = \frac{1}{6}(\chi^3(R) - 3\chi(R)\chi(R^2) + 2\chi(R^3))$$

$$\chi^{S=1/2}(R) = \frac{1}{3}(\chi^3(R) - \chi(R^3))$$

Harris & Bertolucci, p. 328. For derivations see *Antisymmetry* handout; using permutation groups, see D. I. Ford, *J. Chem. Ed.*, **49**, 336-40 (1972).

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Four Equivalent Electrons

- If four electrons occupy orbitals that are at least 4-fold degenerate, one can form singlet, triplet, and quintet states. The characters of the reducible representations of the states are given by:

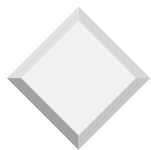
$$\chi^{S=0}(R) = \frac{1}{12}(\chi^4(R) - 4\chi(R)\chi(R^3) + 3\chi^2(R^2))$$

$$\chi^{S=1}(R) = \frac{1}{8}(\chi^4(R) - 2\chi^2(R)\chi(R^2) + 2\chi(R^4) - \chi^2(R^2))$$

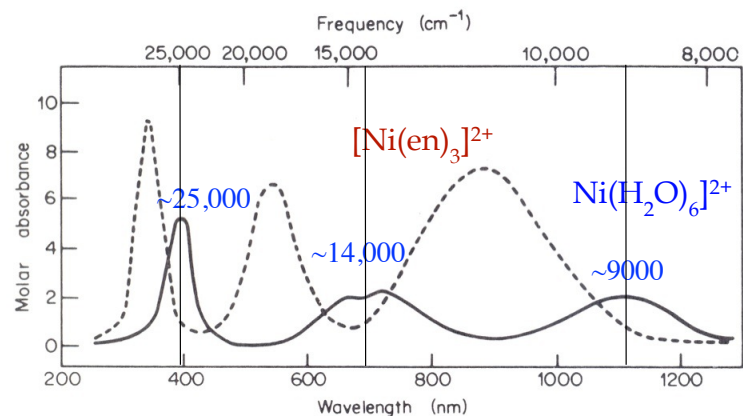
$$\chi^{S=2}(R) = \frac{1}{24}(\chi^4(R) - 6\chi^2(R)\chi(R^2) + 8\chi(R)\chi(R^3) - 6\chi(R^4) + 3\chi^2(R^2))$$

Harris & Bertolucci, p. 328. For derivations using permutation groups, see D. I. Ford, *J. Chem. Ed.*, **49**, 336-40 (1972).

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$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$

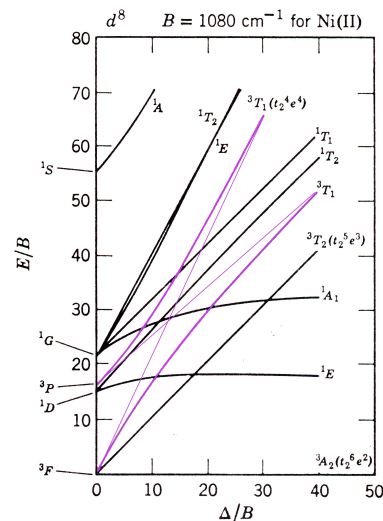


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The Non-crossing Rule

Illustrative Issues:

- What is the strength of the mixing between the ${}^3F({}^3T_{1g})$ and ${}^3P({}^3T_{1g})$ atomic states?
- In the *strong-field limit*, exactly how much of the two ${}^3F({}^3T_{1g})$ and ${}^3P({}^3T_{1g})$ states contribute to the two molecular ${}^3T_{1g}$ states?

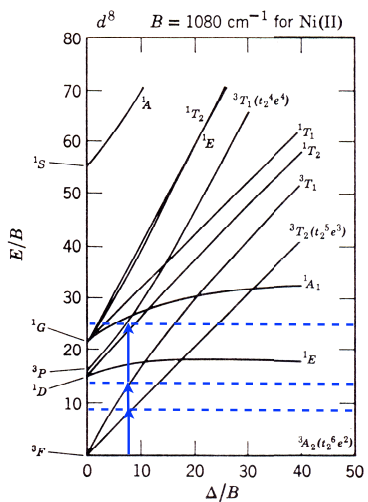


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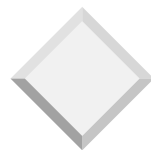


d^8 Tanabe-Sugano Diagram

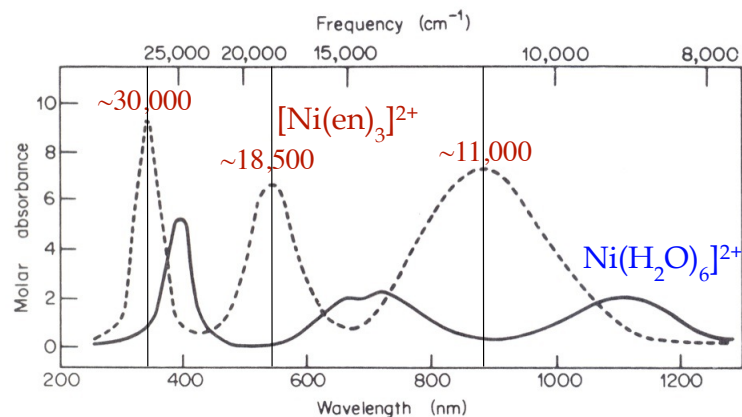
- Quantitative correlation diagram connecting states of free ion and molecule
- In strong-field limit, curves group into families according to slopes, each of which is correlated with a config.
- States of like symmetry never cross.



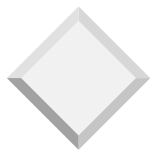
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$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$

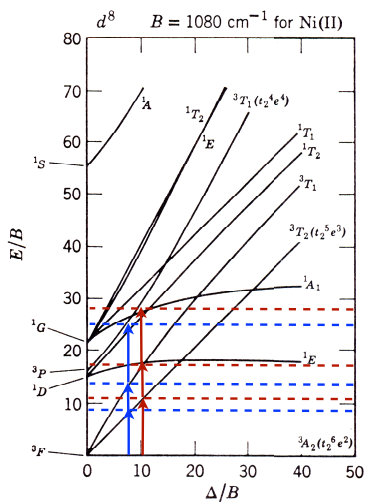


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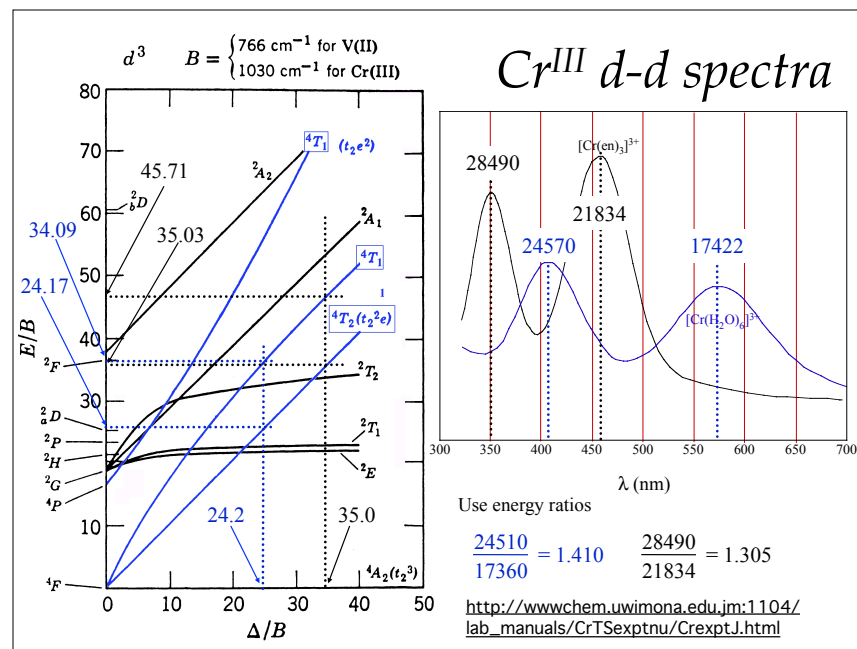


d^8 Tanabe-Sugano Diagram

- Quantitative correlation diagram connecting states of free ion and molecule
- In strong-field limit, curves group into families according to slopes, each of which is correlated with a config.
- States of like symmetry never cross.



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