

## ANTISYMMETRIC WAVEFUNCTIONS: SLATER DETERMINANTS (06/30/16)

Wavefunctions that describe more than one electron must have two characteristic properties. First, since all electrons are identical particles, the electrons' coordinates must appear in wavefunctions such that the electrons are *indistinguishable*. This means that the coordinates of electrons in an atom or molecule must enter into the wavefunction so that in the many-electron probability distribution,  $|\Psi|^2 = \Psi^* \Psi$ , every electron is identical. The second requirement, and this is a more complete and rigorous statement of the *Pauli exclusion principle*, is that the wavefunction for a system of two or more electrons must change sign any time we permute the coordinates of any two electrons,

$$\Psi(1, 2, \dots, \textcolor{blue}{i}, \dots, \textcolor{green}{j}, \dots, N) = -\Psi(1, 2, \dots, \textcolor{green}{j}, \dots, \textcolor{blue}{i}, \dots, N).$$

This is a property of *fermions* (among which are electrons, protons, and other half-integral spin particles); in systems with more than one identical fermion, only probability distributions corresponding to antisymmetric wavefunctions are observed. Let us review the 2-electron case.

If we attempt to construct a two-electron wavefunction as a product of individual electron orbitals,  $\varphi_a$  and  $\varphi_b$ , then neither  $\varphi_a(1)\varphi_b(2)$  nor  $\varphi_a(2)\varphi_b(1)$  alone are satisfactory since we require that the electrons be indistinguishable. The combinations  $\varphi_a(1)\varphi_b(2) \pm \varphi_a(2)\varphi_b(1)$  do meet the requirement of indistinguishability, but these functions just describe the spatial distribution of the electrons; we must also consider their spin. If the two electrons have different spin eigenfunctions, indistinguishability means that neither  $\alpha_1\beta_2$  nor  $\alpha_2\beta_1$  is satisfactory, but  $\alpha_1\beta_2 \pm \beta_1\alpha_2$  are acceptable – as are  $\alpha_1\alpha_2$  and  $\beta_1\beta_2$ , of course. As we've noted, the overall wavefunction for two electrons must be antisymmetric with respect to interchange of the electrons' labels. This admits four possibilities, as long as both  $\varphi_a$  and  $\varphi_b$  are singly occupied (normalization constants included):

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

The left superscripts on  ${}^1\Psi$  and  ${}^3\Psi$  are the spin multiplicities ( $2S + 1$ ); the triplet wavefunctions are all eigenfunctions of  $\hat{S}^2$  with eigenvalue  $S(S + 1) = 2$  and they are degenerate as long as we consider spin-independent contributions to the energy (i.e., there is no applied magnetic field and spin-orbit coupling is neglected). The values of  $M_S$  (=

$m_{s1} + m_{s2}$ , the  $z$ -components of  $\vec{S}$ ) for each wavefunction are given, and the number of values  $M_S$  takes,  $2S + 1$ , for a given  $S$  is the spin multiplicity for the state. Slater pointed out that if we write many-electron wavefunctions as (*Slater*) *determinants*, the antisymmetry requirement is fulfilled. Slater determinants are constructed using *spinorbitals* in which the spatial orbitals are combined with spin functions from the outset. We use the notation  $\phi_a(1) \equiv \varphi_a(1)\alpha_1$  and add a ‘bar’ over the top to indicate ‘spin-down,’  $\bar{\phi}_a(1) \equiv \varphi_a(1)\beta_1$ . Slater determinants are constructed by arranging spinorbitals in columns and electron labels in rows and are normalized by dividing by  $\sqrt{N!}$ , where  $N$  is the number of occupied spinorbitals. This arrangement is universally understood so the notation for Slater determinants can be made very compact; four Slater determinants can be constructed using  $\phi_a$ ,  $\bar{\phi}_a$ ,  $\phi_b$ , and  $\bar{\phi}_b$ :

$$|\phi_a\phi_b|, |\bar{\phi}_a\bar{\phi}_b|, |\phi_a\bar{\phi}_b|, \text{ and } |\bar{\phi}_a\phi_b|$$

What does this notation mean? To see, let’s expand  $|\phi_a\phi_b|$  out, step-by-step:

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

$$\text{Thus, } |\phi_a\phi_b| = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))\alpha_1\alpha_2 = {}^3\Psi(M_S = 1)$$

Notice that the notation assumes the determinant is normalized and that we have adopted the conventions mentioned: running over spinorbitals in columns and over electron labels in rows. Proceeding in the same way for  $|\bar{\phi}_a\bar{\phi}_b|$ ,

$$\begin{aligned} |\bar{\phi}_a\bar{\phi}_b| &\equiv \frac{1}{\sqrt{2!}} \begin{vmatrix} \bar{\phi}_a(1) & \bar{\phi}_b(1) \\ \bar{\phi}_a(2) & \bar{\phi}_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\beta_1 & \varphi_b(1)\beta_1 \\ \varphi_a(2)\beta_2 & \varphi_b(2)\beta_2 \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (\varphi_a(1)\beta_1 \cdot \varphi_b(2)\beta_2 - \varphi_b(1)\beta_1 \cdot \varphi_a(2)\beta_2) \end{aligned}$$

$$\text{Thus, } |\bar{\phi}_a\bar{\phi}_b| = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))\beta_1\beta_2 = {}^3\Psi(M_S = -1)$$

Combinations of  $|\phi_a\bar{\phi}_b|$  and  $|\bar{\phi}_a\phi_b|$  yield the two wavefunctions with  $M_S = 0$ :

$$\begin{aligned} |\bar{\phi}_a\phi_b| &\equiv \frac{1}{\sqrt{2!}} \begin{vmatrix} \bar{\phi}_a(1) & \phi_b(1) \\ \bar{\phi}_a(2) & \phi_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\beta_1 & \varphi_b(1)\alpha_1 \\ \varphi_a(2)\beta_2 & \varphi_b(2)\alpha_2 \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) \cdot \color{blue}{\beta_1\alpha_2} - \varphi_b(1)\varphi_a(2) \cdot \color{red}{\alpha_1\beta_2}) \end{aligned}$$

$$\begin{aligned} |\phi_a\bar{\phi}_b| &\equiv \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_a(1) & \bar{\phi}_b(1) \\ \phi_a(2) & \bar{\phi}_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\alpha_1 & \varphi_b(1)\beta_1 \\ \varphi_a(2)\alpha_2 & \varphi_b(2)\beta_2 \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) \cdot \color{red}{\alpha_1\beta_2} - \varphi_b(1)\varphi_a(2) \cdot \color{blue}{\beta_1\alpha_2}) \end{aligned}$$

$$\frac{1}{\sqrt{2}} (|\bar{\phi}_a\phi_b| + |\phi_a\bar{\phi}_b|) = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)) \cdot \frac{1}{\sqrt{2}} (\color{blue}{\beta_1\alpha_2} + \color{red}{\alpha_1\beta_2}) = {}^3\Psi(M_S = 0)$$

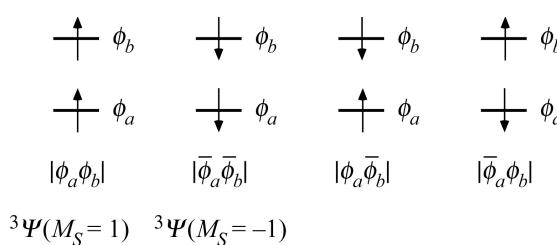
$$\frac{1}{\sqrt{2}} (|\bar{\phi}_a\phi_b| - |\phi_a\bar{\phi}_b|) = \frac{1}{\sqrt{2}} (\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)) \cdot \frac{1}{\sqrt{2}} (\color{blue}{\beta_1\alpha_2} - \color{red}{\alpha_1\beta_2}) = {}^1\Psi(M_S = 0)$$

Take particular note of the fact that the *spatial parts* of all three triplet wavefunctions are identical and are different from the singlet wavefunction. To summarize, in terms of determinants the singlet and triplet wavefunctions are

$${}^3\Psi(M_S=1)=|\phi_a\phi_b|; \quad {}^3\Psi(M_S=0)=\frac{1}{\sqrt{2}}(|\bar{\phi}_a\phi_b|+|\phi_a\bar{\phi}_b|); \quad {}^3\Psi(M_S=-1)=|\bar{\phi}_a\bar{\phi}_b|$$

$${}^1\Psi=\frac{1}{\sqrt{2}}(|\bar{\phi}_a\phi_b|-|\phi_a\bar{\phi}_b|)$$

Determinants can be represented diagrammatically using ‘up-’ and ‘down-arrows’ in orbitals in a manner familiar to chemists. However, the diagrams now take on more precise meanings. While the  $M_S = \pm 1$  components of the triplet state are represented as



The general form of a Slater determinant  
 comports with this discussion. When  ${}^3\Psi(M_S = 0)$  and  ${}^1\Psi(M_S = 0)$   
 expanded, the determinant for  $N$  electrons in  $N$   
 spinorbitals yields  $N!$  terms, generated by the  $N!$  possible permutations of electron labels  
 among the spinorbitals and differing by a multiplicative factor of  $-1$  for terms related by  
 one pairwise permutation. To be explicit, written out in determinantal form we have

single determinants, the singlet wavefunction and the  $M_S = 0$  component of the triplet state should be written as combinations of the determinants:

$$\begin{array}{c} \left[ \begin{array}{c} + \\ - \\ + \end{array} \right] + \left[ \begin{array}{c} + \\ + \\ - \end{array} \right] = \left[ \begin{array}{c} + \\ - \\ + \end{array} \right] \\ \hline ^3\Psi(M_S=0) \end{array} \quad \begin{array}{c} \left[ \begin{array}{c} + \\ - \\ + \end{array} \right] - \left[ \begin{array}{c} + \\ + \\ - \end{array} \right] = \left[ \begin{array}{c} + \\ - \\ + \end{array} \right] \\ \hline ^1\Psi(M_S=0) \end{array}$$

$$\Psi(1,2,\dots,i,\dots,j,\dots,N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{ccccccc} \phi_a(1) & \phi_b(1) & \cdots & \phi_p(1) & \cdots & \phi_q(1) & \cdots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \cdots & \phi_p(2) & \cdots & \phi_q(2) & \cdots & \phi_z(2) \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ \phi_a(i) & \phi_b(i) & \cdots & \phi_p(i) & \cdots & \phi_q(i) & \cdots & \phi_z(i) \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ \phi_a(j) & \phi_b(j) & \cdots & \phi_p(j) & \cdots & \phi_q(j) & \cdots & \phi_z(j) \\ \vdots & \vdots & & \vdots & & \vdots & & \vdots \\ \phi_a(N) & \phi_b(N) & \cdots & \phi_p(N) & \cdots & \phi_q(N) & \cdots & \phi_z(N) \end{array} \right\} \text{Different electrons in rows}$$

Since electronic wavefunctions for two or more electrons should be written as determinants, our goal is to determine the symmetry characteristics of determinants, or more specifically, how the determinants form bases for irreducible representations. Clearly, we want to avoid expanding the determinant out to exhibit  $N!$  terms, if possible. To do that, three properties of determinants can be used (In these expressions, the spinorbitals can carry either spin,  $\phi(i) = \varphi(i) \times [\alpha_i \text{ or } \beta_i]$ :  $i$  = electron label):

- Swap any two rows (or columns) of a determinant, and the sign changes,

$$\left| \phi_A \ \cdots \ \phi_p \ \cdots \ \phi_Q \ \cdots \right| = - \left| \phi_A \ \cdots \ \phi_p \ \cdots \ \phi_Q \ \cdots \right|$$

Therefore, if any two rows (or columns) are identical, the determinant is zero. This guarantees that we can't violate the Pauli principle by using the same spinorbital twice.

- Columns (or rows) can be factored,

$$\begin{aligned} & \left| \phi_A \ \cdots \ \phi_p + \phi_Q \ \cdots \ \phi_R \ \cdots \right| = \\ & \left| \phi_A \ \cdots \ \phi_p \ \cdots \ \phi_R \ \cdots \right| + \left| \phi_A \ \cdots \ \phi_Q \ \cdots \ \phi_R \ \cdots \right| \end{aligned}$$

- Any constant (including  $-1$ ) can be factored out,

$$\left| \phi_A \ \cdots \ c\phi_p \ \cdots \ \phi_R \ \cdots \right| = c \left| \phi_A \ \cdots \ \phi_p \ \cdots \ \phi_R \ \cdots \right|$$

The latter two rules will be useful when evaluating the results of symmetry operations.

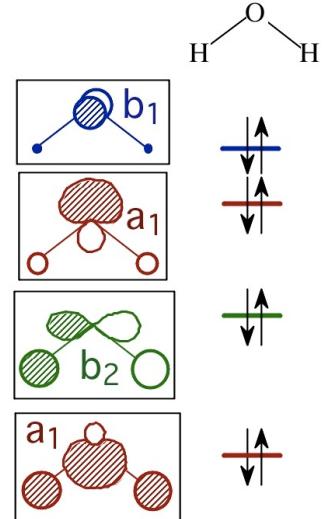
Let's see how these rules apply to a closed-shell molecule, H<sub>2</sub>O, for which we will examine a Slater determinant constructed from the valence MOs. The four valence MOs for water are depicted here and the transformation properties of the MOs are summarized as follows

$a_1 \xrightarrow{R} +a_1$  for all symmetry operations,  $R$ .

$b_1 \xrightarrow{R} +b_1$  for  $R = E, \sigma_{v1}$  and  $-b_1$  for  $R = C_2, \sigma_{v2}$ .

$b_2 \xrightarrow{R} +b_2$  for  $R = E, \sigma_{v2}$  and  $-b_2$  for  $R = C_2, \sigma_{v1}$ .

If we combine the orbital transformation properties with the rules given above for determinants, we can find the symmetry of the ground electronic state wavefunction. Each symmetry operation operates on all the in the determinant and the rules given above will be used to evaluate the irreducible representations to which that ground state determinant belongs:



$$\left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right| \xrightarrow{C_2} \left| 1a_1 \overline{1a_1} (-b_2) \overline{(-b_2)} 2a_1 \overline{2a_1} (-b_1) \overline{(-b_1)} \right| = + \left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right|$$

$$\left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right| \xrightarrow{\sigma_{v1}} \left| 1a_1 \overline{1a_1} (-b_2) \overline{(-b_2)} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right| = + \left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right|$$

$$\left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right| \xrightarrow{\sigma_{v2}} \left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} (-b_1) \overline{(-b_1)} \right| = + \left| 1a_1 \overline{1a_1} b_2 \overline{b_2} 2a_1 \overline{2a_1} b_1 \overline{b_1} \right|$$

This singlet, closed-shell electronic state wavefunction (a Slater determinant) belongs to the totally symmetric representation,  ${}^1A_1$ . Since electrons are paired in orbitals in closed-shell molecules, if the doubly occupied orbitals all belong to one-dimensional representations, the wavefunction will always belong to the totally symmetric

representation. Although it is not as transparently true, this applies to closed-shell molecules with degenerate orbitals as well. To consider just the  $C_3$  operation acting upon the ground state determinant for  $\text{NH}_3$ , we first recall how the orbitals transform:

$$\begin{aligned} a_1 &\xrightarrow{C_3} +a_1 \\ e_x &\xrightarrow{C_3} -\frac{1}{2}e_x + \frac{\sqrt{3}}{2}e_y \quad \text{and} \\ e_y &\xrightarrow{C_3} -\frac{\sqrt{3}}{2}e_x - \frac{1}{2}e_y \end{aligned}$$

Transformation of the determinants is a bit laborious, but straightforward and we can ignore the nondegenerate spinorbitals:

$$\left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right| \xrightarrow{C_3} \left| \cdots \left(-\frac{1}{2}e_x + \frac{\sqrt{3}}{2}e_y\right) \left(-\frac{1}{2}e_x^- + \frac{\sqrt{3}}{2}e_y^-\right) \left(-\frac{\sqrt{3}}{2}e_x^- - \frac{1}{2}e_y^-\right) \left(-\frac{\sqrt{3}}{2}e_x^- - \frac{1}{2}e_y^-\right) \cdots \right|$$

We expand out to four determinants obtained by multiplying through the first two parenthetical factors, ...

$$\begin{aligned} &= \frac{1}{4} \left| \cdots e_x^- e_x^- \left(-\frac{\sqrt{3}}{2}e_x - \frac{1}{2}e_y\right) \left(-\frac{\sqrt{3}}{2}e_x^- - \frac{1}{2}e_y^-\right) \cdots \right| + \frac{3}{4} \left| \cdots e_y^- e_y^- \left(-\frac{\sqrt{3}}{2}e_x - \frac{1}{2}e_y\right) \left(-\frac{\sqrt{3}}{2}e_x^- - \frac{1}{2}e_y^-\right) \cdots \right| \\ &\quad - \frac{\sqrt{3}}{4} \left| \cdots e_y^- e_x^- \left(-\frac{\sqrt{3}}{2}e_x - \frac{1}{2}e_y\right) \left(-\frac{\sqrt{3}}{2}e_x^- - \frac{1}{2}e_y^-\right) \cdots \right| - \frac{\sqrt{3}}{4} \left| \cdots e_x^- e_y^- \left(-\frac{\sqrt{3}}{2}e_x - \frac{1}{2}e_y\right) \left(-\frac{\sqrt{3}}{2}e_x^- - \frac{1}{2}e_y^-\right) \cdots \right| \end{aligned}$$

... expanding this out further, we recall that any determinant with two identical columns is zero, which eliminates all but one term for each of these four determinants, ...

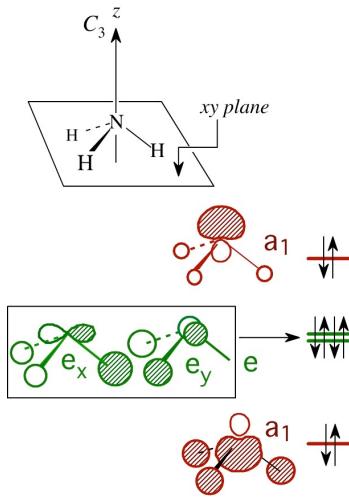
$$= \frac{1}{16} \left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right| + \frac{9}{16} \left| \cdots e_y^- e_y^- e_x^- e_x^- \cdots \right| - \frac{3}{16} \left| \cdots e_y^- e_x^- e_x^- e_y^- \cdots \right| - \frac{3}{16} \left| \cdots e_x^- e_y^- e_y^- e_x^- \cdots \right|$$

... finally we perform two column swaps in the second determinant and one column swap in each of the third and fourth determinants, leaving the sign of the second unchanged and switching the sign of the third and fourth, ...

$$= \frac{1}{16} \left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right| + \frac{9}{16} \left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right| + \frac{3}{16} \left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right| + \frac{3}{16} \left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right|.$$

So we finally conclude that  $\left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right| \xrightarrow{C_3} + \left| \cdots e_x^- e_x^- e_y^- e_y^- \cdots \right|$ . All the other  $C_{3v}$  operations yield the same result. The coefficients ‘work out’ in the end because the symmetry operations are orthogonal transformations (unitary transformations, in the complex case) – readers are encouraged to convince themselves that this is the case.

In the simplest *open-shell* case, a state is represented by a single determinant – with one unpaired electron in a nondegenerate orbital – and the state symmetry is the same as the symmetry of the half-occupied MO. If two nondegenerate orbitals are half occupied, the symmetry of the state is determined by taking the direct product of the two orbitals’ irreducible representations. For the triplet state of methylene ( $: \text{CH}_2$ ), the methylene



valence orbital symmetries are the same as those for water (above) and the triplet state electronic configuration is  $(1a_1)^2(2b_2)^2(2a_1)^1(b_1)^1$ . The  $M_S = \pm 1$  components of the triplet state work out quite simply to transform as  $B_1$ , e.g,

$$\left| 1a_1 \overline{1a}_1 b_2 \overline{b}_2 2a_1 b_1 \right| \xrightarrow{C_2} \left| \cdots 2a_1 (-b_1) \right| = -\left| 1a_1 \overline{1a}_1 b_2 \overline{b}_2 2a_1 b_1 \right|$$

$$\left| 1a_1 \overline{1a}_1 b_2 \overline{b}_2 2a_1 b_1 \right| \xrightarrow{\sigma_{v1}} \left| \cdots 2a_1 b_1 \right| = +\left| 1a_1 \overline{1a}_1 b_2 \overline{b}_2 2a_1 b_1 \right|$$

$$\left| 1a_1 \overline{1a}_1 b_2 \overline{b}_2 2a_1 b_1 \right| \xrightarrow{\sigma_{v2}} \left| \cdots 2a_1 (-b_1) \right| = -\left| 1a_1 \overline{1a}_1 b_2 \overline{b}_2 2a_1 b_1 \right|$$

where the closed shells are not written out. Let's also confirm that the  $M_S = 0$  component also behaves as a  $B_1$  basis function:

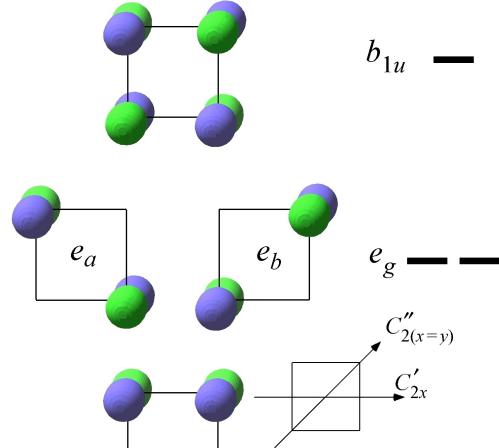
$$\left| \cdots 2a_1 \overline{b}_1 \right| + \left| \cdots \overline{2a}_1 b_1 \right| \xrightarrow{C_2} \left| \cdots 2a_1 (-\overline{b}_1) \right| + \left| \cdots \overline{2a}_1 (-b_1) \right| = -\left( \left| \cdots 2a_1 \overline{b}_1 \right| + \left| \cdots \overline{2a}_1 b_1 \right| \right)$$

$$\left| \cdots 2a_1 \overline{b}_1 \right| + \left| \cdots \overline{2a}_1 b_1 \right| \xrightarrow{\sigma_{v1}} +\left| \cdots 2a_1 \overline{b}_1 \right| + \left| \cdots \overline{2a}_1 b_1 \right|$$

$$\left| \cdots 2a_1 \overline{b}_1 \right| + \left| \cdots \overline{2a}_1 b_1 \right| \xrightarrow{\sigma_{v2}} \left| \cdots 2a_1 (-\overline{b}_1) \right| + \left| \cdots \overline{2a}_1 (-b_1) \right| = -\left( \left| \cdots 2a_1 \overline{b}_1 \right| + \left| \cdots \overline{2a}_1 b_1 \right| \right)$$

Let's examine the electronic states of cyclobutadiene (CB), for which there is a half-occupied degenerate set of orbitals. The four CB  $\pi$  orbitals are depicted below; the lowest-energy configuration is  $(a_{2u})^2(e_g)^2$ . CB is  $D_{4h}$ , but only the  $D_4$  subgroup need be considered because all the states that can arise from this configuration are *gerade*. We focus entirely on the partially occupied  $e_g$  orbitals, which transform as follows,

$$\begin{aligned} e_a &\xrightarrow{C_4} +e_b ; e_b \xrightarrow{C_4} -e_a \\ e_a &\xrightarrow{C_4^2} -e_a ; e_b \xrightarrow{C_4^2} -e_b \\ e_a &\xrightarrow{C'_{2x}} -e_b ; e_b \xrightarrow{C'_{2x}} -e_a \\ e_a &\xrightarrow{C''_{2(x=y)}} e_a ; e_b \xrightarrow{C''_{2(x=y)}} -e_b \end{aligned}$$



There are six determinants of interest:  
 $|e_a e_b|$ ,  $|\overline{e}_a e_b|$ ,  $|e_a \overline{e}_b|$ ,  $|\overline{e}_a \overline{e}_b|$ ,  $|e_a \overline{e}_a|$ , and  $|\overline{e}_b \overline{e}_b|$ .  
The first two clearly belong to a triplet and transform as follows:

$$|e_a e_b| \xrightarrow{C_4} |e_b (-e_a)| = +|e_a e_b|$$

$$|e_a e_b| \xrightarrow{C_4^2} |(-e_a)(-e_b)| = +|e_a e_b|$$

$$|e_a e_b| \xrightarrow{C'_{2x}} |(-e_b)(-e_a)| = |e_b e_a| = -|e_a e_b| ; |e_a e_b| \xrightarrow{C''_{2(x=y)}} |e_a (-e_b)| = -|e_a e_b|$$

This demonstrates that  $|e_a e_b|$  and  $|\overline{e_a} \overline{e_b}|$  belong to the  $A_2$  representation ( $A_{2g}$  in  $D_{4h}$ ). As the reader can readily verify, the combination  $|\overline{e_a} e_b| + |\overline{e_a} \overline{e_b}|$  also belongs to  $A_2$  ( $A_{2g}$ ). It is straightforward to show that  $|\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}|$  has  $B_1$  ( $B_{1g}$ ) symmetry:

$$\begin{aligned} |\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}| &\xrightarrow{C_4} |\overline{e_b}(-e_a)| - |\overline{e_b}(\overline{-e_a})| = -|\overline{e_b} e_a| + |\overline{e_b} \overline{e_a}| = -[|\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}|] \\ |\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}| &\xrightarrow{C_4^2} |(-\overline{e_a})(-\overline{e_b})| - |(-\overline{e_a})(\overline{-e_b})| = +[|\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}|] \\ |\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}| &\xrightarrow{C'_{2x}} |(-\overline{e_b})(-\overline{e_a})| - |(-\overline{e_b})(\overline{-e_a})| = |\overline{e_b} e_a| - |\overline{e_b} \overline{e_a}| = +[|\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}|] \\ |\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}| &\xrightarrow{C''_{2(x=y)}} |\overline{e_a}(-e_b)| - |\overline{e_a}(\overline{-e_b})| = -[|\overline{e_a} e_b| - |\overline{e_a} \overline{e_b}|] \end{aligned}$$

Finally,  $|e_a \overline{e_a}|$  and  $|e_b \overline{e_b}|$  form basis for a reducible representation that yields the  $A_1 \oplus B_2$  ( $A_{1g} \oplus B_{2g}$ ) representations,

$$\begin{aligned} |e_a \overline{e_a}| &\xrightarrow{C_4} |\overline{e_b} \overline{e_b}| \quad ; \quad |e_b \overline{e_b}| \xrightarrow{C_4} |(-\overline{e_a})(\overline{-e_a})| = |e_a \overline{e_a}| \\ |e_a \overline{e_a}| &\xrightarrow{C_4^2} |(-\overline{e_a})(\overline{-e_a})| = |e_a \overline{e_a}| \quad ; \quad |e_b \overline{e_b}| \xrightarrow{C_4^2} |(-\overline{e_b})(\overline{-e_b})| = |e_b \overline{e_b}| \\ |e_a \overline{e_a}| &\xrightarrow{C'_{2x}} |(-\overline{e_b})(\overline{-e_b})| = |e_b \overline{e_b}| \quad ; \quad |e_b \overline{e_b}| \xrightarrow{C'_{2x}} |(-\overline{e_a})(\overline{-e_a})| = |e_a \overline{e_a}| \\ |e_a \overline{e_a}| &\xrightarrow{C''_{2(x=y)}} |e_a \overline{e_a}| \quad ; \quad |e_b \overline{e_b}| \xrightarrow{C''_{2(x=y)}} |(-\overline{e_b})(\overline{-e_b})| = |e_b \overline{e_b}| \end{aligned}$$

The reader can demonstrate that  $|e_a \overline{e_a}| + |e_b \overline{e_b}|$  has  $A_{1g}$  symmetry and  $|e_a \overline{e_a}| - |e_b \overline{e_b}|$  has  $B_{2g}$  symmetry. ( $A_{1g}$  and  $B_{2g}$  projection operators applied to  $|e_a \overline{e_a}|$  or  $|e_b \overline{e_b}|$  will also generate the appropriate combinations.)

In summary, the  $(a_{2u})^2(e_g)^2$  configuration gives rise to  ${}^3A_{2g}$ ,  ${}^1B_{2g}$ ,  ${}^1A_{1g}$ , and  ${}^1B_{2g}$  states and we've established the determinantal wavefunctions for each of these states:

	$M_S$		$M_S$
${}^3A_{2g}$	$\begin{cases}  e_a e_b  & 1 \\ \frac{1}{\sqrt{2}}( \overline{e_a} e_b  +  \overline{e_a} \overline{e_b} ) & 0 \\  \overline{e_a} \overline{e_b}  & -1 \end{cases}$		${}^1B_{1g} : \frac{1}{\sqrt{2}}( \overline{e_a} e_b  -  \overline{e_a} \overline{e_b} ) \quad 0$ ${}^1A_{1g} : \frac{1}{\sqrt{2}}( e_a \overline{e_a}  +  e_b \overline{e_b} ) \quad 0$ ${}^1B_{2g} : \frac{1}{\sqrt{2}}( e_a \overline{e_a}  -  e_b \overline{e_b} ) \quad 0$

## Background: Energies of Determinantal Wavefunctions

Several texts in quantum chemistry offer rigorous and complete derivations for energy expressions of determinantal wavefunctions. In this document, we'll provide a graphical method arriving at the results after providing a ‘physical motivation’ for the method. To accomplish the latter purpose, let’s reexamine the determinants from which the singlet and triplet two-electron wavefunctions were constructed. (A simple example: a helium atom in an excited  $1s^12s^1$  configuration;  $\phi_a = 1s$  and  $\phi_b = 2s$ ):

$$\begin{array}{cccc}
 \begin{array}{c} \uparrow \\ \times \\ \downarrow \end{array} \phi_b & \begin{array}{c} + \\ \times \\ - \end{array} \phi_b & \begin{array}{c} - \\ \times \\ + \end{array} \phi_b & \begin{array}{c} + \\ \times \\ - \end{array} \phi_b \\
 \begin{array}{c} \uparrow \\ \times \\ \downarrow \end{array} \phi_a & \begin{array}{c} + \\ \times \\ - \end{array} \phi_a & \begin{array}{c} - \\ \times \\ + \end{array} \phi_a & \begin{array}{c} + \\ \times \\ - \end{array} \phi_a \\
 |\phi_a\phi_b| & |\bar{\phi}_a\bar{\phi}_b| & |\phi_a\bar{\phi}_b| & |\bar{\phi}_a\phi_b|
 \end{array}$$

$${}^3\Psi(M_S=1) \quad {}^3\Psi(M_S=-1)$$

In the absence of explicitly spin-dependent terms in the Hamiltonian (like an applied magnetic field or spin-orbit coupling), the energies of these wavefunctions are only affected by the spatial distribution of the electrons specified by these expressions, so let’s examine just the spatial factors:

$${}^1\Psi_{space} = \frac{1}{\sqrt{2}}(\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)) \quad ; \quad {}^3\Psi_{space} = \frac{1}{\sqrt{2}}(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2))$$

Let’s evaluate the energies by taking the expectation values of the Hamiltonian (the ‘+’ signs apply to the singlet and the ‘-’ signs apply to the triplet):

$$\begin{aligned}
 {}^{1,3}E &= \frac{1}{2} \iint (\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2)) \mathcal{H}(\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2)) d\tau_1 d\tau_2 \\
 {}^{1,3}E &= \frac{1}{2} \left[ \iint \phi_a(1)\phi_b(2) \mathcal{H} \phi_a(1)\phi_b(2) d\tau_1 d\tau_2 + \iint \phi_b(1)\phi_a(2) \mathcal{H} \phi_b(1)\phi_a(2) d\tau_1 d\tau_2 \pm \right. \\
 &\quad \left. \iint \phi_a(1)\phi_b(2) \mathcal{H} \phi_b(1)\phi_a(2) d\tau_1 d\tau_2 \pm \iint \phi_b(1)\phi_a(2) \mathcal{H} \phi_b(1)\phi_a(2) d\tau_1 d\tau_2 \right]
 \end{aligned}$$

The first two integrals have the same value and are evaluated in a straightforward way,

$$\begin{aligned}
 \iint \phi_a(1)\phi_b(2) \mathcal{H} \phi_a(1)\phi_b(2) d\tau_1 d\tau_2 &= \iint \phi_a(1)\phi_b(2) \left( \hat{h}_1 + \hat{h}_2 + \frac{e^2}{r_{12}} \right) \phi_a(1)\phi_b(2) d\tau_1 d\tau_2 \\
 &= \int \phi_a(1) \hat{h}_1 \phi_a(1) d\tau_1 + \int \phi_b(2) \hat{h}_2 \phi_b(2) d\tau_1 + e^2 \iint \frac{\phi_a^2(1)\phi_b^2(2)}{r_{12}} d\tau_1 d\tau_2 = h_a + h_b + J_{ab}. \\
 &\quad \left( \text{where the normalization has been used: } \int \phi_a^2 d\tau = \int \phi_b^2 d\tau = 1 \right)
 \end{aligned}$$

The operators  $\hat{h}_1$  and  $\hat{h}_2$  would include, for the helium  $1s^12s^1$  case, the kinetic energy operators and electron-nuclear Coulombic attraction terms for each of the electrons – in general they include all the kinetic and potential energy terms that depend only on each electron’s individual coordinates.  $h_a$  and  $h_b$  are hence referred to as ‘one electron’

energies.  $J_{ab}$  is called a *Coulomb integral* and has a semiclassical interpretation in that it can be viewed as the electron-electron repulsion energy between one electron in charge cloud  $\phi_a^2$  and a second electron in charge cloud  $\phi_b^2$ . The last two integrals are equal to each other as well,

$$\begin{aligned} \pm \iint \varphi_a(1) \varphi_b(2) \mathcal{H} \varphi_b(1) \varphi_a(2) d\tau_1 d\tau_2 &= \pm \iint \varphi_a(1) \varphi_b(2) \left( \hat{h}_1 + \hat{h}_2 + \frac{e^2}{r_{12}} \right) \varphi_b(1) \varphi_a(2) d\tau_1 d\tau_2 \\ &= \pm \iint \varphi_a(1) \varphi_b(2) \left( \frac{e^2}{r_{12}} \right) \varphi_b(1) \varphi_a(2) d\tau_1 d\tau_2 = \pm e^2 \iint \frac{\varphi_a \varphi_b(1) \varphi_a \varphi_b(2)}{r_{12}} d\tau_1 d\tau_2 = \pm K_{ab} \\ {}^1 E &= h_a + h_b + J_{ab} + K_{ab} \quad {}^3 E = h_a + h_b + J_{ab} - K_{ab} \end{aligned}$$

$K_{ab}$  is called an *exchange integral* and  $2K_{ab} = {}^1 E - {}^3 E$ , the singlet-triplet energy gap. Note that if we had calculated the expectation values of  $\mathcal{H}$  using  $|\phi_a \bar{\phi}_b|$  or  $|\bar{\phi}_a \phi_b|$  (p. 2), the cross-terms that give the exchange integrals don't survive due to orthogonality of the spin functions, and their ‘energies’ are  $h_a + h_b + J_{ab}$ . Exchange integrals are invariably positive since  $\varphi_a \varphi_b(1)$  and  $\varphi_a \varphi_b(2)$  will tend to have same sign when the integrand has its greatest magnitude (when  $r_{12} \rightarrow 0$ ).<sup>1</sup>  $K_{ab}$  is largest when  $\varphi_a$  and  $\varphi_b$  extend over the same region of space. The antisymmetric nature of the triplet spatial wavefunction guarantees that in the triplet state the electrons in  $\varphi_a$  and  $\varphi_b$  are never at the same location ( ${}^3 \Psi = 0$  if the two electrons have the same coordinates), i.e., the triplet state lies lower in energy because there is less electron-electron repulsion.

*The Rules:* The above background will serve to rationalize the following rules for evaluating energies of determinants, which contain the following terms: (1) a ‘one-electron’ orbital energy,  $\varepsilon_i$ , for each electron.  $\varepsilon_i$  will generally include two-electron terms involving  $e$ - $e$  repulsions with the atomic core electrons (screening) – which distinguishes “ $\varepsilon_i$ ” from the symbol “ $h_i$ ” used above, (2) for each pairwise  $e^-$ - $e^-$  repulsion, a Coulomb term (a  $J_{ij}$  contribution), and (3) an exchange ‘stabilization’ (a  $-K_{ij}$  contribution) for each *like-spin*  $e^-$ - $e^-$  interaction. As an example, consider the five determinants illustrated here.

Associated with each of these determinants are six Coulomb integral contributions since there must be six unique pairwise repulsions with four electrons. The two determinants with  $M_S = \pm 1$  are associated with *three* exchange

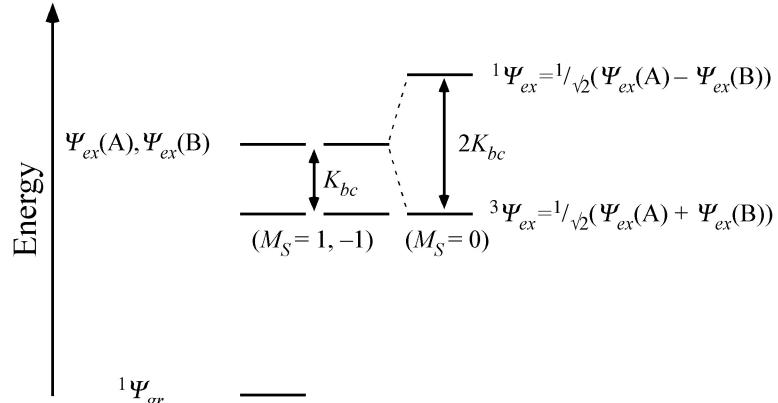
$\overline{\overline{\phi_c}}$	$\overline{\overline{\uparrow \phi_c}}$	$\overline{\downarrow \phi_c}$	$\overline{\downarrow \phi_c}$	$\overline{\overline{\uparrow \phi_c}}$
$\overline{\downarrow \uparrow \phi_b}$	$\overline{\uparrow \phi_b}$	$\overline{\downarrow \phi_b}$	$\overline{\uparrow \phi_b}$	$\overline{\downarrow \phi_b}$
$\overline{\downarrow \uparrow \phi_a}$	$\overline{\downarrow \downarrow \phi_a}$	$\overline{\uparrow \phi_a}$	$\overline{\downarrow \uparrow \phi_a}$	$\overline{\downarrow \downarrow \phi_a}$
${}^1 \Psi_{gr}$	${}^3 \Psi_{ex}$ $(M_S = 1)$	${}^3 \Psi_{ex}$ $(M_S = -1)$	$\Psi_{ex}(A)$	$\Psi_{ex}(B)$
${}^3 \Psi_{ex} = 1/\sqrt{2}(\Psi_{ex}(A) + \Psi_{ex}(B))$				
${}^1 \Psi_{ex} = 1/\sqrt{2}(\Psi_{ex}(A) - \Psi_{ex}(B))$ $(M_S = 0)$				

<sup>1</sup> Proof: Slater, J. C. *Quantum Theory of Atomic Structure, Vol. I*, McGraw-Hill: New York, 1960, p. 486.

stabilizations while those with  $M_S = 0$  are associated with *two* exchange stabilizations. This is algebraically summarized as

$$\begin{aligned}
 E_{gr} &= 2\epsilon_a + 2\epsilon_b + J_{aa} + J_{bb} + 4J_{ab} - 2K_{ab} \\
 E_{ex}^{(3)} &= 2\epsilon_a + \epsilon_b + \epsilon_c + J_{aa} + 2J_{ab} + 2J_{ac} + J_{bc} - (K_{ab} + K_{ac}) - K_{bc} \\
 E_{ex}^A = E_{ex}^B &= 2\epsilon_a + \epsilon_b + \epsilon_c + J_{aa} + 2J_{ab} + 2J_{ac} + J_{bc} - (K_{ab} + K_{ac}) \\
 E_{ex}^{A+B} + E_{ex}^{A-B} &= E_{ex}^A + E_{ex}^B ; \text{ but } E_{ex}^{A+B} = E_{ex}^{(3)} \therefore E_{ex}^{(1)} = E_{ex}^{A-B} = E_{ex}^A + E_{ex}^B - E_{ex}^{(3)} \\
 E_{ex}^{(1)} &= 2\epsilon_a + \epsilon_b + \epsilon_c + J_{aa} + 2J_{ab} + 2J_{ac} + J_{bc} - (K_{ab} + K_{ac}) + K_{bc} ; E_{ex}^{(1)} - E_{ex}^{(3)} = +2K_{bc}
 \end{aligned}$$

Mixing of the two  $M_S = 0$  determinants,  $\Psi_{ex}(A)$  and  $\Psi_{ex}(B)$ , yields a triplet and a singlet wavefunction. The triplet energy must be equal to the energies for the  $M_S = \pm 1$  triplet wavefunctions that are representable as single determinants.



### States arising from degenerate orbitals with two or more electrons

Molecules and ions with open shell electronic configurations are quite common in transition metal chemistry. Before proceeding further with applications, however, let's derive some formulas that allow us to work with characters in deriving states for multi-electron configurations in degenerate orbital sets.

When  $n$ -fold degenerate orbitals  $\{\varphi_1, \dots, \varphi_n\}$  belonging to irreducible representation  $\Gamma_i$  are occupied by, say, two electrons or two ‘holes’, one cannot simply evaluate a direct product to determine the states that derive from such configurations. The  $n^2$ -dimensional direct ‘squared’ representation  $(\Gamma_i \otimes \Gamma_i)$  will have the  $n^2$  pairwise products of these orbitals,  $\{\varphi_1^2, \dots, \varphi_n^2, \varphi_i \varphi_j, i \neq j\}$ , as basis functions. The characters,  $\chi_{\Gamma_i \otimes \Gamma_i}(R)$ , are just  $\chi_{\Gamma_i}^2(R)$ . Now, if we are constructing permissible *singlet/triplet* state wavefunctions, the spatial part of the wavefunctions are symmetric/antisymmetric with respect to permutation of the electron labels while the spin function is antisymmetric/symmetric:

$$\begin{aligned}
 &\text{Symmetric} \\
 1\Psi = &\left( \begin{array}{c} \varphi_1(1)\varphi_1(2) \\ \vdots \\ \varphi_n(1)\varphi_n(2) \\ \frac{1}{\sqrt{2}}(\varphi_i(1)\varphi_j(2) + \varphi_j(1)\varphi_i(2)), i < j \end{array} \right) \overbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}^{\text{Antisymmetric}}
 \end{aligned}$$

$$^3\Psi = \frac{1}{\sqrt{2}} \left( \varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2) \right), i < j$$

Antisymmetric
Symmetric

$$\left\{ \begin{array}{c} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{array} \right\}$$

The set,  $\{\varphi_1, \dots, \varphi_n\}$ , is the basis for an irreducible representation so the character for each operation within a class with respect to this basis will be the same, and independent of any choice of orthogonal linear combinations of these orbitals we make. Suppose that we've singled out a particular operation  $R$  from each class and assume that we have chosen linear combinations of the orbitals such that the matrix for each  $R$  is diagonal:<sup>2</sup>

$$\varphi_i \xrightarrow{R} r_i \varphi_i \quad i = 1, \dots, n \quad ; \quad \mathbf{R} = \begin{bmatrix} r_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & r_n \end{bmatrix} \quad ; \quad \chi(R) = r_1 + \dots + r_n$$

The combinations of basis functions that diagonalize  $\mathbf{R}$  will generally be different for each operation, but the characters are, as always, the same for every member of a class. Operating on the spatial parts of the wavefunctions for both the singlets and the triplets,

$$\begin{aligned} \varphi_1(1)\varphi_1(2) &\xrightarrow{R} r_1 \varphi_1(1) \cdot r_1 \varphi_1(2) = r_1^2 \varphi_1(1)\varphi_1(2) \\ &\vdots \\ \varphi_n(1)\varphi_n(2) &\xrightarrow{R} r_n^2 \varphi_n(1)\varphi_n(2) \\ (\varphi_i(1)\varphi_j(2) + \varphi_j(1)\varphi_i(2)) &\xrightarrow{R} r_i r_j (\varphi_i(1)\varphi_j(2) + \varphi_j(1)\varphi_i(2)) \quad i < j \\ (\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)) &\xrightarrow{R} r_i r_j (\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)) \quad i < j \end{aligned}$$

So the characters for the operations in the basis spanned by all the symmetric singlet ( $\chi^+$ ) and antisymmetric triplet ( $\chi^-$ ) wavefunctions are

$$\chi^+(R) = \sum_{i=1}^n r_i^2 + \sum_{i < j} r_i r_j \quad ; \quad \chi^-(R) = \sum_{i < j} r_i r_j$$

As noted above, the characters for the normal direct product basis are just

$$\chi^2(R) = \left( \sum_{i=1}^n r_i \right)^2 = \sum_{i=1}^n r_i^2 + \sum_{i \neq j} r_i r_j = \sum_{i=1}^n r_i^2 + 2 \sum_{i < j} r_i r_j$$

and since the basis functions are chosen so our class representative operations have diagonal matrices, the characters for the squares of the operations are diagonal as well,

$$\varphi_i \xrightarrow{R^2} r_i^2 \varphi_i \quad i = 1, \dots, n \quad ; \quad \mathbf{R}^2 = \begin{bmatrix} r_1^2 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & r_n^2 \end{bmatrix} \quad ; \quad \chi(R^2) = \sum_{i=1}^n r_i^2$$

---

<sup>2</sup> The linear combinations are the eigenvectors of  $\mathbf{R}$ ;  $r_1, \dots, r_n$  are the eigenvalues. Since  $\mathbf{R}$  is an orthogonal (or unitary) diagonal matrix, for all  $r_i, |r_i| = 1$ ; in general,  $r_i$  could be a complex number,  $r_i = e^{ia}$ .

If we take the sum and difference of the expressions for  $\chi^2(R)$  and  $\chi(R^2)$  and divide each by two, we obtain formulas for the antisymmetric and symmetric direct products,

$$\boxed{\begin{aligned}\chi^+(R) &= \chi^{S=0}(R) = \frac{1}{2}(\chi^2(R) + \chi(R^2)) \\ \chi^-(R) &= \chi^{S=1}(R) = \frac{1}{2}(\chi^2(R) - \chi(R^2))\end{aligned}}$$

where the context of the derivation given makes it clear that these two formulas are only defined when taking a direct product of a degenerate irreducible representation with itself and they're used to handle two-electron (or two-hole) cases.

It is easy to show that these formulae recover our results for cyclobutadiene. The  $D_4$  subgroup is again sufficient, since the  $(e_g)^2$  configuration will generate only *gerade* states:

$D_4$	$E$	$2C_4$	$C_2(C_4^2)$	$2C'_2$	$2C''_2$	
$[E \otimes E]^-$	1	1	1	-1	-1	$= A_2$
$[E \otimes E]^+$	3	-1	3	1	1	$= A_1 \oplus B_1 \oplus B_2$

Formulas for three electrons (or three holes) in a 3-fold- or higher-degenerate set of orbitals can be derived using permutation group theory<sup>3</sup> and are

$$\boxed{\begin{aligned}\chi^{S=1/2}(R) &= \frac{1}{3}(\chi^3(R) - \chi(R^3)) \\ \chi^{S=3/2}(R) &= \frac{1}{6}(\chi^3(R) - 3\chi(R)\chi(R^2) + 2\chi(R^3))\end{aligned}}$$

and for four electrons (or four holes) in a 4-fold- or higher-degenerate set of orbitals:

$$\boxed{\begin{aligned}\chi^{S=0}(R) &= \frac{1}{12}(\chi^4(R) - 4\chi(R)\chi(R^3) + 3\chi^2(R^2)) \\ \chi^{S=1}(R) &= \frac{1}{8}(\chi^4(R) - 2\chi^2(R)\chi(R^2) + 2\chi(R^4) - \chi^2(R^2)) \\ \chi^{S=2}(R) &= \frac{1}{24}(\chi^4(R) - 6\chi^2(R)\chi(R^2) + 8\chi(R)\chi(R^3) - 6\chi(R^4) + 3\chi^2(R^2))\end{aligned}}$$

### Applications to Ligand Field Theory

An understanding of bonding in transition-metal complexes, particularly classical ‘Werner’ complexes, demands that we account for electron-electron repulsion on an equal footing with the ‘quasi-independent electron’ terms implicit in our focus on molecular orbitals and their respective orbital energies. In ligand-field theory, one seeks to correlate atomic (ion) *state* energies (i.e., Russell-Saunders terms) with molecular states built up from molecular orbital configurations. In the ligand-field approach, the open-shell wavefunctions are assumed to retain their *d*-like character and the ligand contribution to the partially-filled orbitals is accounted for through their effect on orbital energy splitting and by treating the *d-d* repulsion energies as adjustable parameters (mainly the Racah parameter *B*) that will generally be smaller than in free ions because when the electrons are delocalized onto ligands, repulsions are lessened by the relief of their crowding into

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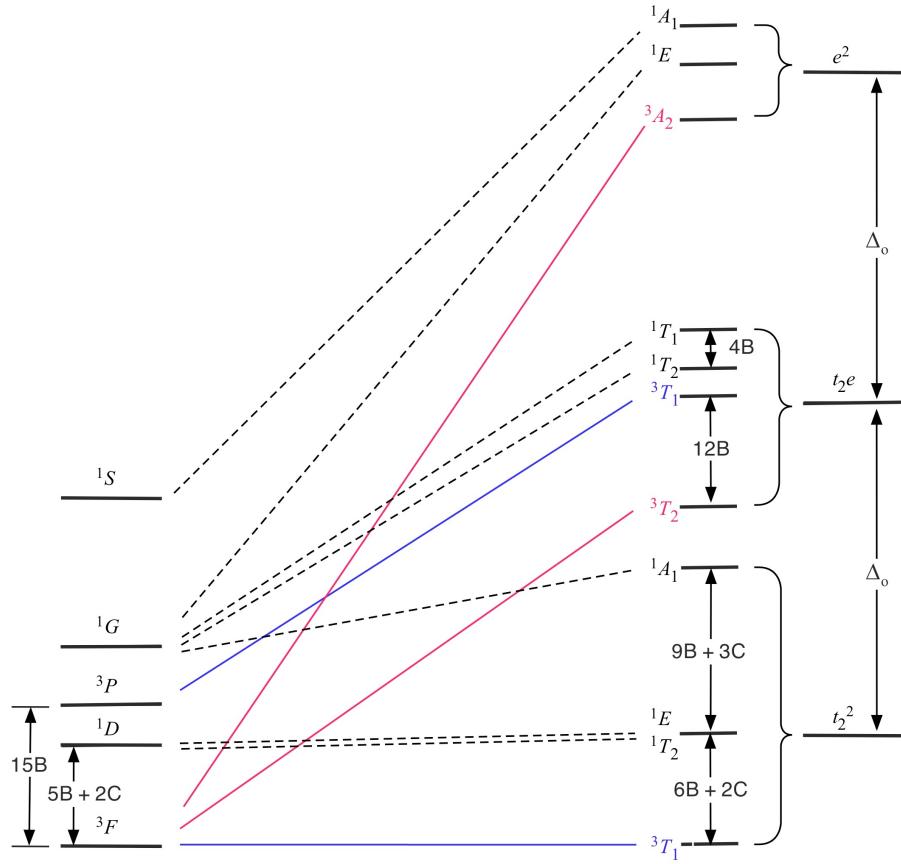
<sup>3</sup> See D. I. Ford, *J. Chem. Ed.*, **49**, 336-40 (1972). Appendix 2 below gives proof of the three electron formulae.

relatively contracted  $d$  orbitals. These are matters we will refer to only tangentially - our focus will remain on the symmetry-controlled characteristics of ligand field theory.

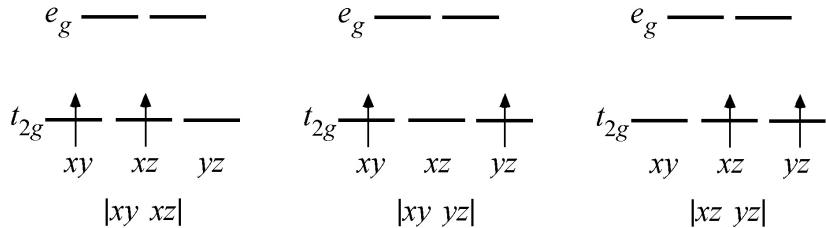
Let's turn our attention to the electronic states of octahedrally-coordinated  $d^2$  ions, for which there are three possible configurations:  $(t_{2g})^2$ ,  $(t_{2g})^1(e_g)^1$ , and  $(e_g)^2$ . The singly-excited  $(t_{2g})^1(e_g)^1$  configuration is handled easily: there are six assignments of the  $t_{2g}$  electron (three orbitals, spin-up or spin-down) and four assignments of the  $e_g$  electron, so the state wavefunctions from this configuration are written in terms of 24 determinants. The symmetries of the states are easily determined by taking the direct product,  $t_{2g} \otimes e_g = {}^{1,3}T_1 \oplus {}^{1,3}T_2$  where the left superscripts indicate that both singlets and triplets can be formed for each symmetry (with one electron each in  $t_{2g}$  and  $e_g$ , no Pauli Principle violations occur). We'll return to the issue of finding wavefunctions for these states below.

$O$	$E$	$8C_3$	$3C_2$ $(= C_4^2)$	$6C_4$	$6C'_2$		
$A_1$	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		$(xy, xz, yz)$
$T_2 \otimes E$	6	0	-2	0	0	${}^{1,3}T_1 \oplus {}^{1,3}T_2$	
$[T_2 \otimes T_2]^-$	3	0	-1	1	-1	${}^3T_1$	
$[T_2 \otimes T_2]^+$	6	0	2	0	2	$\Rightarrow {}^1A_1 \oplus {}^1E \oplus {}^1T_2$	
$[E \otimes E]^-$	1	1	1	-1	-1	${}^3A_2$	
$[E \otimes E]^+$	3	0	3	1	1	${}^1A_1 \oplus {}^1E$	

To find the states arising from the  $(t_{2g})^2$  and  $(e_g)^2$  configurations, the formulas derived in the preceding section are applied, the results of which are shown in the augmented character table above for the  $O$  group (the  $g$  symmetry of the  $d$  orbitals is understood). If we correlate the  $d^2$  ion atomic states with these molecular states, the diagram shown here emerges. This is a modified version of Figure 9.4 given in Cotton's text. Atomic states are at left, molecular orbital configurations are shown at far right. The diagram also shows some energy splittings that are not given in the corresponding diagram found in Cotton's text. In the Cotton's Figure 9.4, the configurations are labeled as “∞ Strong interaction” – referring the the strength of the ligand-metal interaction. Note that even in the strong ligand field limit, the electron-electron repulsion that causes the state splitting would still be present. The figure given on the following page also includes energy splittings between some of the states on both sides of the diagram – the origins of which shall be explained below.



Now let's find wavefunctions for some of these states. For the  $(t_{2g})^2$  configuration, Hund's rule predicts that the lowest energy state will be the triplet,  ${}^3T_{1g}$ . The  $M_S = 1$  determinants are simple to illustrate graphically and are shown below the correlation diagram:



To verify that these determinants do indeed belong to the  $T_{1g}$  representation, we first apply the symmetry operations to the orbitals...

$$\begin{aligned}
 & xy \xrightarrow{C_3} yz ; yz \xrightarrow{C_3} xz ; xz \xrightarrow{C_3} xy ; xy \xrightarrow{C_{4z}} -xy ; xz \xrightarrow{C_{4z}} yz ; yz \xrightarrow{C_{4z}} -xz \\
 & xy \xrightarrow{C_{4z}^2} xy ; xz \xrightarrow{C_{4z}^2} -xz ; yz \xrightarrow{C_{4z}^2} -yz \\
 & xy \xrightarrow{C'_{2(x=y)}} xy ; xz \xrightarrow{C'_{2(x=y)}} -yz ; yz \xrightarrow{C'_{2(x=y)}} -xz
 \end{aligned}$$

...then apply these to the determinants, which do indeed behave as  $T_{1g}$  basis functions:

$$|xy\ xz| \xrightarrow{C_3} |yz\ xy| = -|xy\ yz| ; \quad |xy\ yz| \xrightarrow{C_3} |yz\ xz| = -|yz\ xz| ;$$

$$|xz\ yz| \xrightarrow{C_3} |xy\ xz| \Rightarrow \chi(C_3) = 0$$

$$|xy\ xz| \xrightarrow{C_{4z}} |-xy\ yz| = -|xy\ yz| ; \quad |xy\ yz| \xrightarrow{C_{4z}} |-xy\ -xz| = |xy\ xz| ;$$

$$|xz\ yz| \xrightarrow{C_{4z}} |yz\ -xz| = |xz\ yz| \Rightarrow \chi(C_4) = 1$$

$$|xy\ xz| \xrightarrow{C_{4z}^2} |xy\ -xz| = -|xy\ xz| ; \quad |xy\ yz| \xrightarrow{C_{4z}^2} |xy\ -yz| = -|xy\ yz| ;$$

$$|xz\ yz| \xrightarrow{C_{4z}^2} |-xz\ -yz| = |xz\ yz| \Rightarrow \chi(C_4^2) = -1$$

$$|xy\ xz| \xrightarrow{C'_{2(x=y)}} |xy\ -yz| = -|xy\ yz| ; \quad |xy\ yz| \xrightarrow{C'_{2(x=y)}} |xy\ -xz| = -|xy\ xz| ;$$

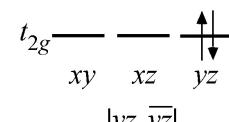
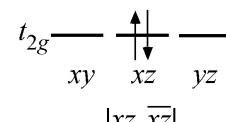
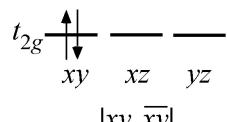
$$|xz\ yz| \xrightarrow{C'_{2(x=y)}} |-yz\ -xz| = -|xz\ yz| \Rightarrow \chi(C'_2) = -1$$

The determinants  $|xy\ xz|$ ,  $|xz\ yz|$ , and  $|xy\ yz|$  are likewise the wavefunctions with  $M_S = -1$  for the  ${}^3T_{1g}$  state. The  $M_S = 0$  wavefunctions belonging to  ${}^3T_{1g}$  are combinations of determinants:  $\sqrt[3]{2}(|xy\ xz| + |xy\ xz|)$ ,  $\sqrt[3]{2}(|xz\ yz| + |xz\ yz|)$  and  $\sqrt[3]{2}(|xy\ yz| + |xy\ yz|)$ . The reader may verify by direct operation that the  ${}^1T_{2g}$  wavefunctions are the orthogonal combinations of the same determinants:  $\sqrt[3]{2}(|xy\ xz| - |xy\ xz|)$ ,  $\sqrt[3]{2}(|xz\ yz| - |xz\ yz|)$ , and  $\sqrt[3]{2}(|xy\ yz| - |xy\ yz|)$ . Finally, we can construct a reducible representation spanned

$e_g \text{ --- ---}$

$e_g \text{ --- ---}$

$e_g \text{ --- ---}$



by determinants corresponding to two electrons in each one of the  $t_{2g}$  orbitals. Reduction of that representation shows that these determinants form the  ${}^1A_{1g}$  and  ${}^1E_g$  states.

$O$	$E$	$8C_3$	$3C_2(C_4^2)$	$6C_4$	$6C'_2$	
$ xy\ \bar{xy} ,  xz\ \bar{xz} ,  yz\ \bar{yz} $	3	0	3	1	1	${}^1A_1 \oplus {}^1E$

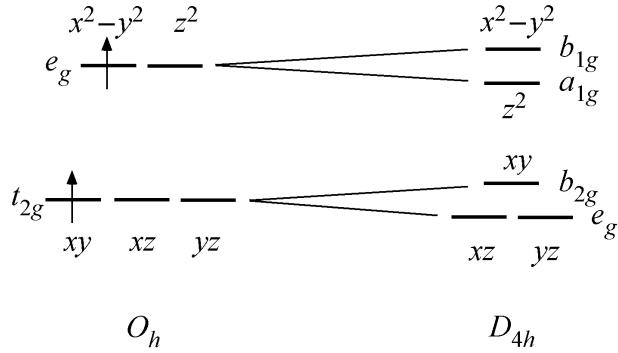
The combinations of these determinants for these two states, derivation of which is left as an exercise, are as follows:

$$\Psi(^1A_{1g}) = \frac{1}{\sqrt{3}} \left( |xy\bar{xy}| + |xz\bar{xz}| + |yz\bar{yz}| \right)$$

$$\Psi_a(^1E_g) = \frac{1}{\sqrt{6}} \left( 2|xy\bar{xy}| - |xz\bar{xz}| - |yz\bar{yz}| \right) ; \quad \Psi_b(^1E_g) = \frac{1}{\sqrt{2}} \left( |xz\bar{xz}| - |yz\bar{yz}| \right).$$

### Descent in symmetry as a tool for deriving electronic wavefunctions

Let's consider the states we derived for the  $(t_{2g})^1(e_g)^1$  configuration:  ${}^{1,3}T_{1g} \oplus {}^{1,3}T_{2g}$ . Perhaps the simplest way to find determinantal wavefunctions for each of these is to proceed by lowering the symmetry (in this case, from  $O_h$  to  $D_{4h}$ ) and exploiting the symmetry correlations that apply to *both* the orbitals and the states. When  $O_h$  symmetry is lowered to  $D_{4h}$  symmetry, the correlation of  $d$  orbitals goes as illustrated here:



The parent  $(t_{2g})^1(e_g)^1$  configuration can yield four descendent configurations in  $D_{4h}$ :  $(e_g)^1(a_{1g})^1$ ,  $(e_g)^1(b_{1g})^1$ ,  $(b_{2g})^1(a_{1g})^1$ , and  $(b_{2g})^1(b_{1g})^1$ , which respectively give rise to  ${}^{1,3}E_g$ ,  ${}^{1,3}E_g$ ,  ${}^{1,3}B_{2g}$ , and  ${}^{1,3}A_{2g}$  states, as determined by evaluating direct products using the  $D_{4h}$  orbitals. However, the  $D_{4h}$  descendent states must also correlate directly with their  $O_h$  parent states,  ${}^{1,3}T_{1g}(O_h) \rightarrow {}^{1,3}E_g$ ,  ${}^{1,3}A_{2g}(D_{4h})$ ,  ${}^{1,3}T_{2g}(O_h) \rightarrow {}^{1,3}E_g$ ,  ${}^{1,3}B_{2g}(D_{4h})$ . We can conclude that  $(b_{2g})^1(a_{1g})^1$  and  $(b_{2g})^1(b_{1g})^1$  configurations and their corresponding determinants in  $D_{4h}$  must respectively derive from  ${}^{1,3}T_{2g}$  and  ${}^{1,3}T_{1g}$  in  $O_h$ . We therefore know some representative wavefunctions for each of these two states,

	$M_S$		$M_S$
$ xy\bar{z}^2 $	1	$ xy\bar{x}^2-y^2 $	1
${}^3T_{2g} :  \overline{xy}\bar{z}^2  +  xy\bar{\overline{z}}^2 $	0	${}^3T_{1g} :  \overline{xy}\bar{x}^2-y^2  +  xy\bar{x}^2-\overline{y}^2 $	0
$ \overline{xy}\bar{z}^2 $	-1	$ \overline{xy}\bar{x}^2-\overline{y}^2 $	-1
${}^1T_{2g} :  \overline{xy}\bar{z}^2  -  xy\bar{\overline{z}}^2 $	0	${}^1T_{1g} :  \overline{xy}\bar{x}^2-y^2  -  xy\bar{x}^2-\overline{y}^2 $	0

### Relative State Energies

Now we will depart from a purely symmetry-based analysis and evaluate the energies of the triplet states and several of the singlet states for an octahedral  $d^2$  system. Just as for the qualitative correlation diagram, the two limiting cases are the atomic ions and the strong ligand field limit. Let's begin with the strong-field limit:

$$\begin{aligned}
E(^3T_{1g}, t_{2g}^2) &= 2\epsilon_{t_{2g}} + J_{xy,xz} - K_{xy,xz} = 2\epsilon_{t_{2g}} + (A - 2B + C) - (3B + C) = 2\epsilon_{t_{2g}} + A - 5B \\
E(^3T_{2g}, t_{2g}^1 e_g^1) &= \epsilon_{t_{2g}} + \epsilon_{e_g} + J_{xy,z^2} - K_{xy,z^2} = \epsilon_{t_{2g}} + \epsilon_{e_g} + (A - 4B + C) - (4B + C) = \epsilon_{t_{2g}} + \epsilon_{e_g} + A - 8B \\
E(^3T_{1g}, t_{2g}^1 e_g^1) &= \epsilon_{t_{2g}} + \epsilon_{e_g} + J_{xy,x^2-y^2} - K_{xy,x^2-y^2} = \epsilon_{t_{2g}} + \epsilon_{e_g} + (A + 4B + C) - (C) = \epsilon_{t_{2g}} + \epsilon_{e_g} + A + 4B \\
E(^3A_{2g}, e_g^2) &= 2\epsilon_{e_g} + J_{z^2,x^2-y^2} - K_{z^2,x^2-y^2} = 2\epsilon_{e_g} + (A - 4B + C) - (4B + C) = 2\epsilon_{e_g} + A - 8B \\
E(^1T_{2g}, t_{2g}^2) &= 2\epsilon_{t_{2g}} + J_{xy,xz} + K_{xy,xz} = 2\epsilon_{t_{2g}} + (A - 2B + C) + (3B + C) = 2\epsilon_{t_{2g}} + A + B + 2C \\
E(^1T_{2g}, t_{2g}^1 e_g^1) &= \epsilon_{t_{2g}} + \epsilon_{e_g} + J_{xy,z^2} + K_{xy,z^2} = \epsilon_{t_{2g}} + \epsilon_{e_g} + (A - 4B + C) + (4B + C) = \epsilon_{t_{2g}} + \epsilon_{e_g} + A + 2C \\
E(^1T_{1g}, t_{2g}^1 e_g^1) &= \epsilon_{t_{2g}} + \epsilon_{e_g} + J_{xy,x^2-y^2} + K_{xy,x^2-y^2} = \epsilon_{t_{2g}} + \epsilon_{e_g} + (A + 4B + C) + (C) = \epsilon_{t_{2g}} + \epsilon_{e_g} + A + 4B + 2C
\end{aligned}$$

In practice, we are interested in the relative energies of these states, so let's take energy differences to get the excited state energies relative to the ground state,  $E(^3T_{1g}, t_{2g}^2)$ :

$$\begin{aligned}
E(^3T_{2g}, t_{2g}^1 e_g^1) - E(^3T_{1g}, t_{2g}^2) &= \epsilon_{e_g} - \epsilon_{t_{2g}} - 3B = \Delta_o - 3B & -3B \\
E(^3A_{2g}, e_g^2) - E(^3T_{1g}, t_{2g}^2) &= 2\epsilon_{e_g} - 2\epsilon_{t_{2g}} - 3B = 2\Delta_o - 3B & -3B \\
E(^3T_{1g}, t_{2g}^1 e_g^1) - E(^3T_{1g}, t_{2g}^2) &= \Delta_o + 9B & 9B \\
E(^1T_{2g}, t_{2g}^2) - E(^3T_{1g}, t_{2g}^2) &= 6B + 2C & \xrightarrow{\Delta_o \rightarrow 0} 6B + 2C \\
E(^1T_{2g}, t_{2g}^1 e_g^1) - E(^3T_{1g}, t_{2g}^2) &= \Delta_o + 5B + 2C & 5B + 2C \\
E(^1T_{1g}, t_{2g}^1 e_g^1) - E(^3T_{1g}, t_{2g}^2) &= \Delta_o + 9B + 2C & 9B + 2C
\end{aligned}$$

At this point, we need to recognize that these expressions are based on the assumption that each state arises from a single (strong field) configuration. As  $\Delta_o \rightarrow 0$ , the energies of the  $^3T_{2g}$ ,  $^3A_{2g}$ , and the lowest  $^3T_{1g}$  states must be equal since all three states correlate back to the same atomic state ( $^3F$ ). In the above expressions, however, we can see that the energy of the first two states is  $-3B$  relative to the the lowest  $^3T_{1g}$  state as  $\Delta_o \rightarrow 0$ . The resolution of this difficulty lies in configuration interaction (CI). There are two  $^3T_{1g}$  states, for which we've written ligand-field single-determinant wavefunctions in the preceding discussion, and they must interact with each other since they are of the same symmetry. The wavefunctions written above are very good approximations for large  $\Delta_o$ ; the extent of CI is small when the energy difference between these like-symmetry determinants from two different configurations is large. As  $\Delta_o \rightarrow 0$ , however, these wavefunctions mix to yield the  $^3P$  atomic state and a component of the  $^3F$  atomic state. Since the  $^3T_{2g}$  state is the only triplet state of that symmetry, it correlates back to the  $^3F$  atomic state without any mixing with other configurations. We therefore choose the energy of the  $^3T_{2g}$  state at  $\Delta_o = 0$  as the zero of energy, so that at  $\Delta_o = 0$ ,  $E(^3T_{1g}, t_{2g}^2) = 3B$  and  $E(^3T_{1g}, t_{2g}^1 e_g^1) = 12B$ . Now, we know that if the mixing between the two  $^3T_{1g}$  states is accounted for, the lower of the two states must have  $E = 0$  when  $\Delta_o = 0$ . We can therefore write a secular equation that accounts for the CI and it must be of the form,

$$\begin{vmatrix} 12B-E & x \\ x & 3B-E \end{vmatrix} = 0, \text{ when } \Delta_o = 0 \Rightarrow E^2 - (15B)E + 36B^2 - x^2 = 0$$

where  $x$  is the matrix element due to the interaction of the two  ${}^3T_{1g}$  states.<sup>4</sup> The lower energy solution is  $E = 0$ , which is satisfied if  $x^2 = 36B^2$ ; the higher energy root is therefore  $E = 15B$ . The interaction between the two states is due to electron-electron repulsion and is therefore independent of the ligand-field splitting, i.e., even for nonzero  $\Delta_o$ , the off-diagonal entry in the secular equation is  $6B$ :

$$\begin{vmatrix} \Delta_o + 12B - E & -6B \\ -6B & 3B - E \end{vmatrix} = 0$$

$$\frac{E_{\pm}({}^3T_{1g})}{B} = \frac{1}{2} \left[ \left( \frac{\Delta_o}{B} \right) + 15 \pm \sqrt{\left( \frac{\Delta_o}{B} \right)^2 + 18 \left( \frac{\Delta_o}{B} \right) + 225} \right]$$

Since the lower of the two  ${}^3T_{1g}$  states is the ground state and we wish to express all the other states' energies relative to the ground state, we must subtract  $E_-({}^3T_{1g})$  from each. In particular, for the triplet states we obtain

$$\boxed{\frac{E_+({}^3T_{1g})}{B} - \frac{E_-({}^3T_{1g})}{B} = \sqrt{\left( \frac{\Delta_o}{B} \right)^2 + 18 \left( \frac{\Delta_o}{B} \right) + 225}}$$

$$\boxed{\frac{E({}^3T_{2g}, t_{2g}^1 e_g^1)}{B} - \frac{E_-({}^3T_{1g})}{B} = \frac{1}{2} \left[ \left( \frac{\Delta_o}{B} \right) - 15 + \sqrt{\left( \frac{\Delta_o}{B} \right)^2 + 18 \left( \frac{\Delta_o}{B} \right) + 225} \right]}$$

$$\boxed{\frac{E({}^3A_{2g}, e_g^2)}{B} - \frac{E_-({}^3T_{1g})}{B} = \frac{1}{2} \left[ 3 \left( \frac{\Delta_o}{B} \right) - 15 + \sqrt{\left( \frac{\Delta_o}{B} \right)^2 + 18 \left( \frac{\Delta_o}{B} \right) + 225} \right]}$$

The  ${}^1T_{2g}$  singlet determinants also mix via CI, and we know that as  $\Delta_o \rightarrow 0$ , the energies of the higher  ${}^1T_{2g}$  state and the  ${}^1T_{1g}$  state both correlate to the  ${}^1G$  atomic state with energy  $2\varepsilon_d + A + 4B + 2C$ . We can therefore write a secular equation (applicable as  $\Delta_o \rightarrow 0$ ) that accounts for the CI,

$$\begin{vmatrix} 2C - E & x \\ x & B + 2C - E \end{vmatrix} = 0, \text{ when } \Delta_o = 0 \Rightarrow x^2 = 12B^2 \text{ if } E_+ = 4B + 2C.$$

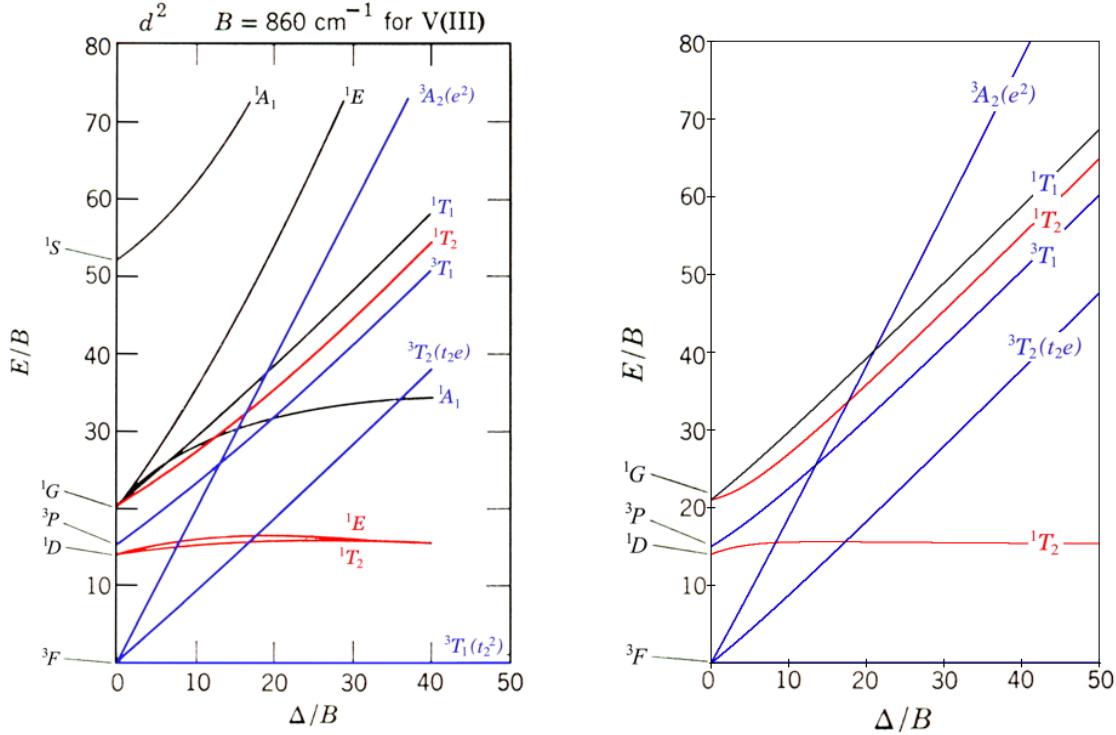
As before,  $x^2 = 12B^2$  for *all* values of  $\Delta_o$ . The general CI secular equation and its roots:

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<sup>4</sup> A symmetry argument is used here to deduce the off-diagonal matrix element. A direct calculation is given in Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*, McGraw-Hill: New York, 1980, p. 58.

$$\begin{aligned}
& \left| \begin{array}{cc} (B+2C)-E & -\sqrt{12}B \\ -\sqrt{12}B & (\Delta_o + 2C) - E \end{array} \right| = 0 \\
& \left( \frac{E}{B} \right)_\pm = 2 \left( \frac{C}{B} \right) + \frac{1}{2} \left[ \left( \frac{\Delta_o}{B} \right) + 1 \pm \sqrt{\left( \frac{\Delta_o}{B} \right)^2 - 2 \left( \frac{\Delta_o}{B} \right) + 49} \right] \\
& \left( \frac{E}{B} \right)_\pm - \left( \frac{E_-({}^3T_{1g})}{B} \right) = 2 \left( \frac{C}{B} \right) - 7 + \frac{1}{2} \sqrt{\left( \frac{\Delta_o}{B} \right)^2 + 18 \left( \frac{\Delta_o}{B} \right) + 225} \pm \frac{1}{2} \sqrt{\left( \frac{\Delta_o}{B} \right)^2 - 2 \left( \frac{\Delta_o}{B} \right) + 49} \\
& \frac{E({}^1T_{1g}, t_{2g}^1 e_g^1)}{B} - \left( \frac{E_-({}^3T_{1g})}{B} \right) = 2 \left( \frac{C}{B} \right) + \frac{9}{2} + \frac{1}{2} \left[ \left( \frac{\Delta_o}{B} \right) + \sqrt{\left( \frac{\Delta_o}{B} \right)^2 + 18 \left( \frac{\Delta_o}{B} \right) + 225} \right]
\end{aligned}$$

The reader may now compare these results with those published by Tanabe and Sugano in the eponymously-named diagram for a  $d^2$  ion:



Left: a reproduction of the Tanabe-Sugano diagram for a  $d^2$  ion; Right: Plots of the state energies for selected states of a  $d^2$  ion as derived in this document for the parameter choice  $C = 4.5B$ .

## Appendix 1: Relations Involving Coulomb and Exchange Integrals

### p orbitals

$$\begin{aligned} J_{0,0} &= J_{z,z} = J_{x,x} = J_{y,y} \\ J_{1,1} &= J_{-1,-1} = J_{-1,1} = \left(\frac{1}{2}\right)(J_{x,x} + J_{x,y}) \\ J_{1,0} &= J_{-1,0} = J_{x,y} = J_{x,z} = J_{y,z} \\ K_{1,-1} &= K_{-1,1} = 2K_{x,y} = J_{x,x} - J_{x,y} \\ K_{1,0} &= K_{-1,0} = K_{x,y} = K_{x,z} = K_{y,z} \end{aligned}$$

### definitions

$$\begin{aligned} J_{i,j} &= \int \varphi_i^*(1) \varphi_j^*(2) \left(\frac{1}{r_{12}}\right) \varphi_i(1) \varphi_j(2) d\tau_1 d\tau_2; \\ K_{i,j} &= \int \varphi_i^*(1) \varphi_j^*(2) \left(\frac{1}{r_{12}}\right) \varphi_i(2) \varphi_j(1) d\tau_1 d\tau_2 \end{aligned}$$

### d orbitals

$$\begin{aligned} J_{0,0} &= J_{z^2,z^2} \\ J_{2,2} &= J_{-2,-2} = J_{2,-2} = \left(\frac{1}{2}\right)(J_{xy,xy} + J_{x^2-y^2,xy}) \\ J_{2,1} &= J_{-2,-1} = J_{2,-1} = J_{-2,1} = J_{xy,xz} \\ J_{2,0} &= J_{-2,0} = J_{xy,z^2} \\ J_{1,1} &= J_{-1,-1} = J_{1,-1} = \left(\frac{1}{2}\right)(J_{xz,xz} + J_{xz,yz}) \\ J_{1,0} &= J_{-1,0} = J_{xz,z^2} \\ K_{1,-1} &= 2K_{xz,yz} = J_{xz,xz} - J_{xz,yz} \\ K_{2,-2} &= 2K_{xy,x^2-y^2} = J_{xy,xy} - J_{xy,x^2-y^2} \\ K_{2,1} &= K_{-2,-1} = K_{xy,xz} - \int \varphi_{xz}(1) \varphi_{xy}(2) \left(\frac{1}{r_{12}}\right) \varphi_{yz}(1) \varphi_{x^2-y^2}(2) d\tau_1 d\tau_2 \\ K_{2,-1} &= K_{-2,1} = K_{xy,xz} + \int \varphi_{xz}(1) \varphi_{xy}(2) \left(\frac{1}{r_{12}}\right) \varphi_{yz}(1) \varphi_{x^2-y^2}(2) d\tau_1 d\tau_2 \\ K_{2,0} &= K_{-2,0} = K_{xy,z^2} \\ K_{1,0} &= K_{-1,0} = K_{xz,z^2} \end{aligned}$$

Energies of real *d* orbital integrals in terms of Racah parameters

$J_{xy,xy} = J_{xz,xz} = J_{yz,yz} = J_{z^2,z^2} = J_{x^2-y^2,x^2-y^2}$	$A + 4B + 3C$
$J_{xz,yz} = J_{xy,yz} = J_{xy,xz} = J_{x^2-y^2,yz} = J_{x^2-y^2,xz}$	$A - 2B + C$
$J_{xy,z^2} = J_{x^2-y^2,z^2}$	$A - 4B + C$
$J_{yz,z^2} = J_{xz,z^2}$	$A + 2B + C$
$J_{x^2-y^2,xy}$	$A + 4B + C$
$K_{xy,yz} = K_{xz,yz} = K_{xy,xz} = K_{x^2-y^2,yz} = K_{x^2-y^2,xz}$	$3B + C$
$K_{xy,z^2} = K_{x^2-y^2,z^2}$	$4B + C$
$K_{yz,z^2} = K_{xz,z^2}$	$B + C$
$K_{x^2-y^2,xy}$	$C$
$\int \varphi_{xz}(1) \varphi_{xy}(2) \left(\frac{1}{r_{12}}\right) \varphi_{yz}(1) \varphi_{x^2-y^2}(2) d\tau_1 d\tau_2$	$-3B$

Energies of complex  $d$  orbital integrals in terms of Racah parameters

$J_{0,0}$	$A + 4B + 3C$
$J_{2,2} = J_{-2,-2} = J_{2,-2}$	$A + 4B + 2C$
$J_{2,1} = J_{-2,-1} = J_{2,-1} = J_{-2,1}$	$A - 2B + C$
$J_{2,0} = J_{-2,0}$	$A - 4B + C$
$J_{1,1} = J_{-1,-1} = J_{1,-1}$	$A + B + 2C$
$J_{1,0} = J_{-1,0}$	$A + 2B + C$
$K_{1,-1}$	$6B + 2C$
$K_{2,-2}$	$C$
$K_{2,1} = K_{-2,-1}$	$6B + C$
$K_{2,-1} = K_{-2,1}$	$C$
$K_{2,0} = K_{-2,0}$	$4B + C$
$K_{1,0} = K_{-1,0}$	$B + C$

For 1<sup>st</sup>-row transition metal ions, Racah parameters  $B$  and  $C$  have typical ranges:

$B \approx 650 - 1100 \text{ cm}^{-1}$ ,  $C \approx 3800 - 5500 \text{ cm}^{-1}$ . (State energy differences don't involve  $A$ .)

We've chosen to express the Coulomb and Exchange integrals in terms of Racah parameters, but the Slater-Condon parameters are also commonly encountered. Slater-Condon parameters are integrals involving  $R_{nl}$ , the radial parts of the hydrogenic orbitals, and defined by

$$F^k \equiv e^2 \int_0^\infty r_1^2 \left[ \int_0^\infty r_2^2 \frac{r_-^k}{r_+^{k+1}} |R_{nl}(r_1)|^2 |R_{nl}(r_2)|^2 dr_2 \right] dr_1 ; \quad \frac{r_-^k}{r_+^{k+1}} = \begin{cases} \frac{r_1^k}{r_2^{k+1}} & \text{if } r_2 > r_1 \\ \frac{r_2^k}{r_1^{k+1}} & \text{if } r_1 > r_2 \end{cases}$$

$$\text{and (in the } d\text{-shell): } F_0 \equiv F^0, F_2 = \frac{F^2}{49}, F_4 = \frac{F^4}{441}$$

The Racah parameters are related to the Slater-Condon parameters by

$$A = F_0 - 49F_4$$

$$B = F_2 - 5F_4$$

$$C = 35F_4$$

## Appendix 2: States from three electrons in three or more degenerate orbitals

We can extend the method used to derive 2-electron antisymmetric direct product formulae to handle 3-electron configurations involving 3 or more degenerate orbitals. If we are constructing permissible *quartet* state ( $S = 3/2$ ) wavefunctions, the wavefunction can be factored into separate spatial and spin parts, and just as for the two-electron triplet wavefunctions case, the spatial part of the wavefunctions is antisymmetric with respect to permutation of the electron labels while the spin functions are symmetric:

$${}^4\Psi = \underbrace{\frac{1}{\sqrt{6}}(\varphi_i(1)\varphi_j(2)\varphi_k(3) - \varphi_i(2)\varphi_j(1)\varphi_k(3) - \varphi_i(1)\varphi_j(3)\varphi_k(2) + \varphi_i(3)\varphi_j(2)\varphi_k(1) + \varphi_i(2)\varphi_j(3)\varphi_k(1) + \varphi_i(3)\varphi_j(1)\varphi_k(2))}_{\text{Antisymmetric}} , i < j < k$$

	Symmetric	$M_S$
$\alpha_1\alpha_2\alpha_3$	3/2	
$\frac{1}{\sqrt{3}}(\alpha_1\alpha_2\beta_3 + \alpha_1\beta_2\alpha_3 + \beta_1\alpha_2\alpha_3)$	1/2	
$\frac{1}{\sqrt{3}}(\alpha_1\beta_2\beta_3 + \beta_1\alpha_2\beta_3 + \beta_1\beta_2\alpha_3)$	-1/2	
$\beta_1\beta_2\beta_3$	-3/2	

when operated on by operation  $R$ , each of the terms in the spatial wavefunction yield the same eigenvalue:  $r_i r_j r_k$ . The set  $\{\varphi_1, \dots, \varphi_n\}$  is the basis for an irreducible representation so the character for each operation within a class with respect to this basis will be the same, and independent of any choice of orthogonal linear combinations of these orbitals we make. As before (p. 11), we suppose that we've singled out a particular operation  $R$  from each class and have chosen a linear combination of the orbitals such that the matrix for each  $R$  is diagonal:

$$\chi^-(R) = \chi^{3/2}(R) = \sum_{i < j < k}^n r_i r_j r_k$$

Let's show that the formula given on p. 12,  $\chi^{S=3/2}(R) = \frac{1}{6}(\chi^3(R) - 3\chi(R)\chi(R^2) + 2\chi(R^3))$ , yields just this result:

$$\begin{aligned} \chi^3(R) &= \left( \sum_i^n r_i \right)^3 = \sum_i^n r_i^3 + 3 \sum_i^n \sum_{j \neq i}^n r_i^2 r_j + 6 \sum_i^n \sum_{j \neq i}^n \sum_{k \neq i, k \neq j}^n r_i r_j r_k \\ -3\chi(R)\chi(R^2) &= -3 \left( \sum_i^n r_i \right) \left( \sum_i^n r_i^2 \right) = -3 \sum_i^n r_i^3 - 3 \sum_i^n \sum_{j \neq i}^n r_i^2 r_j \\ + 2\chi(R^3) &= +2 \sum_i^n r_i^3 \end{aligned}$$

Which, when we take the sum and divide by 6, yields the desired result for  $\chi^{3/2}(R)$ . Using the first and last of these equations, we obtain

$$\frac{1}{3}(\chi^3(R) - \chi(R^3)) = \sum_i^n \sum_{j \neq i}^n r_i^2 r_j + 2 \sum_i^n \sum_{j \neq i}^n \sum_{k \neq i, k \neq j}^n r_i r_j r_k$$

The reader may verify that with a set  $n$  degenerate orbitals one can construct  $n(n - 1)(n - 2)/2$  distinct determinants with  $M_S = 1/2$  (or  $-1/2$ ) in which three different orbitals ( $\varphi_i, \varphi_j, \varphi_k$ ) are occupied and  $n(n - 1)$  distinct determinants with  $M_S = 1/2$  (or  $-1/2$ ) in which one orbital ( $\varphi_i$ ) is doubly occupied and one orbital ( $\varphi_j$ ) is singly occupied. The characters for each of the determinant of the first type are  $r_i r_j r_k$  and those of the second type have characters  $r_i^2 r_j$ . The formula  $\chi^{1/2}(R) = \frac{1}{3}(\chi^3(R) - \chi(R^3))$  follows from taking the sum over all the basis determinants of both types.

### Appendix 3: *Bosons*

As it happens, vibrational excitations behave like *bosons*, among which are deuterons, alpha particles, and other integer-spin particles. In solids, vibrational excitations are customarily given a particle-like name: *phonons*. The wavefunction for a system of two or more bosons must retain the same sign any time we permute the coordinates of any two particles,

$$\Psi(1,2,\dots\textcolor{blue}{i},\dots,\textcolor{green}{j},\dots N) = +\Psi(1,2,\dots\textcolor{green}{j},\dots,\textcolor{blue}{i},\dots N).$$

Consider, for example, an overtone or combination energy level in which a molecule has two quanta of vibrational excitation. In the harmonic approximation, the vibrational Hamiltonian for a molecule can be expressed as a sum of separate contributions from each normal mode,

$$\mathcal{H}_{vib} = \sum_{k=1}^{3N-6} \mathcal{H}_k; \quad \mathcal{H}_k = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \lambda_k Q_k^2$$

and therefore the vibrational wavefunctions are a product of individual harmonic oscillator wavefunctions for each mode and the vibrational energy is sum of the energies of individual modes. Consider, for example, an overtone or combination energy level in which a molecule has two quanta of vibrational excitation, one each in the  $j^{\text{th}}$  and  $k^{\text{th}}$  modes,

$$\Psi_{vib} = \left\{ \prod_{i \neq j,k}^{3N-6} \psi_i(0) \right\} \psi_j(1) \psi_k(1); \quad E = \frac{1}{2} \sum_{i \neq j,k}^{3N-6} h\nu_i + \frac{3}{2} h(\nu_j + \nu_k)$$

where mode quantum numbers,  $n_i$ , are indicated in parentheses.

Recall that the ground state ( $n_i = 0$ ) vibrational wavefunctions all transform as the totally symmetric representation, so the symmetry of a combination level involving nondegenerate modes is given by the direct product,  $\Gamma_j \otimes \Gamma_k$ . If the  $j^{\text{th}}$  and  $k^{\text{th}}$  modes are members of a degenerate representation,  $\Gamma_p$ , three wavefunctions are possible,  $\psi_j(2)$ ,  $\psi_k(2)$ , and  $\psi_j(1)\psi_k(1)$ . There is, of course, no physical distinction between the functions  $\psi_j(1)\psi_k(1)$  and  $\psi_k(1)\psi_j(1)$ . Thus, the wavefunctions for a degenerate overtone vibrational states form the basis for the *symmetric* direct product representation  $[\Gamma_p \otimes \Gamma_p]^+$ , the characters of which are determined using the formula derived on p. 12,

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

For three quanta, the formula is<sup>5</sup>

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

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<sup>5</sup> A more complete and general treatment is found in Wilson, E.B. Jr., Decius, J.C., Cross, P.C., *Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra*, Dover: New York, 1980, pp. 151-5.