

Electronic Configurations

- The standard labelling convention for a state of spin S that transforms as a basis function for irrep Γ of the point group in question is $^{2S+1}\Gamma$.
- Closed shells contribute nothing, that is, they are totally symmetric singlets.
- One electron in an orbital of symmetry Γ transforms as $^2\Gamma$, since we have

$$G\psi_{\Gamma i} = \sum_j \psi_{\Gamma j} D_{ji}^{\Gamma}(G),$$

and a single electron is a doublet.

- Thus b_2^1 gives 2B_2 in C_{2v} , e^1 gives 2E in C_{3v} , and d^1 gives 2D in $SO(3)$.



Electronic Configurations

- Consider multiple singly-occupied orbitals (possibly degenerate) $\psi_\alpha^1 \psi_\beta^1 \psi_\gamma^1 \dots$. The overall spin symmetry is given by the reduction of $D^{\frac{1}{2}} \otimes D^{\frac{1}{2}} \otimes \dots$ in $SU(2)$ (as many factors as electrons).
- This reduces to $S = 0, 1 \dots \frac{N}{2}$ for N even or $S = \frac{1}{2}, \frac{3}{2} \dots \frac{N}{2}$ for N odd.
- Note that except for the maximum S value, which occurs only once, each spin state can occur multiple times as shown in the branching diagram.



Electronic Configurations

- The spatial symmetry labels of the configurations arising from $\psi_\alpha^1 \psi_\beta^1 \psi_\gamma^1 \dots$ are obtained by reducing the direct product representation $D^\alpha \otimes D^\beta \otimes D^\gamma \otimes \dots$ in the point group of the system.
- For example, $e^1 e'^1$ in C_{3v} symmetry gives rise to 1A_1 , 1A_2 , 1E , 3A_1 , 3A_2 , and 3E states. Total “degeneracy” 16.
- $d^1 d'^1$ in $SO(3)$ symmetry gives rise to 1S , 1P , 1D , 1F , 1G , 3S , 3P , 3D , 3F , 3G states, with total degeneracy 100.
- One “hole” in an orbital behaves analogously — this is the same as $(2p - 1)$ electrons in an p -fold degenerate orbital.



Equivalent Electrons

- This obviously does not cover all possible cases. What happens in the case of a p -fold degenerate orbital with more than one (and less than $2p - 1$) electrons (*equivalent electrons*)?
- The problem is the Pauli principle. In a case like $d^1 d'^1$ all occupations of the orbitals can be combined with the possible spin functions and still satisfy the Pauli principle.
- But it is not possible to have a nonzero antisymmetric wave function when two electrons with the same spin can occupy the same orbital.
- We must explicitly ensure we can make the wave function antisymmetric.



Equivalent Electrons

- This is done by looking at the permutational symmetry of the possible wave functions.
- We will give here only the formulas.
- For the case of ψ_α^2 , where α is a degenerate irrep of the point group (including $SO(3)$), the character of the representation spanned by the singlet states is

$$\chi^{S=0}(G) = \frac{1}{2} \left([\chi^\alpha(G)]^2 + \chi^\alpha(G^2) \right),$$

and for the triplet states

$$\chi^{S=1}(G) = \frac{1}{2} \left([\chi^\alpha(G)]^2 - \chi^\alpha(G^2) \right),$$

- Thus in C_{3v} e^2 gives rise to 1A_1 , 1E , and 3A_2 .



Equivalent Electrons

- Sidebar: d^2 .
- The more general case of $e^2 e'^2$ and similar is handled by first forming the states to which the equivalent electrons give rise to, and then forming and reducing all possible products.
- We consider the case of $e^2 t_2^2$ in T_d .
- The first step is to enumerate the cases of e^2 and t_2^2 .



$e^2t_2^2$ in T_d

- e^2

	E	$8C_3$	$6\sigma_d$	$6S_4$	$3C_2$
E	2	-1	0	0	2
$[\chi(G)]^2$	4	1	0	0	4
$\chi(G^2)$	2	-1	2	2	2
$\chi^0(G)$	3	0	1	1	3
$\chi^1(G)$	1	1	-1	-1	1

- This gives ${}^1A_1, {}^1E, {}^3A_2$.



$e^2t_2^2$ in T_d

- t_2^2

	E	$8C_3$	$6\sigma_d$	$6S_4$	$3C_2$
T_2	3	0	1	-1	-1
$[\chi(G)]^2$	9	0	1	1	1
$\chi(G^2)$	3	0	3	-1	3
$\chi^0(G)$	6	0	2	0	2
$\chi^1(G)$	3	0	-1	1	-1

- This gives 1A_1 , 1E , 1T_2 , and 3T_1 .



$e^2t_2^2$ in T_d

- We obtain for the product $e^2t_2^2$

$$\{^1A_1, ^1E, ^3A_2\} \otimes \{^1A_1, ^1E, ^1T_2, \text{ and } ^3T_1\},$$

which reduces to $(2)^1A_1$, 1A_2 , $(3)^1E$, 1T_1 , $(3)^1T_2$, 3A_2 , 3E , $(3)^3T_1$, $(2)^3T_2$, and 5T_2 .

- This can be applied to any number of terms in the product.



Three Equivalent Electrons

- The formula for two electrons also works for $2p - 2$ electrons in a p -fold degenerate orbital.
- For three electrons (and an irrep that is at least triply degenerate) the formulas are

$$\chi^{S=\frac{1}{2}}(G) = \frac{1}{3} \left([\chi^\alpha(G)]^3 - \chi^\alpha(G^3) \right)$$

$$\chi^{S=\frac{3}{2}}(G) = \frac{1}{6} \left([\chi^\alpha(G)]^3 - 3\chi^\alpha(G)\chi^\alpha(G^2) + 2\chi^\alpha(G^3) \right).$$

- Sidebar: t_2^3 in T_d .
- Four and more equivalent electrons occur only in very special cases.



Four or More Equivalent Electrons

- Two cases are of interest.
- Atoms: d^4 , f^6 , etc. All these situations have been analyzed using symmetric group methods and the irreps of the groups $SU(2j + 1)$. Look in the books! (Hamermesh and references therein).
- The four- and five-fold degenerate irreps of I and I_h . The five-fold degenerate case can be treated by looking at d^4 or d^5 for an atom and subducing the various $SO(3)$ irreps in I .
- If you need the four-fold degenerate case, you can work it out or send me Email. . . .



Coupling Between Angular Momenta

- All of our reasoning so far has been based on a separation of spin and orbital angular momentum.
- These angular momenta can couple at various levels. We have assumed so far that the orbital angular momenta couple to give an overall spatial symmetry, and the spin angular momenta couple to give an overall spin.
- If we continue with this assumption, we can finally couple the spin and spatial angular momentum to get the *total angular momentum J*.



Coupling Between Angular Momenta

- We obtain from the usual Clebsch-Gordan formula for an atom

$$J = L + S, L + S - 1 \dots |L - S|,$$

for example.

- These J levels are all degenerate if the Hamiltonian contains no spin-space coupling terms (such as a magnetic field or spin-orbit coupling).
- States of a given J are themselves $(2J + 1)$ -fold degenerate.
- Thus, for example, a 3P state yields three J values, 0, 1, and 2.
- These are respectively singly, triply and five-fold degenerate (total degeneracy nine).
- Note that states with zero angular momenta (spatial or spin) yield only a single J value.

