

P423 - Lecture 13: How to write down wavefunctions for atomic ground states

How to write down many particle wave fns from single particle states: Slater determinant

If a many particle state has one electron in state a_1 , one in a_2 , ... the Fermion wave fn is

$$\Psi(\vec{n}_1, \vec{n}_2, \dots, \vec{n}_m) = \frac{1}{\sqrt{m!}} \sum_{\text{all } P} (-1)^P \hat{P} \Psi_{a_1}(\vec{n}_1) \Psi_{a_2}(\vec{n}_2) \Psi_{a_3}(\vec{n}_3) \dots \Psi_{a_m}(\vec{n}_m)$$

(m! of them!)

where \hat{P} is a permutation operator, e.g. $\hat{P}_{23} \Psi_{a_1}(\vec{n}_1) \Psi_{a_2}(\vec{n}_2) \Psi_{a_3}(\vec{n}_3) = \Psi_{a_1}(\vec{n}_1) \Psi_{a_3}(\vec{n}_2) \Psi_{a_2}(\vec{n}_3)$

and P is the order of the operator (how many 2 particle permutations are required to form the P):

e.g. $\hat{P}_{1234 \rightarrow 2143} = \hat{P}_{12} \hat{P}_{34}$ has order 2 so $(-1)^P = 1$.

It is more convenient to write this as a determinant:

$$\Psi(\vec{n}_1, \vec{n}_2, \dots, \vec{n}_m) = \frac{1}{\sqrt{m!}} \begin{vmatrix} \Psi_{a_1}(\vec{n}_1) & \Psi_{a_1}(\vec{n}_2) & \dots & \Psi_{a_1}(\vec{n}_m) \\ \Psi_{a_2}(\vec{n}_1) & \Psi_{a_2}(\vec{n}_2) & \dots & \Psi_{a_2}(\vec{n}_m) \\ \dots & \dots & \dots & \dots \\ \Psi_{a_m}(\vec{n}_1) & \Psi_{a_m}(\vec{n}_2) & \dots & \Psi_{a_m}(\vec{n}_m) \end{vmatrix}$$

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Example: write down the 3 electron wave for the ground state of $Li = (1s)^2(2s)$
one electron $1s, \uparrow$, another $1s, \downarrow$ and another $2s \uparrow$ or \downarrow :

$$\psi_{Li}^{(\uparrow)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{100}(1)|\uparrow\rangle & \psi_{100}(2)|\uparrow\rangle & \psi_{100}(3)|\uparrow\rangle \\ \psi_{100}(1)|\downarrow\rangle & \psi_{100}(2)|\downarrow\rangle & \psi_{100}(3)|\downarrow\rangle \\ \psi_{200}(1)|\uparrow\rangle & \psi_{200}(2)|\uparrow\rangle & \psi_{200}(3)|\uparrow\rangle \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}} \left\{ \begin{aligned} & \left[\psi_{100}(1)\psi_{100}(2)\psi_{200}(3)|\uparrow\downarrow\uparrow\rangle + \psi_{100}(1)\psi_{200}(2)\psi_{100}(3)|\downarrow\uparrow\uparrow\rangle \right. \\ & \left. + \psi_{200}(1)\psi_{100}(2)\psi_{100}(3)|\uparrow\uparrow\downarrow\rangle \right] \\ & - \left[\psi_{200}(1)\psi_{100}(2)\psi_{100}(3)|\uparrow\downarrow\uparrow\rangle + \psi_{100}(1)\psi_{200}(2)\psi_{100}(3)|\uparrow\uparrow\downarrow\rangle \right. \\ & \left. + \psi_{100}(1)\psi_{100}(2)\psi_{200}(3)|\downarrow\uparrow\uparrow\rangle \right] \end{aligned} \right\}$$

$$= \frac{1}{\sqrt{3}} \left\{ \begin{aligned} & \psi_{100}(1)\psi_{100}(2)\psi_{200}(3) \frac{1}{\sqrt{2}} (|\uparrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\rangle) \quad \text{"singlet 1-2"} \\ & + \psi_{100}(1)\psi_{200}(2)\psi_{100}(3) \frac{1}{\sqrt{2}} (|\downarrow\uparrow\uparrow\rangle - |\uparrow\uparrow\downarrow\rangle) \quad \text{"singlet 1-3"} \\ & + \psi_{200}(1)\psi_{100}(2)\psi_{100}(3) \frac{1}{\sqrt{2}} (|\uparrow\uparrow\downarrow\rangle - |\uparrow\downarrow\uparrow\rangle) \quad \text{"singlet 2-3"} \end{aligned} \right\}$$

Note how the $(1s)^2$ state forms a singlet. This is typical of a closed shell.

How to find the ground state of an atom: Hund's rules

$$H = \sum_{j=1}^Z \left[\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} + \underbrace{\left(\frac{Ze^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2} \right) \frac{1}{r_j^3} \vec{S}_j \cdot \vec{L}_j}_{\text{Spin-orbit interaction}} \right] + \frac{1}{4\pi\epsilon_0} \sum_{j < k} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

'LS coupling'

Approximation: $\sum_{j=1}^Z \left(\frac{Ze^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2} \right) \frac{1}{r_j^3} \vec{S}_j \cdot \vec{L}_j \approx \eta_{\text{eff}} \left(\sum_i \vec{S}_i \right) \cdot \left(\sum_j \vec{L}_j \right) = \eta_{\text{eff}} \vec{S} \cdot \vec{L}$

$$= \frac{\eta_{\text{eff}}}{2} \left[\underbrace{(\vec{S} + \vec{L})^2}_{\vec{J}} - (\vec{S})^2 - (\vec{L})^2 \right]$$

The approximate Hamiltonian ^{approx} has the following symmetries:

$$\left[H, \underbrace{\left(\sum_j \vec{L}_j + \vec{S}_j \right)}_{\vec{J}} \right] = 0 \quad (\text{Symmetry of exact } H!)$$

$$\left[H_{\text{approx}}, \underbrace{\left(\sum_i \vec{S}_i \right)^2}_{S^2} \right] = 0 \quad (\text{only for } H_{\text{approx}}!)$$

$$\left[H_{\text{approx}}, \underbrace{\left(\sum_i \vec{L}_i \right)^2}_{L^2} \right] = 0 \quad (||)$$

Note: without spin-orbit coupling, all these symmetries are exact!

⇒ Pick $(L^2), (S^2), (J^2), J_z$ and H as a set of commuting observables.

⇒ We can label our eigenenergies as ^{eigenvalues of} S^2, L^2, J^2 , the total angular momentum quantum numbers.

$|E\rangle \rightarrow |n, s, l, j\rangle$

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Russell-Saunders term-symbol notation:

$$2S+1 L_J \quad \text{where } L \text{ is written as a letter: } L = S, P, D, F, G, \dots$$

and S, J are written as numbers.

Any ground or excited atom configuration can be written in this notation.

Example: Show Table 5.1

$$Fe = (Ar) (4s)^2 (3d)^6 \quad 5D_4 \Rightarrow \begin{cases} S=2 \\ L=2 \\ J=4 \end{cases}$$

Note: rule (0): "Aufbau principle" - Fill (n,l) shells diagonally.

Hund's rules to find ground state term-symbol: In order of priority:

How to determine value of S:

- 1) Consistent with Pauli exclusion, the state with highest S will have the lowest energy.
 - Why? e-e interaction is minimized by space-antisymmetric wavefunctions (so that $\tau=0$ when $\vec{s}_1 = \vec{s}_2 = \dots = \vec{s}_n$).

For Fe, look at $(3d)^6$: $\begin{array}{cccccc} -2 & -1 & m_l=0 & 1 & 2 \\ \uparrow & \uparrow & \uparrow & \uparrow & \uparrow\downarrow \end{array} \Rightarrow \text{Max}(\sum_j (m_{s_j})) = 4 \times \frac{1}{2} + (\frac{1}{2} - \frac{1}{2}) = 2 //$

$\Rightarrow S=2 //$

How to determine value of L:

- 2) Highest L consistent with antisymmetrization will have lowest energy.

For Fe: $\text{Max}(\sum_{j=1}^6 (m_{l_j})) = +2 \quad \begin{array}{cccccc} -2 & -1 & 0 & 1 & 2 \\ \uparrow & \uparrow & \uparrow & \uparrow & \downarrow \end{array} \quad \text{and} \quad \text{Min}(m_L) = -2 \quad \begin{array}{cccccc} -2 & -1 & 0 & 1 & 2 \\ \downarrow & \downarrow & \downarrow & \downarrow & \uparrow \end{array}$

$\equiv m_L$

So the maximum allowed L is 2, which is D.

(Note: You can't have $m_L \geq 3$, it would require a violation of either Hund's (1) or Pauli:

like $\begin{array}{cccccc} -2 & -1 & 0 & 1 & 2 \\ \uparrow & \uparrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \end{array}$ or $\begin{array}{cccccc} -2 & -1 & 0 & 1 & 2 \\ \uparrow & \uparrow & \uparrow & \uparrow\downarrow & \uparrow \end{array}$

Why? Highest total L "spreads out" electrons, increasing their separation

⇒ minimizes e-e repulsion.

Hund's rule 3

3) If a subshell ^(n, l) is less than half filled, total J equal to |L-S| has the lowest energy;
 if subshell is more than half filled, total J equal to |L+S| has the lowest energy.

(note if subshell is half filled, L=0 and J=S).

For Fe, (3d)⁶ =

↑	↑	↑	↑	↓
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 is more than half filled, so J = |L+S| = 2+2 = 4

Why? μ_{eff} in LS Coupling is positive when subshell is less than half filled ⇒ Minimize J to minimize energy.

And μ_{eff} is negative when subshell is more than half filled ⇒ Maximize J.

(Because spin orbit can be described for holes instead of electrons ⇒ holes have positive charge flipping the sign of spin-orbit coupling).

Examples:

$$Mn = (Ar)(4s)^2(3d)^5 \Rightarrow \begin{array}{|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array} \Rightarrow S = \frac{5}{2}, L = 0, J = \frac{5}{2} \Rightarrow {}^6S_{5/2}$$

$$V = (Ar)(4s)^2(3d)^3 \Rightarrow \begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \uparrow \\ \hline \end{array} \Rightarrow S = \frac{3}{2}, L = 3, J = \frac{3}{2} \Rightarrow {}^4F_{3/2}$$

$$Se = (Ar)(4s)^2(3d)^4(4p)^1 \Rightarrow \begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \uparrow \\ \hline \end{array} \Rightarrow S = 1, L = 1, J = 2 \Rightarrow {}^3P_2$$

$$-(Kr)(2s)^2(2p)^2 \Rightarrow \begin{array}{|c|c|} \hline \uparrow & \uparrow \\ \hline \end{array} \Rightarrow S = 1, L = 1, J = 0 \Rightarrow {}^3P_0$$

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How to write down these wave fns?

Consider $C = (\text{He})(2s)^2(2p)^2, {}^3P_0$.

The $J=0$ comes from the addition of $S=1$ and $L=1$, so look at

the Clebsch-Gordan table $1 \otimes 1$:

$$|0,0\rangle = \frac{1}{\sqrt{3}} \left\{ \underbrace{|1,1\rangle}_{\text{orbit}} \underbrace{|1,-1\rangle}_{\text{Spin}} - \underbrace{|1,0\rangle}_{\text{orbit}} \underbrace{|1,0\rangle}_{\text{Spin}} + \underbrace{|1,-1\rangle}_{\text{orbit}} \underbrace{|1,1\rangle}_{\text{Spin}} \right\}$$

For the full 6-electron system, the spin states are $S=1, m_S=1, 0, -1$ states formed from

$\frac{1}{2} \otimes \dots \otimes \frac{1}{2}$. This is complicated! And the orbit states are $L=1, m_L=1, 0, -1$ formed from

$$\underbrace{0 \otimes \dots \otimes 0}_{4 \text{ electrons}} \otimes 1 \otimes 1$$

But we know that (He) and $(2s)^2$ are forming singlets. So let's write down the 2-electron wave fns for $(2p)^2$: (we can later multiply by the singlets and antisymmetrize, but $6! = 720$ states!)

$$S=1 \text{ Spin states are } \begin{cases} |1,1\rangle = |\uparrow\uparrow\rangle \\ |1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ |1,-1\rangle = |\downarrow\downarrow\rangle \end{cases}$$

The $L=1$ orbital states arise from $1 \otimes 1 = 2 \oplus 1 \oplus 0$. Look at Clebsch-Gordan:

$$\begin{cases} |1,1\rangle = \frac{1}{\sqrt{2}} [\psi_{211}(1)\psi_{210}(2) - \psi_{210}(1)\psi_{211}(2)] \\ |1,0\rangle = \frac{1}{\sqrt{2}} [\psi_{211}(1)\psi_{21-1}(2) - \psi_{21-1}(1)\psi_{211}(2)] \\ |1,-1\rangle = \frac{1}{\sqrt{2}} [\psi_{210}(1)\psi_{21-1}(2) - \psi_{21-1}(1)\psi_{210}(2)] \end{cases}$$

Plug all these in the spin-orbit wave fns $|0,0\rangle$ above and you get your $(2p)^2$ state!