

# Periodic Table

A multiple electron atom has a Hamiltonian of the form

$$H = \underbrace{\sum_i \left[ \frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right]}_{\text{Hydrogen-like}} + \underbrace{\frac{1}{2} \cdot \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{interaction}}$$

$Z$  = atomic number       $e$  = charge of electron  
 $m$  = mass of electron.

If we stupidly ignore the interaction term, the SE separates into  $Z$  hydrogen-like equations. The total wave function is a product of hydrogen-like wave functions

$$\psi = \psi_{n_1, l_1, m_{l1}} \psi_{n_2, l_2, m_{l2}} \dots \vec{S}(\vec{s}_1, \vec{s}_2, \vec{s}_3, \dots)$$

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$n$  = principle quantum number  
 $n = 1, 2, 3, \dots$

$l$  = total orbital angular momentum  
 $L^2 = l(l+1)\hbar^2$

$$l = n-1, n-2, \dots, 0$$

$m_l$  = z-component of orbital angular momentum

$$L_z = m_l \hbar$$

$$m_l = l, l-1, \dots, -l$$

We will also need the z-component of the spin

$$m_s = \pm \frac{1}{2}$$

$\Rightarrow$  No  $S$  is always  $\frac{1}{2}$  so

$$S^2 = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 = \frac{3}{4} \hbar^2$$

Crazy abbreviations for  $l$  that you need to know. (spectroscopic notation)

$l$		
0	s	sharp
1	p	principle
2	d	diffuse
3	f	fundamental
4	g	
5	h	

Without the ~~tan~~ interaction term, the total energy depends only on the ~~interaction~~ principle quantum number  $n$ . We can place two electrons (Pauli) into any hydrogen orbital  $\psi_{nlm}$ . Therefore each energy state is degenerate.

$l$		$m_l$	# $m_l$	# electrons
0	s	0	1	2
1	p	1, 0, -1	3	6
2	d	2, 1, 0, -1, -2	5	10
3	f	3, 2, 1, 0, -1, -2, -3	7	14

In general, because of the interaction term, states with higher  $l$  have higher energy for the same  $n$ . Higher  $l$  states are on average farther from the nucleus.

Therefore, to build the ground state of a non-interacting  $Z$  electron atom fill the lowest  $n$  then the lowest  $l$  for that  $n$ .

Now, an abbreviation from chemistry. We will write the  $\psi_{nl??}$  as  $n l_{\text{spectroscopic}}$

so  $\psi_{21??} = 2p$

We will also indicate the number of electrons in the state by an exponent. So  $(2p)^3$  has 3 electrons in the  $n=2, l=1$  state.

# Ground states

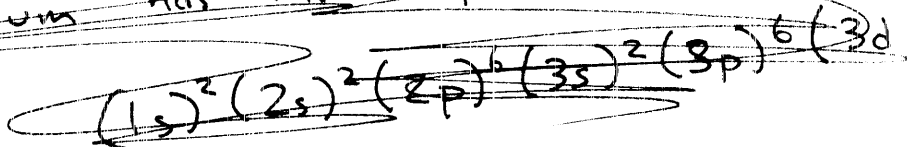
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Z		
1	H	(1s)
2	He	(1s) <sup>2</sup>
3	Li	(1s) <sup>2</sup> (2s)
4	Be	(1s) <sup>2</sup> (2s) <sup>2</sup>
5	B	(1s) <sup>2</sup> (2s) <sup>2</sup> (2p)
10	Ne	(1s) <sup>2</sup> (2s) <sup>2</sup> (2p) <sup>6</sup>

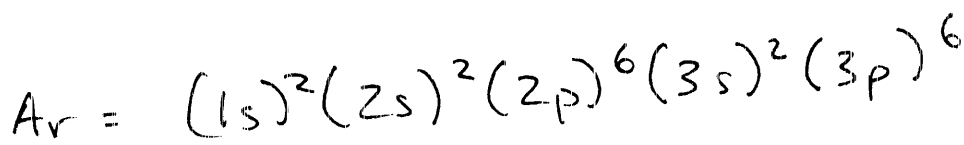
~~This stops working (the interaction term wins)~~

~~at ~~Ca~~ Ca, Z=20.~~

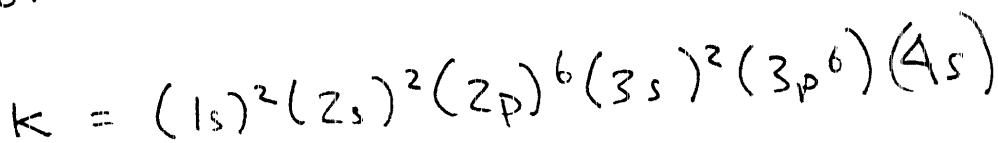
~~Calcium has the expected~~



This stops working, interaction and other effects win at Argon, Ar Z=18

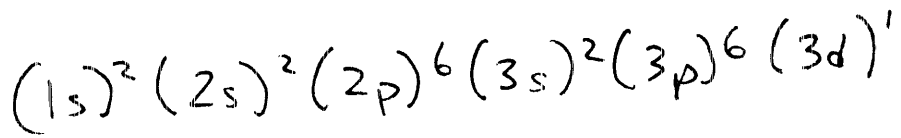


but Potassium's (K, Z=21) ground state is



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not



This process only gives the values of  $n$  and  $l$  for each electron. We would also like to know  $m_l$ ,  $m_s$  and the total spin angular momentum  $S$ , the total orbital angular momentum  $L$ , and the total angular momentum  $J$ .

$J \equiv$  Total Angular Momentum  
(spin + orbital)

$L \equiv$  Total Orbital Angular Momentum

$S \equiv$  Total Spin Angular Momentum.

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Symbolically the total angular momentum state is represented by

$$2S+1 \quad L \quad J$$

with

L	symbol
0	S
1	P
2	D
3	F

$S_0$

$$^1S_0 \Rightarrow s=0, l=0, j=0$$

## Example - Hydrogen

$$H = (1s)^1 \Rightarrow l = 0$$

one electron so  $s = 1/2$ . Total angular momentum

$$j = |l+s| \dots |l-s|$$

$$= |0+1/2| \dots |0-1/2| = 1/2$$

$$H = 2^{1/2+1} S_{1/2} = {}^2S_{1/2}$$

Ex Helium - Another electron can be placed in the  $n=1, l=0$  state. Its ~~spin~~ spin must be opposite that of the first electron so, if the first electron had  $m_{s1} = +1/2$ , then  $m_{s2} = -1/2$ .

The total spin is

$$S = S_1 + S_2 \dots |S_1 - S_2|$$

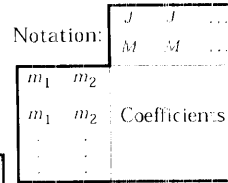
$$= 1/2 + 1/2 \dots |1/2 - 1/2|$$

$$= 1, 0$$



### 34. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND $d$ FUNCTIONS

Note: A square-root sign is to be understood over every coefficient, e.g., for  $-8/15$  read  $-\sqrt{8/15}$ .



$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$

$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$

$Y_2^0 = \sqrt{\frac{5}{4\pi}} \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$

$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$

$Y_2^2 = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\phi}$

$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$

$d_{m,0}^\ell = \sqrt{\frac{4\pi}{2\ell+1}} Y_\ell^m e^{-im\phi}$

$\langle j_1 j_2 m_1 m_2 | j_1 j_2 J M \rangle = (-1)^J J^{-1} J_2 (j_2 J_1 m_2 m_1 j_2 J_1 J M)$

$d_{m',m}^j = (-1)^{m-m'} d_{m,m'}^j = d_{-m,-m'}^j$

$d_{1,0}^1 = \cos \theta$

$d_{1/2,1/2}^{1/2} = \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\sin \frac{\theta}{2}$

$d_{1,1}^1 = \frac{1+\cos \theta}{2}$

$d_{1,0}^1 = -\frac{\sin \theta}{\sqrt{2}}$

$d_{1,-1}^1 = \frac{1-\cos \theta}{2}$

$d_{3/2,3/2}^{3/2} = \frac{1+\cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,1/2}^{3/2} = -\sqrt{3} \frac{1+\cos \theta}{2} \sin \frac{\theta}{2}$

$d_{3/2,-1/2}^{3/2} = \sqrt{3} \frac{1-\cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,-3/2}^{3/2} = -\frac{1-\cos \theta}{2} \sin \frac{\theta}{2}$

$d_{1/2,1/2}^{3/2} = \frac{3\cos \theta - 1}{2} \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{3/2} = -\frac{3\cos \theta + 1}{2} \sin \frac{\theta}{2}$

$d_{2,2}^2 = \left( \frac{1+\cos \theta}{2} \right)^2$

$d_{2,1}^2 = -\frac{1+\cos \theta}{2} \sin \theta$

$d_{2,0}^2 = \frac{\sqrt{6}}{4} \sin^2 \theta$

$d_{2,-1}^2 = -\frac{1-\cos \theta}{2} \sin \theta$

$d_{2,-2}^2 = \left( \frac{1-\cos \theta}{2} \right)^2$

$d_{1,1}^2 = \frac{1+\cos \theta}{2} (2\cos \theta - 1)$

$d_{1,0}^2 = -\sqrt{\frac{3}{2}} \sin \theta \cos \theta$

$d_{1,-1}^2 = \frac{1-\cos \theta}{2} (2\cos \theta + 1)$

$d_{2,0,0}^2 = \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$

**Figure 34.1:** The sign convention is that of Wigner (*Group Theory*, Academic Press, New York, 1959), also used by Condon and Shortley (*The Theory of Atomic Spectra*, Cambridge Univ. Press, New York, 1953), Rose (*Elementary Theory of Angular Momentum*, Wiley, New York, 1957), and Cohen (*Tables of the Clebsch-Gordan Coefficients*, North American Rockwell Science Center, Thousand Oaks, Calif., 1974). The coefficients here have been calculated using computer programs written independently by Cohen and at LBNI.

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So two spin configurations are possible.

The spatial wave functions are identical for the two particles

$$(1s) = \psi_{100} = R_{10} Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} R_{10}$$

so the spatial part is symmetric under particle exchange

$$\begin{aligned}\psi(\vec{r}_1, \vec{r}_2) &= \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \\ &= \psi_{100}(\vec{r}_2) \psi_{100}(\vec{r}_1) = \psi(\vec{r}_2, \vec{r}_1)\end{aligned}$$

therefore the spin wave function must be anti-symmetric.

The two single particle spins are  $|\frac{1}{2} \frac{1}{2}\rangle$  and  $|\frac{1}{2} -\frac{1}{2}\rangle$ . The eigenstates of  $S^2, S_z$  that can be made of these states are

$$|00\rangle = \frac{1}{\sqrt{2}} \left( |\frac{1}{2} \frac{1}{2}\rangle |\frac{1}{2} -\frac{1}{2}\rangle - |\frac{1}{2} -\frac{1}{2}\rangle |\frac{1}{2} \frac{1}{2}\rangle \right)$$

singlet

$$|110\rangle = \frac{1}{\sqrt{2}} \left( |\frac{1}{2} \frac{1}{2}\rangle |\frac{1}{2} -\frac{1}{2}\rangle + |\frac{1}{2} -\frac{1}{2}\rangle |\frac{1}{2} \frac{1}{2}\rangle \right)$$

triplet

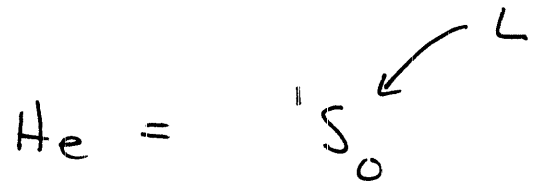
The singlet state is anti-symmetric under particle exchange, so the total wave function must be

$$\psi = \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) |00\rangle$$

$$\Rightarrow S=0, S_z=0$$

$\Rightarrow$  We know  $L=0$  from the wave function

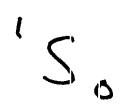
$$\Rightarrow J=0 = |L+S| \dots |L-S|$$



Helium has a completed filled  $n=1$  energy level, called a shell. Helium has a filled shell.

A filled shell has  $J=0, S=0, L=0$ .

The atoms with filled shells are the noble gases, He, Ne, Ar, Kr, Rn and all are



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Both a filled shell ( $n$ ) and a filled subshell ( $n\ell$ ) have  $L=0, S=0, J=0$ .

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Ex Carbon  $Z=6$

$$C = \underbrace{(1s)^2(2s)^2(2p)^2}_{\text{filled shells / subshells}}$$

$J=0, L=0, S=0$

$\Rightarrow$  Only unfilled shells contribute.

$\Rightarrow$  We have two electrons in  $\ell=1$  states

Possible values

$$S = s_1 + s_2 \quad \dots \quad |s_1 - s_2| = \frac{1}{2} + \frac{1}{2} \quad \dots \quad \left| \frac{1}{2} - \frac{1}{2} \right| = 1, 0$$

$$L = \ell_1 + \ell_2 \quad \dots \quad |\ell_1 - \ell_2| = 1 + 1 \quad \dots \quad |1 - 1| = 2, 1, 0$$

$$J = \cancel{J_1 + J_2} \quad \dots \quad |s - \ell| = 3, 2, 1, 0$$

## Possible States of Carbon

$L=0$	${}^1S_0$	${}^3S_1$
$L=1$	${}^1P_1$	${}^3P_{2,1,0}$
$L=2$	${}^1D_2$	${}^3D_{3,2,1}$

The total wave function must be anti-symmetric.

The radial part of each electron is identical  $R_{nl}$ ,  
so the radial part is symmetric under particle exchange

$\Rightarrow$  <sup>Orbital</sup> Angular Momentum  $\otimes$  Spin must be anti-symmetric.

Spin is symmetric if  $s=1$  antisymmetric if  $s=0$ .

The Clebsch-Gordan tables show angular momentum  
is symmetric if  $l$  is even  $\Rightarrow$  S, D states  
and anti-symmetric if  $l$  odd, P states.

	orbital	spin	total	
$^3D$	$l=2$ (sym)	$s=1$ (sym)	sym	BAD
$^1P$	$l=1$ (anti)	$s=0$ (anti)	sym	
$^3S$	$l=0$ (sym)	$s=1$ (sym)	sym	
$^1D$	$l=2$ (sym)	$s=0$ (anti)	anti	GOOD
$^3P$	$l=1$ (anti)	$s=1$ (sym)	anti	
$^1S$	$l=0$ (sym)	$s=0$ (anti)	anti	

Possible states that obey symmetrization

$$^1D_2, \quad ^3P_{2,1,0}, \quad ^1S_0$$

Now we need criteria to choose between these states, to select the ground state.

Hund's Rules

(1) The highest spin state will have the lowest energy

then (2) For a given spin state, the highest  $L$  will have the lowest energy.

then (3) If a subshell is no more than half-filled,  
 $J = |L - S|$  otherwise  $J = L + S$ .

Rule (1) - The  $^3P$  states have highest spin

Rule (2) - No help, all have  $L = 1$ .

Rule (3) - The shell is less than half filled

$$\text{so } J = |L - S| = |1 - 1| = 0$$

Ground state of Carbon

