8. Atomic Physics, 2

lecture 29, November 6, 2017

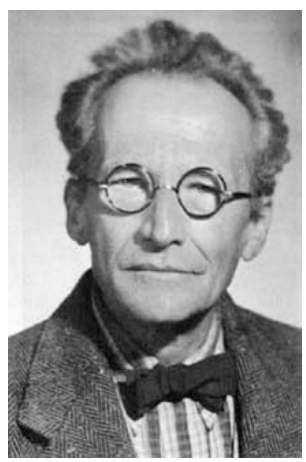
housekeeping

Honors project

- By tonight I need to know via email:
  - *if you're doing the honors project*
  - *that you've completed the first part*
- I have data sets to give you,
  - *but they're personally assigned…hence I need your name*

today

Hydrogen atom, more



$$\psi_T(x_1 y_1 z_1 x_2 y_2 z_2) = \phi(x_1 y_1 z_1)\,\eta(x_2 y_2 z_2) = \phi(1)\,\eta(2)$$

Pauli Exclusion Principle

In multi-electron atoms there can be no more than 1 electron in the same quantum state.

"State" = wavefunction defined by quantum numbers $n, l, m_l, \underline{m_s}$

$$\psi_S \equiv \frac{1}{\sqrt{2}}\left[\phi(1)\eta(2) + \phi(2)\eta(1)\right] \qquad \text{symmetric}$$

$$\psi_A = \frac{1}{\sqrt{2}}\left[\phi(1)\eta(2) - \phi(2)\eta(1)\right] \qquad \text{antisymmetric}$$

Insured by requiring that the total wavefunction for electrons is ψ_A

which for 2: $\quad \psi_A = \frac{1}{\sqrt{2}}\left[\phi(1)\phi(2) - \phi(2)\phi(1)\right] = 0$

True for any spin ½ system

Helium...

ψ_T = (space wavefunction) × (spin wave function)

$\downarrow$ ψ_A or ψ_S

$\downarrow$ not a "function" per se

something that depends on m_s

Cartoons:

$m_s = +\frac{1}{2}$ " $\uparrow$ " "spin up"

$m_s = -\frac{1}{2}$ " $\downarrow$ " "spin down"

TOTAL SPIN

$\vec{S} = \vec{S}_1 + \vec{S}_2$

$|S| = \hbar\sqrt{s(s+1)}$

$S_z = m_s \hbar$

$m_s = -s \ldots +s$

Combine them: $S_1 = \uparrow$ or $\downarrow$

$S_2 = \uparrow$ or $\downarrow$

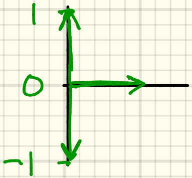
like

$\begin{matrix} S_2 \uparrow \\ S_1 \uparrow \end{matrix}$ or $\begin{matrix} S_1 \uparrow \\ S_2 \uparrow \end{matrix} \Rightarrow \uparrow\uparrow \} = 1$

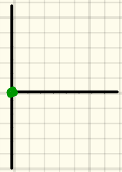
or $\quad s_1 \uparrow\downarrow s_2$ or $s_1 \downarrow\uparrow s_2 \Rightarrow \cdot \} = 0$

so... $\quad S = S_1 + S_2 = 1$ or 0

$S = 1$



$S = 0$



Spin wavefunctions

$$\Sigma(m_{s_1}, m_{s_2}) \qquad \text{so} \qquad m_{s_1} = 1/2 \;,\; m_{s_2} = -1/2$$

$$\Sigma = (\uparrow, \downarrow)$$

Can also make A and S:

$$\left.\begin{aligned} \Sigma_S &= (\uparrow, \uparrow) \\ \Sigma_S &= \frac{1}{\sqrt{2}}\left[(\uparrow, \downarrow) + (\downarrow, \uparrow)\right] \\ \Sigma_S &= (\downarrow, \downarrow) \end{aligned}\right\} \text{a "triplet" 3 S states}$$

$$\Sigma_A = \frac{1}{\sqrt{2}}\left[(\uparrow, \downarrow) - (\downarrow, \uparrow)\right] \Big\} \text{a "singlet" 1 A state}$$

How?

Eigenvectors that are little matrices $\psi \rightarrow \begin{pmatrix} \psi \\ \psi \end{pmatrix}$

"spin up" $\psi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

"spin down" $\psi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$\Big\}$ mixed state $\psi_M = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

and operators that are 2x2 matrices "Pauli Matrices"

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$S_i = \frac{\hbar}{2}\sigma_i \longrightarrow S^+ = S_x + i S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

so in the energy term: $S^+\psi_M \rightarrow \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$$S^-\psi_M \rightarrow \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

all of the angular momentum vectors? $\rightarrow$ matrices which form IRR of some group ahem...

Bach to Helium...

Pauli Exclusion Principle requires

$$\psi_T(e_1, e_2) = \text{antisymmetric}$$

$$= \psi_S \Sigma_A \qquad \text{singlet} \qquad \text{parahelium}$$

or

$$= \psi_A \Sigma_S \qquad \text{triplet} \qquad \text{orthohelium}$$

Energy... first pass

$$E_T = \frac{-\mu z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n_1^2} - \frac{\mu z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar n_2^2}$$

$z=2$

$$E_T = -\frac{4(13.6\,\text{eV})}{n_1^2} - \frac{4(13.6\,\text{eV})}{n_2^2}$$

Ground state: $n_1 = n_2 = 1$

$$E_T(gs) = -(4+4)(13.6\,\text{eV}) = \boxed{-109\,\text{eV}}$$

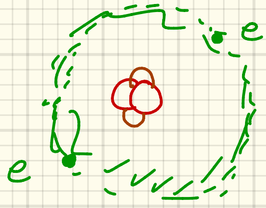
1st excited state $n_1 = 1 \quad n_2 = 2$ or $n_1 = 2 \quad n_1 = 1$

$$E_T(1^{st}) = -(4+1)(13.6\,\text{eV}) = \boxed{-68\,\text{eV}}$$

Energy... second pass

Coulomb repulsion raises these values

Energy... third pass

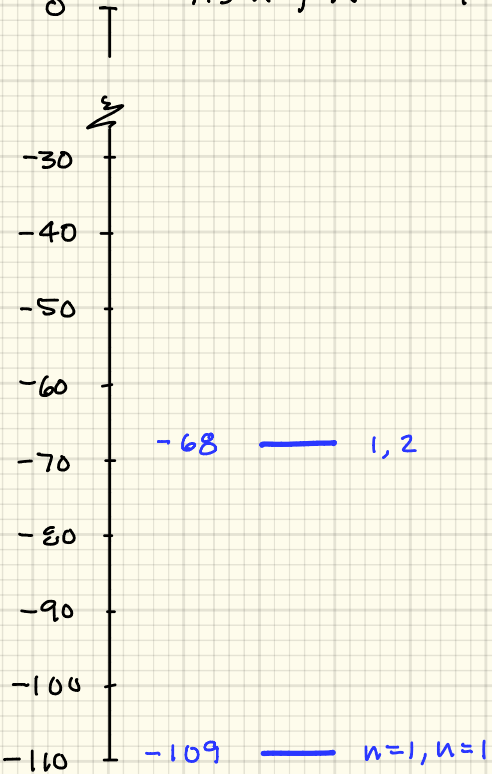


other electron's wavefunction "screens" the Z protons' positive charge

$\rightarrow$ "effective" $Z^* \simeq 1.7e$ not $2e$

G.S.: $E_T(gs) \cong -(1.7^2 + 1.7^2)(13.6) = \boxed{-79\,eV}$

As if just 2 hydrogen

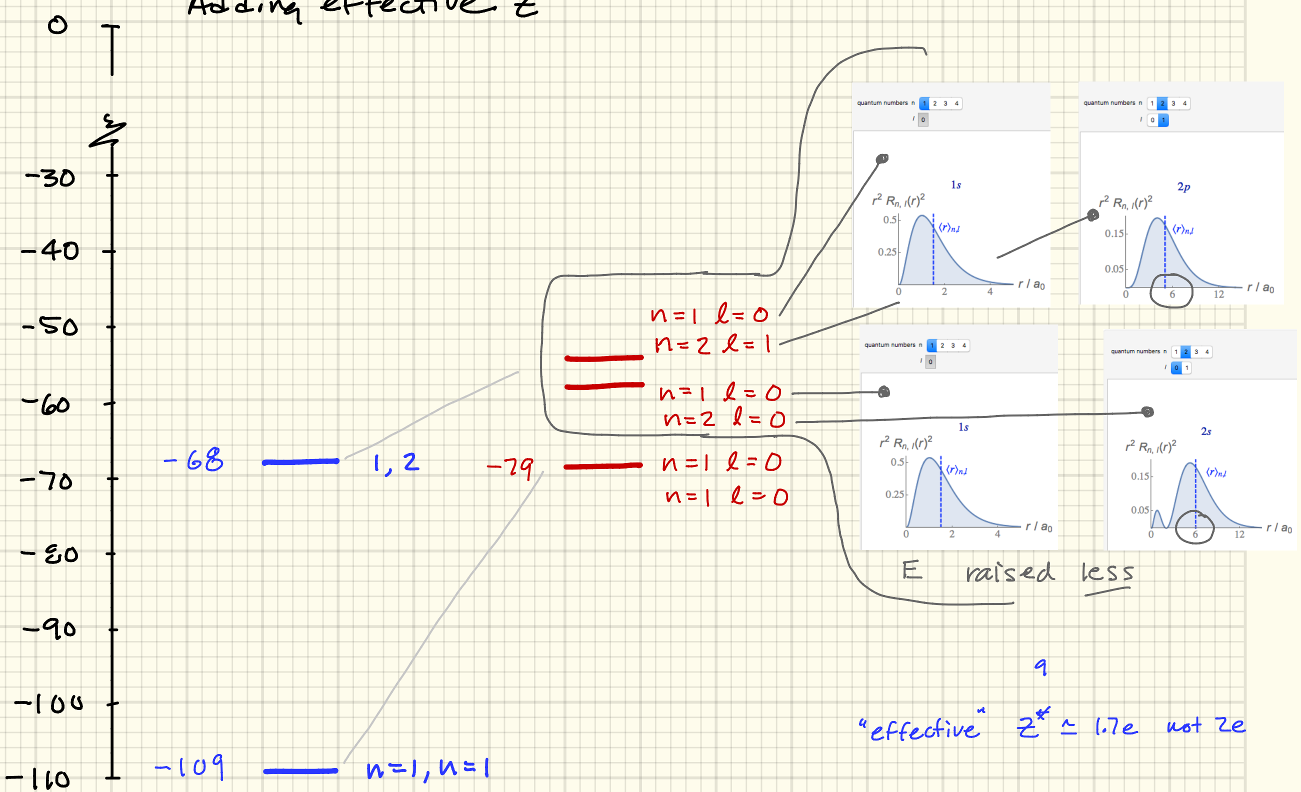


v) = $\boxed{-109\ eV}$

=2 $n_1 = 1$

v) = $\boxed{-68\ eV}$

Adding effective Z^*

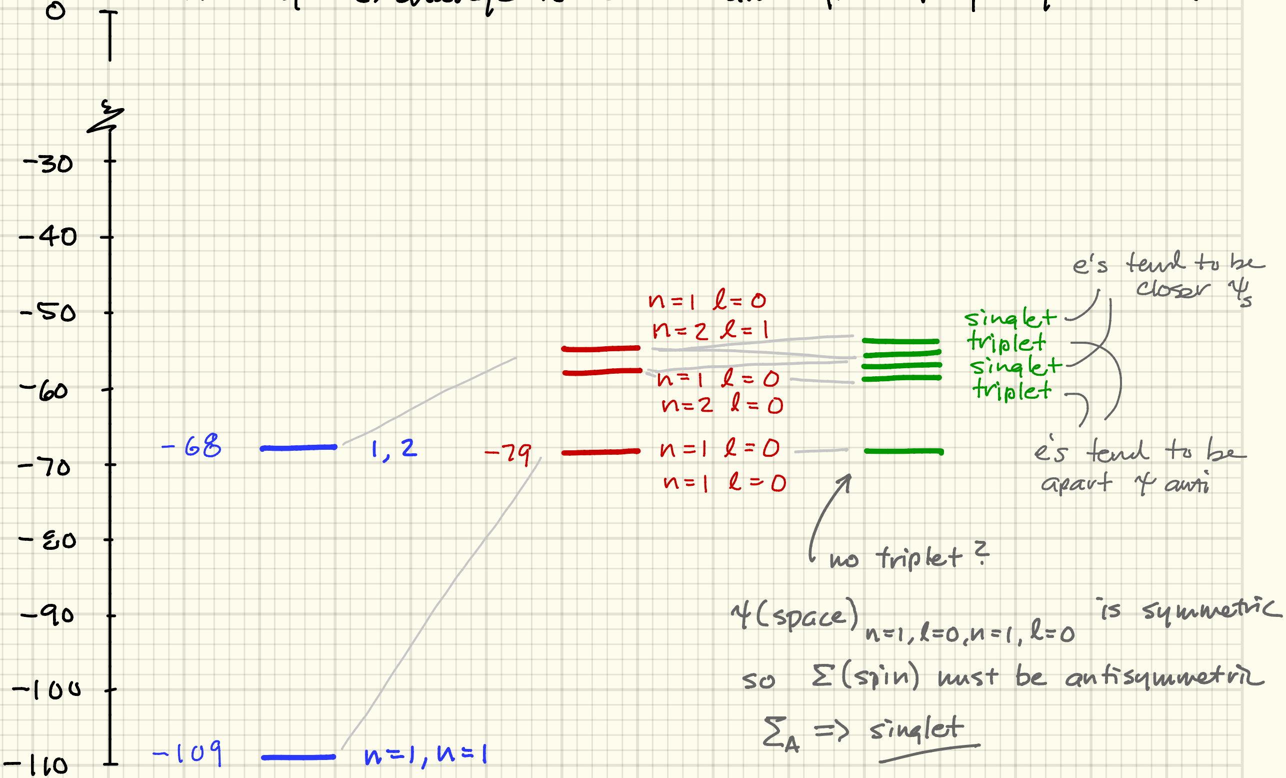


9

"effective" $Z^* \simeq 1.7e$ not $2e$

$17^2)(13.6) = \boxed{-79\,\text{eV}}$

Adding "exchange force" → antisymmetry requirement



$\psi(\text{space})_{n=1,\ell=0,n=1,\ell=0}$ is symmetric

so $\Sigma(\text{spin})$ must be antisymmetric

$\Sigma_A \Rightarrow$ singlet

So! Even Helium is complicated!

Rest of Periodic Table is also

Rules of thumb:
1. electrons tend to be in lowest energy states
2. Pauli Exclusion Principle always at work.

Notation:

$n =$	1	2	3	4
	K	L	M	N

Energy of states primarily depends on $n \longrightarrow$ "shells"

$\ell \longrightarrow$ "subshells"

atomic electron state: (n, ℓ, m_ℓ, m_s)

No magnetic field? .. no dependence on m_ℓ or m_s

BUT: proton has spin $\longrightarrow$ magnetic moment $\longrightarrow \vec{B}$
$\vec{L} \longrightarrow$ magnetic moment $\longrightarrow \vec{B}$

Internal magnetism!

Sloppy language -- but hard to avoid thinking this way.

we imagine building the periodic table by "filling the shells"

How many states can we "fill"?

m_ℓ

$\ell=0$ "s" $(2\ell+1) = (2\cdot 0+1) = 1$ $m_\ell = 0$

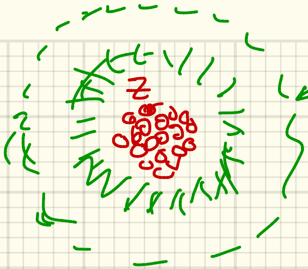
$\ell=1$ "p" $= (2\cdot 1+1) = 3$ $m_\ell = -1, 0, +1$

$\ell=2$ "d" $= (2\cdot 2+1) = 5$ $m_\ell = -2, -1, 0, 1, 2$

m_s for each m_ℓ, $m_s = \pm 1/2$

n	ℓ	sub-shell	$2\ell+1$	m_ℓ	max m_s	max states
1	0	1s	1	0	$\frac{1}{2}$ & $-\frac{1}{2}$ ↑↓	2
2	0	2s	1	0	$\frac{1}{2}$ & $-\frac{1}{2}$ ↑↓	2
2	1	2p	3	−1	↑↓	
				0	↑↓	6
				+1	↑↓	
3	0	3s	1	0	↑↓	2
3	1	3p	3	−1	↑↓	
				0	↑↓	6
				+1	↑↓	
3	2	3d	5	−2	↑↓	
				−1	↑↓	
				0	↑↓	10
⋮				+1	↑↓	
				+2	↑↓	

Shielding

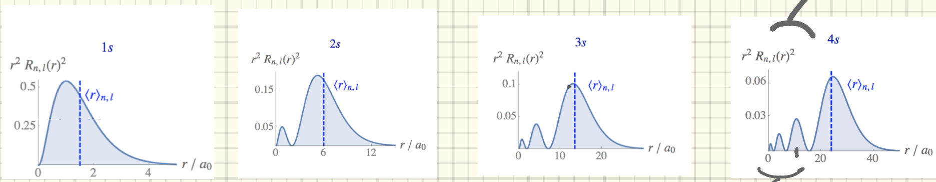


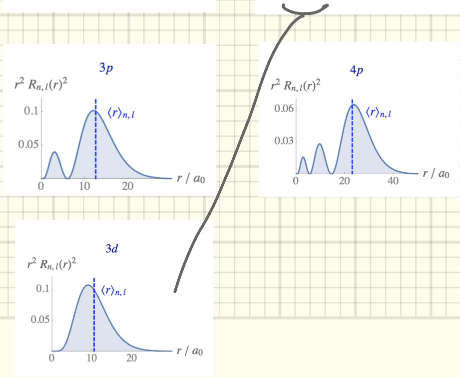
outer electrons "see" something less than Z

And – inner electrons tighter-bound

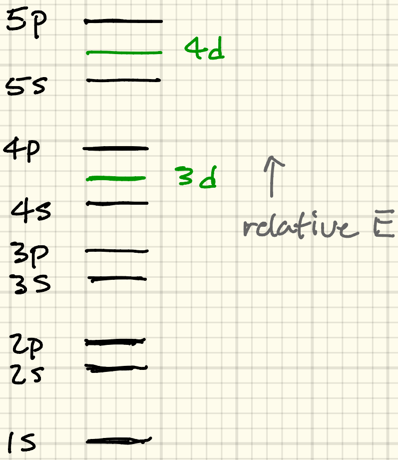
And outer shell s states can be "inside"...

spends lots of time near nucleus

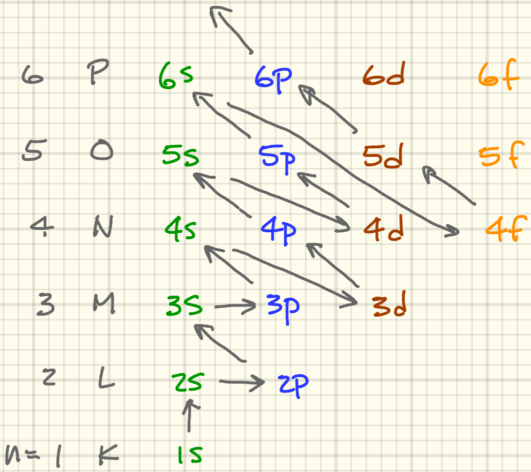




so ordering can be unexpectedly non-n...



so "filling"
is sort of
hectic



Complicated calculations

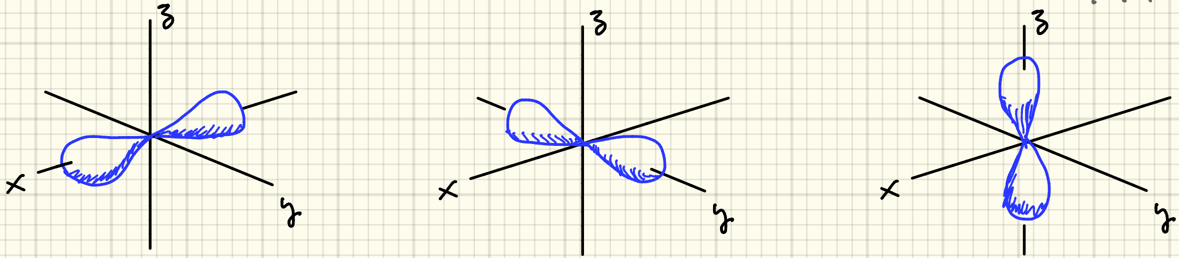
Periodic Table explained:

Z							
1	H	$(\uparrow, \ )$ $1s^1$					
2	He	$(\uparrow, \downarrow)$ $1s^2$					FULL
3	Li	$(\uparrow, \downarrow)$ $1s^2$	$(\uparrow, \ )$ $2s^1$				
4	Be	$(\uparrow, \downarrow)$ $1s^2$	$(\uparrow, \downarrow)$ $2s^2$				
5	B	$(\uparrow, \downarrow)$	$(\uparrow, \downarrow)$	$(\uparrow, \ )$	$(\ , \ )$ $2p^1$	$(\ , \ )$	
6	C	$(\uparrow, \downarrow)$	$(\uparrow, \downarrow)$	$(\uparrow, \ )$	$(\uparrow, \ )$ $2p^2$	$(\ , \ )$	
7	N	$(\uparrow, \downarrow)$	$(\uparrow, \downarrow)$	$(\uparrow, \ )$	$(\uparrow, \ )$ $2p^3$	$(\uparrow, \ )$	
	⋮						
10	Ne	$(\uparrow, \downarrow)$	$(\uparrow, \downarrow)$	$(\uparrow, \downarrow)$	$(\uparrow, \downarrow)$ $2p^6$	$(\uparrow, \downarrow)$	FULL

Carbon is interesting 6 C $1s^2 2s^2 2p^2$

where?

$\rightarrow$ involve Y_{11}, Y_{10}, Y_{1-1}



1p electron into some lobe...

2^{nd} p electron into an orthogonal one

they can get away from one another — minimizing repulsion energy

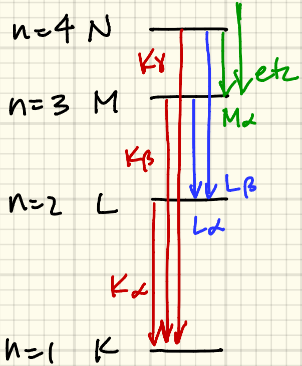
raising ionization energy

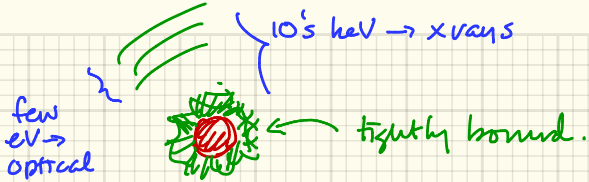
&

$1s^2 2s^2 2p^2 \xrightarrow[\text{easy}]{\text{energetically}} 1s^2 \underbrace{2s^1 2p^3}$

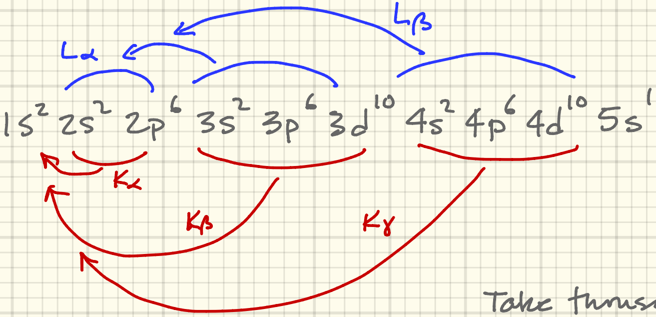
strongly bonding to other stuff

Xrays ...

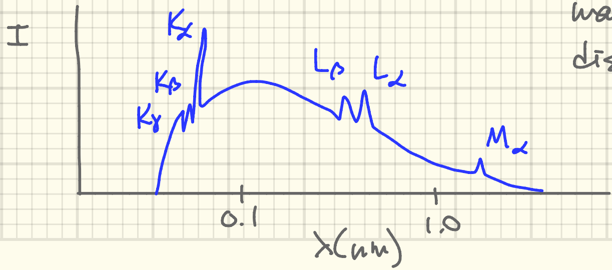




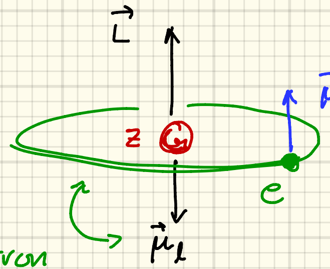
Silver Z = 47



Take thousands of volts to run xray machine → hard to displace s electrons



Lots of internal magnetic action

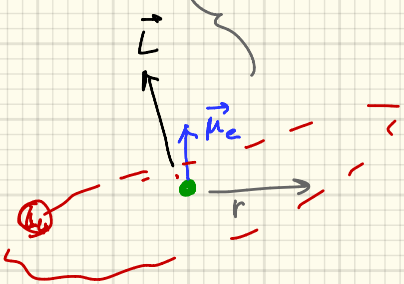


$\vec{\mu}_e$ – electron's intrinsic magnetic moment – spin, $\vec{\mu}_e$

electron current around protons

From electron frame:

these interact



like an internal Zeeman Effect

$$\vec{B} = \frac{\mu_0}{4\pi}(-Ze)\frac{\vec{v}\times\vec{r}}{r^3} \longleftarrow$$

$\vec{B}$ field "seen" by electron

$\vec{B}_{int}$

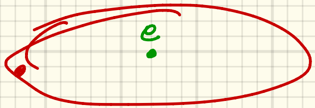
We have a magnetic moment, $\vec{\mu}_e$

We have a magnetic field, $\vec{B}_{int}$

} potential energy & a precession

$$\Delta E_{\mu B} = -\vec{\mu}_e \cdot \vec{B}_{int}$$

Estimate amount for 2p H state (s cannot contribute)



$$B = \frac{\mu_0 I}{2r}$$

$$I = \frac{+e}{T} = fe$$

$$B = \frac{\mu_0 fe}{2r}$$

$$f = \frac{v}{2\pi r} = 8.4 \times 10^{14}\ s^{-1}$$

$$r = n^2 a_0 = 4a_0 = 2.1 \times 10^{-10}\ m$$

$$B = \frac{(4\pi \times 10^{-7}\ T \cdot m/A)(8.4 \times 10^{14}\ s^{-1})(1.6 \times 10^{-19}\ C)}{2(2.1 \times 10^{-10}\ m)} = 0.4\ T \quad \text{large!}$$

$$|\Delta E_{\mu B_{int}}| \cong \mu B = \frac{e\hbar}{2m}(0.4) = 3.7 \times 10^{-24}\ J = 2.3 \times 10^{-5}\ eV$$

"Spin-orbit Interaction"

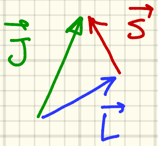
splits every l state into 2

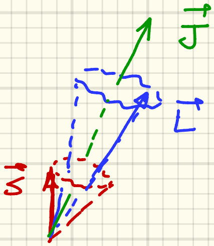
"Fine structure"

So: $\vec{S}$ and $\vec{L}$ are coupled

$\vec{J} = \vec{S} + \vec{L}$

"total angular momentum"





now: instead of (n, l, m_l, m_s)

the more complete set:

(n, l, j, m_j)

Total Angular Momentum

concentrate on alkali's $\rightarrow$ one electron

$$\vec{J} = \vec{L} + \vec{S}$$

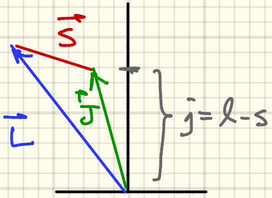
$|\vec{J}| = \hbar\sqrt{j(j+1)}$ $\quad$ j = total angular momentum quantum #

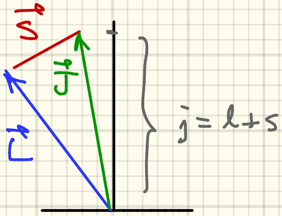
$J_z = m_j \hbar$ $\quad$ $m_j = \underbrace{-j, \text{------} \; +j}_{2j+1 \text{ multiplicity}}$

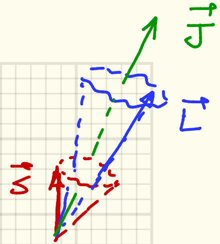
Combining angular momenta is standard job

pictures or an elegant algebra. —

Pictures



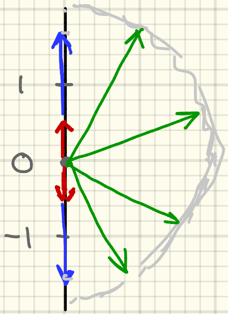




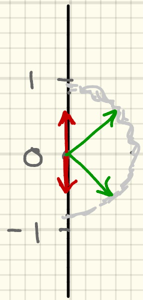
$s = 1/2 \qquad L = 1$

$j = l \oplus s \Rightarrow 1/2,\ 3/2$

$J = \hbar\sqrt{j(j+1)}$



$j = 3/2$



$j = 1/2$

Adding Quantum Mechanical Angular Momenta — algebraically.

$\vec{D} = \vec{A} + \vec{B}$

$|\vec{D}| = \hbar\sqrt{d(d+1)}$

$D_z = m_d \hbar$

$|\vec{A}| = \hbar\sqrt{a(a+1)}$ a : Q.N.

$A_z = m_a \hbar$

$|\vec{B}| = \hbar\sqrt{b(b+1)}$

$B_z = m_b \hbar$

Calculate the d's easily:

$d = a \oplus b$ special addition

$a \oplus b = |a-b|, |a-b|+1, \cdots a+b-1, a+b$

$\Rightarrow$ a <u>set</u> of possible values of d each with own family of m_d's example

$\vec{C} = \vec{A} + \vec{B}$

A & B are electron spins

$a = 1/2$ $m_a = -1/2 , 1/2$

$b = 1/2$ $m_b = -1/2 , 1/2$

$c = a \oplus b$

$= |a-b|, \ldots (a+b)$

$c = 0, 1$ two values for c

$c = 0$ $m_0 = 0$ singlet.

$c = 1$ $m_c = -c \ldots c = -1, 0, 1$ triplet

General Rules $\qquad \vec{C} = \vec{A} + \vec{B}$

$\boxed{\tfrac{1}{2}+\tfrac{1}{2}}$

A	m_A
$\tfrac{1}{2}$	$\tfrac{1}{2}, -\tfrac{1}{2}$

B	m_B
$\tfrac{1}{2}$	$\tfrac{1}{2}, -\tfrac{1}{2}$

C	m_C
0	0
1	$-1, 0, 1$

$\boxed{\tfrac{1}{2}+1}$

A	m_A
$\tfrac{1}{2}$	$\tfrac{1}{2}, -\tfrac{1}{2}$

B	m_B
1	$-1, 0, 1$

C	m_C
$\tfrac{1}{2}$	$-\tfrac{1}{2}, \tfrac{1}{2}$
$\tfrac{3}{2}$	$-\tfrac{3}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2}$

$\boxed{1+1}$

A	m_A
1	$-1, 0, 1$

B	m_B
1	$-1, 0, 1$

$C = |1-1| \ldots (1+1)$

$C = 0, 1, 2$

C	m_C
0	0
1	$-1, 0, 1$
2	$-2, -1, 0, 1, 2$

Selection Rules

single photon transitions

$\Delta n =$ anything

$\Delta j = 0,$ or ± 1 (no $0 \to 0$)

$\Delta m_j = 0$ or ± 1

$\Delta l = \pm 1$

States are labeled

$$n\,^{2S+1}L_j$$

multiplicity

orbital angular momentum S, P, D ...

total angular momentum

principle quantum number

Hydrogen

remember $S \cdot L$ coupling only $\geq p$ states

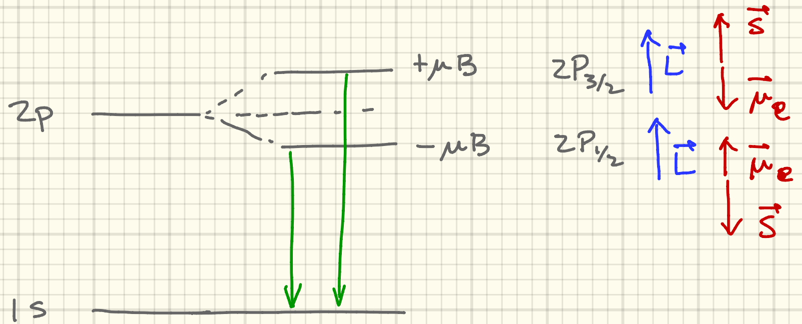
Table $\quad S = A = 1/2 \quad$ spin

$L = B = 1 \quad$ P state L

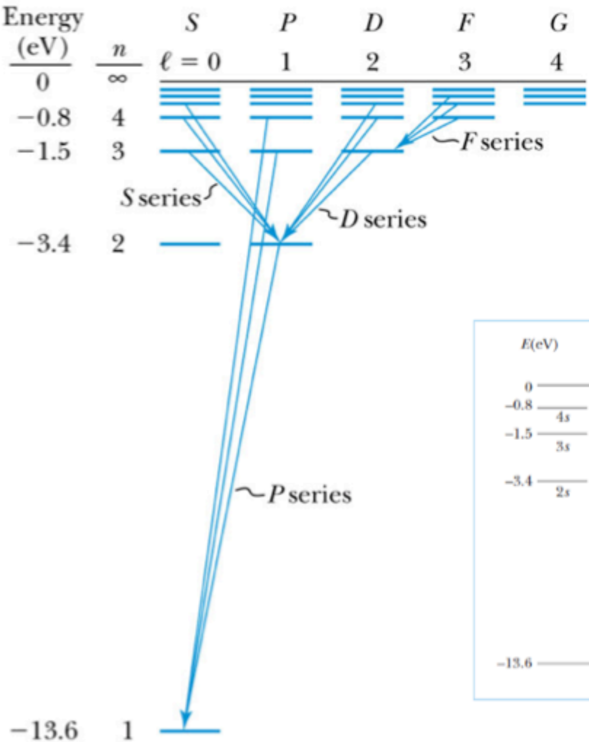
C	m_C
$1/2$	$-1/2, 1/2$
$3/2$	$-3/2, -1/2, 1/2, 3/2$

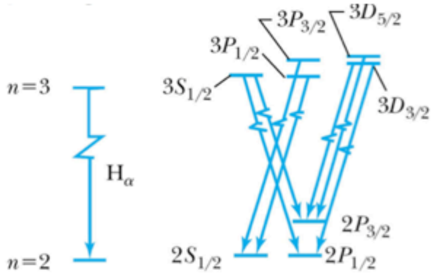
$J = 1/2$ and $3/2$

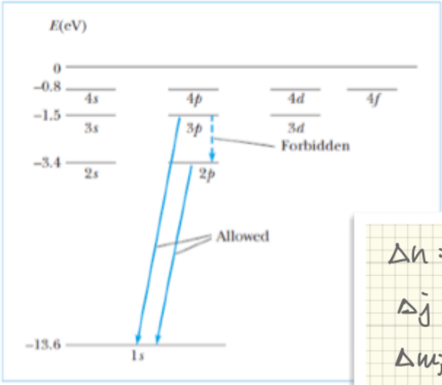
$\longrightarrow$ each P state splits into doublet



$\Delta E = 5 \times 10^{-5}\ \mathrm{eV}$







Δn = anything

$\Delta j = 0$, or ± 1 (no $0 \to 0$)

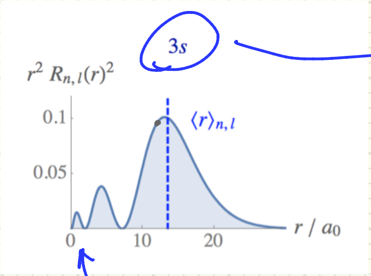
$\Delta m_j = 0$ or ± 1

$\Delta \ell = \pm 1$

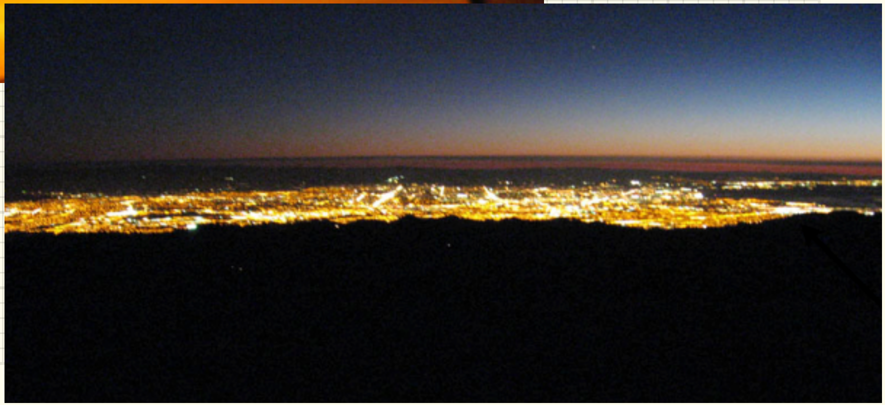
Everyone's favorite: sodium

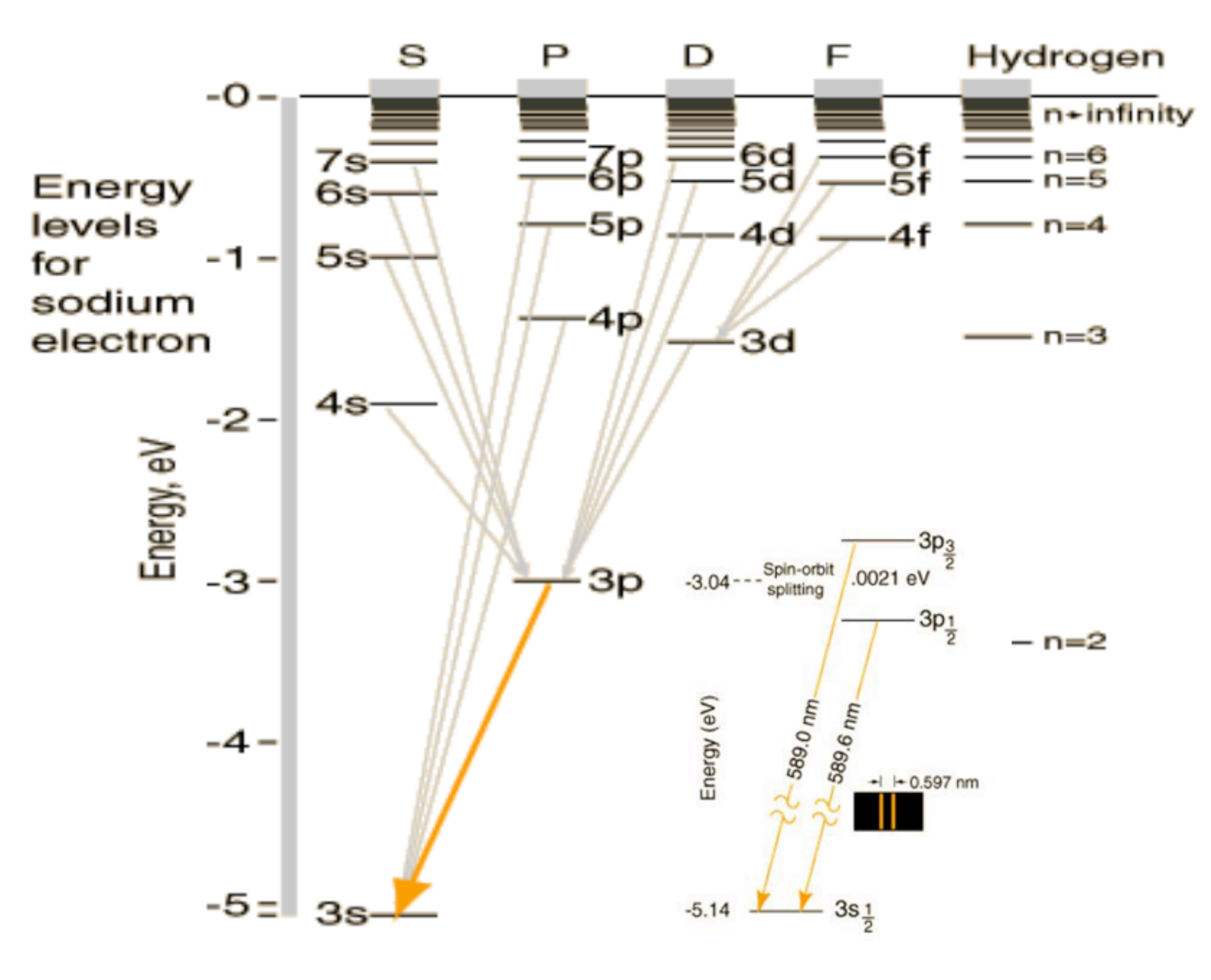
1 e outside of a closed shell

Na $Z = 11$ $1s^2 2s^2 2p^6 3s^1$



that little bit – overlap of 3s – 1s – increases 3s binding relative to 3p


S
P
D
F
Hydrogen
-0
-1
-2
-3
-4
-5
Energy levels for sodium electron
Energy, eV
n→infinity
7s
6s
5s
4s
3s
7p
6p
5p
4p
3p
6d
5d
4d
3d
6f
5f
4f
n=6
n=5
n=4
n=3
n=2
-3.04
Spin-orbit splitting
.0021 eV
3p3/2
3p1/2
589.0 nm
589.6 nm
0.597 nm
Energy (eV)
-5.14
3s1/2

Fraunhofer lines