Multi-electron atoms

Electronic configuration

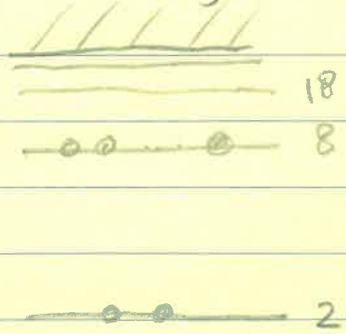
1st approximation = H-like ion of nuclear charge Ze.

Drop electrons one by one into H-like states.

Electrons are fermions so satisfy Pauli exclusion principle:

one elec per state,

2 spin states per H-like state: ↑ or ↓.



$2n^2$ elecs per n-shell

Electrons in configuration specified by $n\ell$.

Conventional notation:

ℓ	notation	
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental
4	g	↓ alphabetical
5	h	
⋮	⋮	

$2(2\ell+1)$ elecs per $n\ell$ shell.

Electronic configuration is written

2 elecs in 1s state

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d \ldots$

Abbreviated 3d (drop filled shells)

n n

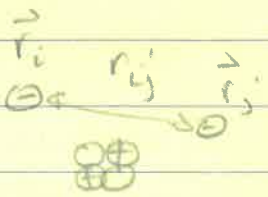
$\ell=0$ $\ell=0$ $\ell=1$

Electronic parity $= (-)^{\sum_{\text{elecs}} \ell}$ = what here?

$= \pm 1$ even, odd

Term

Electrostatic elec-elec interactions



$$V_{elec} = \sum_{\substack{elecs \\ i>j}} \frac{e^2}{r_{ij}}$$

r_{ij}: what is this? Operator on wavefunc.

Perturbs H-like approximation.

nl configuration → different LS terms

Can still track configuration by turning on elec. interaction slowly.

Unperturbed $\mathring{H}$ and interaction $H' = V_{elec}$

$\mathring{H}$: what is this? Hydrogenic Hamiltonian

both commute with

L^2 and S^2 (and L_z and S_z)

L^2: total orbital ang mom squared

S^2: total elec spin squared

and therefore leave L and S of energy levels unsplit.

Why L unsplit? Overall rot symmetry: no preferred direction.

Why S unsplit? Rot symm plus $\mathring{H} + V_{elec}$ contain no $\vec{L} - \vec{S}$ interaction

Each LS term designated

$^{2S+1}L^{o}$ (optional "o" if odd parity)

$(2S+1)(2L+1)$-fold degenerate

Does total spin S affect energy level?
Yes: it affects position of elecs through exclusion principle — see PS 6 Q2
Opposite spins ↑↓ attract; like spins ↑↑ repel.

Level

Relativistic effects couple $\vec{L}$ and $\vec{S}$
$\vec{L}$: total elec orb ang mom; $\vec{S}$: total elec spin

through LS (spin-orbit) coupling

$$H_{LS} \propto \vec{L} \cdot \vec{S}$$

(See this in more detail in later lecture)

$\vec{L}, \vec{S}$ interaction still commutes with

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

$\vec{J}$: total elec ang mom; $\vec{L}$: orb; $\vec{S}$: spin

$J = |L-S|$ to $|L+S|$ integer spaced

Why? Total rotational symmetry.
So states with same J remain unsplit.
Levels are designated

$$L_J^{2S+1}$$

each J-level $(2J+1)$-fold degen

Term ^{2S+1}L ——— { various J levels = "fine structure"

Each J-level has $2J+1$ states

$$M_J = -J, \ldots, J$$

M_J: eigenvalue of L_z

Hyperfine structure

If nucleus has spin, then interaction between nuclear spin and electrons splits levels

$$\vec{F} \equiv \vec{J}_{elec} + \vec{S}_{nuc}$$

$\vec{F}$: total elec + nuc ang mom.

level $^{2S+1}L_J$ — various F hyperfine levels = "hyperfine structure"

Order of filling of shells of ground elec config

$1s^2$
$2s^2$
$2p^6$
$3s^2$
$3p^6$
$3d$ } but now starts getting out of order
$4s$ } because of strong electrostatic interactions

eg. Ca I $3p^6 4s^2$
Fe I $3d^6 4s^2$
Fe-like Ni III $3d^8$ (higher Z ⇒ closer to H-like)

Filled shells have $L = S = 0$ (zero ang mom).
Outermost-shell electrons are "valence" electrons.

Q: Why don't nuclei fly apart under elec repulsion?
Q: proton uud 3 valence quarks
neutron dud in colorless combo.

Very heavy atoms

Above designation of levels by $^{2S+1}L_J$ is called LS coupling, which works for most ions of astronomical interest

In higher Z atoms & ions interactions grow strong enough that eigenstates are mixes of L, S levels. Other designations may be used, such as

j - j coupling

in which the total angular momentum $\vec{j} = \vec{l} + \vec{s}$ of each electron is approximately conserved

Excited states

Can be designated in various ways

Ex/

OI $2p^3\,(^4S)\,3p\;^3P$

consists (approximately) of OII "core" $2p^3\;^4S$ with 3p electron tacked on top, such that total LS is ^3P ($S=1$, $L=1$) $\quad J = ?\ 0, 1, 2$

How to construct terms of elec. configuration

Ex / $2p^3$ In full? # elecs = ?

e.g.? NI , OII

Each of the 3 2p electrons can belong to one of 6 2p states with

$m = -1, 0, 1$ orb

$m_s = -\frac{1}{2}, \frac{1}{2}$ spin

		m = -1	0	1
m_s	$-\frac{1}{2}$			
	$\frac{1}{2}$			

3 elecs in 6 slots is $\frac{6 \times 5 \times 4}{3!} = 20$ states

Various possible arrangements give summed $M = \Sigma m$

$M_s = \Sigma m_s$

M_s \ M	-2	-1	0	1	2
$-\frac{3}{2}$			1S		
$-\frac{1}{2}$	1D	2D	3SD	2D	1D
$\frac{1}{2}$	1D	2D	3SD	2D	1D
$\frac{3}{2}$			1S		

eg 3 is

Look at most extreme cases.

Largest $M_S = 3/2$ requires $L = 0$.

So there is an LS term

with $^4S_{3/2}$ ← J must be ? $\frac{3}{2}$

$S = 3/2$, $L = 0$

Term must contain 4 states.

$M_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

Largest $M = 2$ requires $M_S = \pm\frac{1}{2}$.

So there is an LS term

^2D $\quad M_S = \pm\frac{1}{2}$ 2 states } 10 states

$S = \frac{1}{2}$ $L = 2$ $\quad M_L = -2, \ldots, 2$ 5 states }

Vector model of addition of ang mom requires

$$|L - S| \le J \le L + S$$

So $J = 2 \pm \frac{1}{2} = \frac{3}{2}$ or $\frac{5}{2}$.

$^2D_{3/2}$ contains $M_J = -\frac{3}{2}, \ldots, \frac{3}{2}$ 4 states

$^2D_{5/2}$ " $M_J = -\frac{5}{2}, \ldots, \frac{5}{2}$ 6 states

10 states ✓

S and D account for 14 of 20 states, leaving

M_S \ M	−2	−1	0	1	2
−3/2					
−1/2		1	1	1	
1/2		1	1	1	
3/2					

Again look at extreme cases

Largest $M_S = \frac{1}{2}$ requires $L = 1$

" $M = 1$ requires $S = \frac{1}{2}$

So there is an LS term

^2P $\quad M_s = \pm\frac{1}{2}$ $\quad$ 2 states } 6 states
$S = \frac{1}{2}$, $L = 1$ $\quad M_L = -1, 0, 1$ $\quad$ 3 " }

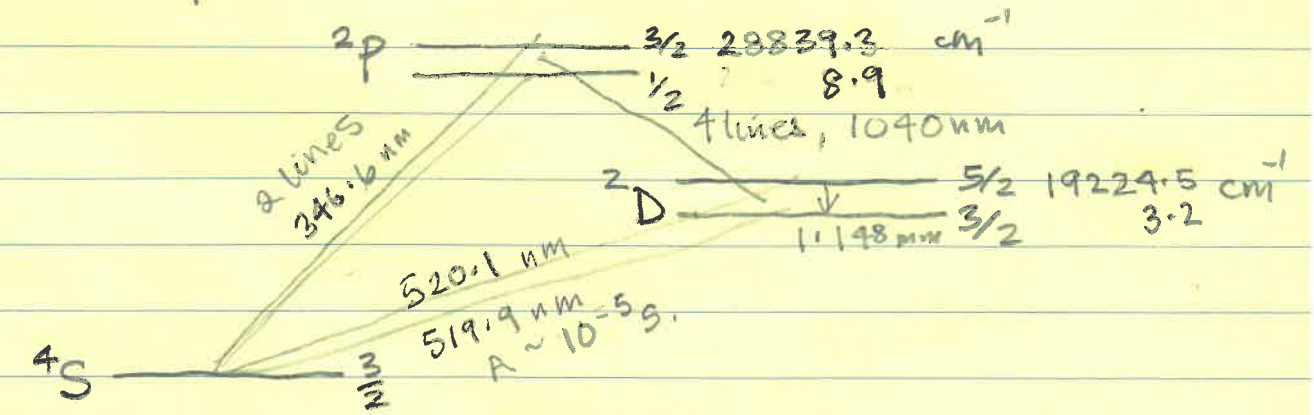
$J = 1 \pm \frac{1}{2} = \frac{1}{2}$ or $\frac{3}{2}$.

$^2P_{1/2}$ has $M_J = -\frac{1}{2}, \frac{1}{2}$ 2 states
$^2P_{3/2}$ $\quad -\frac{3}{2}, \ldots, \frac{3}{2}$ 4 states
6 states ✓

Hund's (empirical) rules usually, not always, work for ordering of energy levels in elec config in order of precedence:

(1) Largest S has lowest energy
(Exclusion principle makes electrons far apart)
(2) Largest L has lowest energy
(Large L makes electrons further apart)
(3) $\leq \frac{1}{2}$-filled config: smallest J lowest energy
$>$ " " : largest J " "

Ex/ NI $2p^3$



PI $3p^3$ has similar structure.