

Multi-electron atoms (11) – 09 update

Extend the H-atom picture to more than 1 electron:

H-atom sol'n use for N-elect., assume product wavefct.

$$\Psi = \prod_{i=1}^n \phi_{n_i \ell_i m_i} \quad \text{where: } \psi - \text{multi electron w/fct}$$

$\phi_{n_i \ell_i m_i}$ – one electron w/fct

we might expect the lowest energy state like H-atom
with $n_i = 1$ for all electrons $i = 1 \rightarrow N$

but this is **not an allowed multielectron wavefunction**

Election Spin changes how things work for electrons:

Pauli Principle:

a. Every wavefunction for fermion (spin 1/2 particle)
must be anti-symmetric with respect to exchange of
identical particles

b. For electrons in atoms this turns out to mean –
each electron has different set of quantum numbers
But there is also spin quantum number, $\pm 1/2$, so
for each $n \ell m_\ell$ – 2 electrons maximum

“Spin” – intrinsic magnetic moment

or angular momentum – no physical picture

no functional form - represent as: α, β

$$\mathbf{S}_z \alpha = m_s \hbar \alpha = \frac{1}{2} \hbar \alpha$$

$$\mathbf{S}_z \beta = m_s \hbar \alpha = -\frac{1}{2} \hbar \beta$$

$$\mathbf{S}^2 \alpha = s(s+1) \hbar^2 \alpha = \frac{3}{4} \hbar^2 \alpha$$

Multi-electron Atoms -- Simplest idea

- if H-atom describes electrons around nucleus
- use solutions to describe multi-electron atom

Problem – potential has – **electron-electron repulsion**

$$V(r) = \sum_{i=1}^N -Ze^2/r_i + \sum_{i=1}^N \sum_{j=1}^N e^2/r_{ij} \quad \leftarrow \text{added repulsion term}$$

term

$$r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}$$

distance between electrons ($r_i - e^-$ nucl)

$$H = T + V = \underbrace{\sum_{i=1}^N -\hbar^2/2m \nabla_i^2}_{\text{K.E. sum over } e^-} + \underbrace{\sum_{i=1}^N -Ze^2/r_i}_{\text{attraction}} + \underbrace{1/2 \sum_i \sum_j e^2/r_{ij}}_{\text{repulsion}}$$

assume C of M

if ignore 3rd term → $H_0 \sim \sum_{i=1}^N h_i(r_i)$ - separable

each $h_i(r_i)$ is H-atom problem with solution that we know

$$E_0 = \sum_{i=1}^N \epsilon_i \quad \psi_0 = \prod_{i=1}^N \phi_i(r_i)$$

sum of orbital E_i product ↑ H-atom solution

Which orbitals to use?

- Could put all e^- in 1s – lowest energy, but Pauli prevent that
- Put $2e^-$ each orbital (opposite spin), fill in order of increasing energy

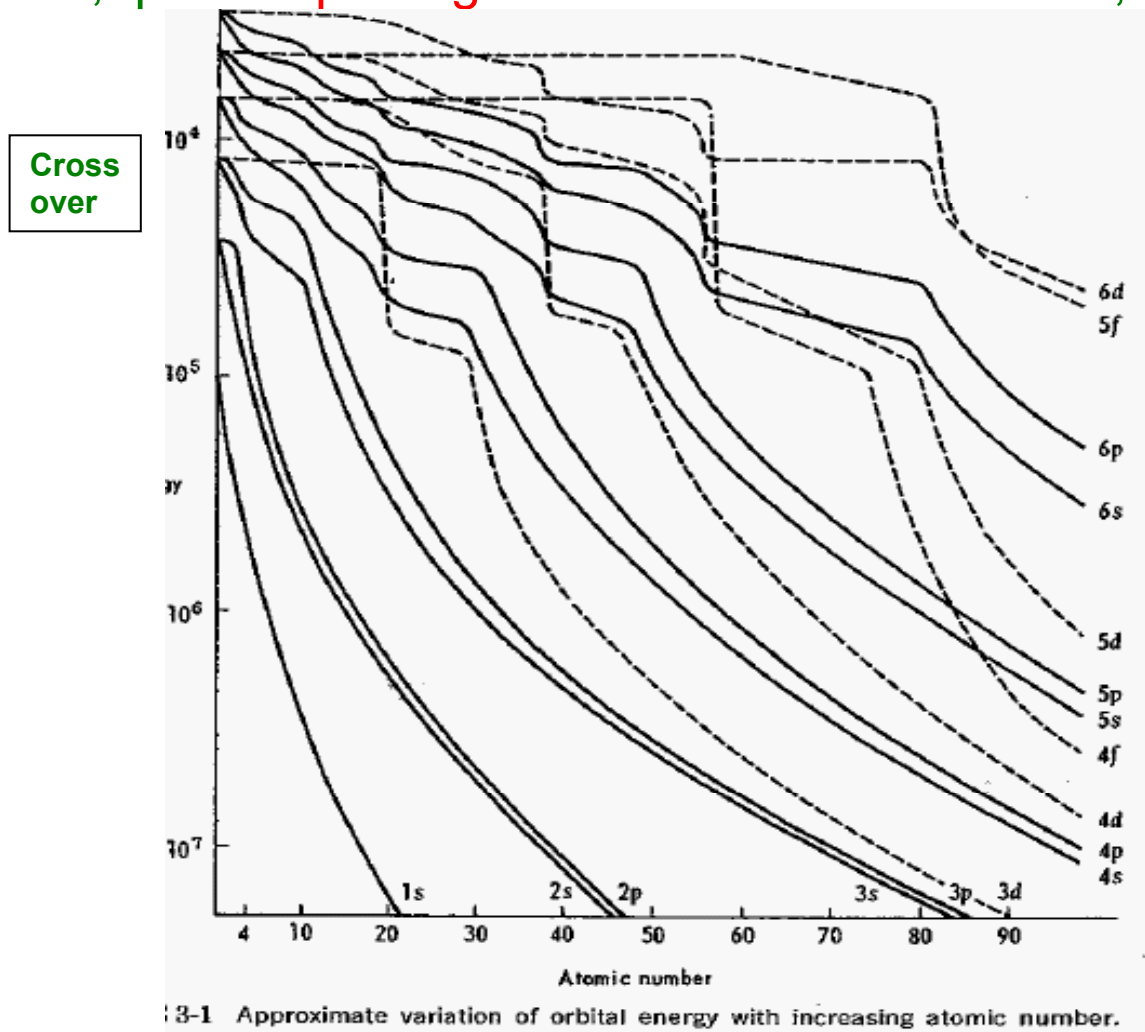
Order of filling – Aufbau (build up)

in order of **increasing n** – (idea: low to high energy)
and **increasing l** – (skip one n for d and again for f)

1s → 2s – 2p → 3s – 3p → 4s – 3d – 4p →
5s – 4d – 5p → 6s – 4f – 5d – 6p → 7s – 5f ...

Multi-electron atoms, need to account for electron repulsion, radial node structure (# nodes = $n-l-1$) leads to **split of s,p,d,f energies** for multi-electron atoms,

Cross-over of dashed lines – e.g. see 3d go above 4s,4p so **skip filling in order** - same for other d,f orbitals



Atomic Orbital Energy (ϵ_j) vs. Atomic Number (Z)

Why this order? → relates back to the d and f orbitals being smaller because fewer nodes

Added electrons shield outer electron from attraction to nucleus (3rd term left out)

i.e. as Z increases → 1s has more negative energy

Same for $n=2$ etc. but each shielded by $2e^-$ in 1s and $2e^-$ in 2s, 6 in 2p, etc.

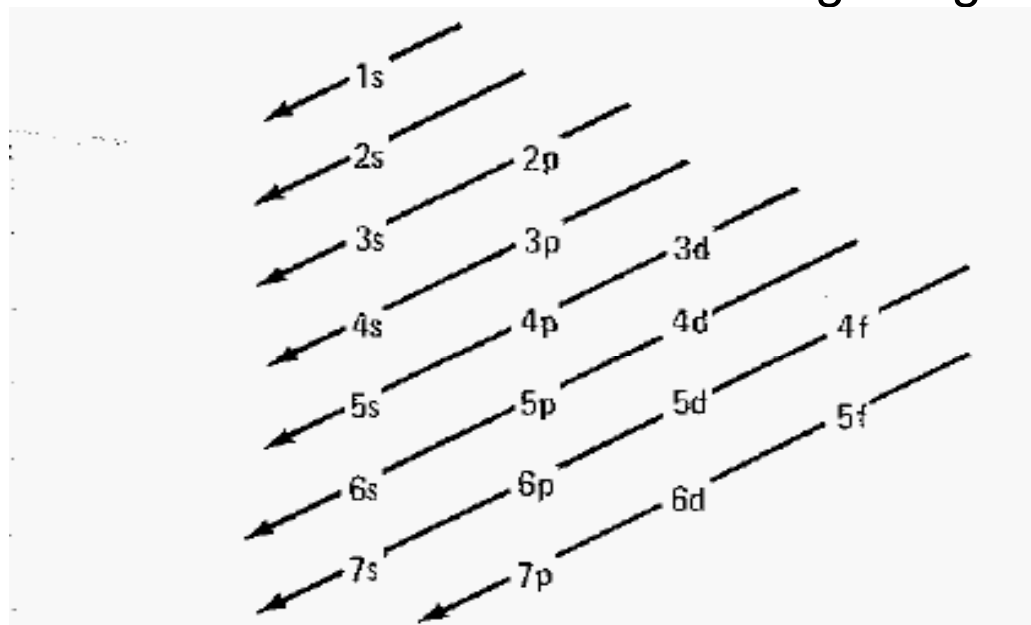
Different s and p radii cause: n-level split with l : $E \rightarrow E_{nl}$

But d, f abnormal – do not fill until fill (s + p) higher n

Seems counter-intuitive, but goes like nodes

– more nodes e^- get sucked in close to nucleus

Aufbau mnemonic for remembering filling order:



Key: use spin and Pauli Principle – $2 e^-$ per orbital

Atomic w/f build up (Aufbau) or fill in the order of:

~ $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^2 (3d)^{10} (4p)^6 \dots$ etc.

For **atoms**, number of electrons equals atomic #, **neutral**

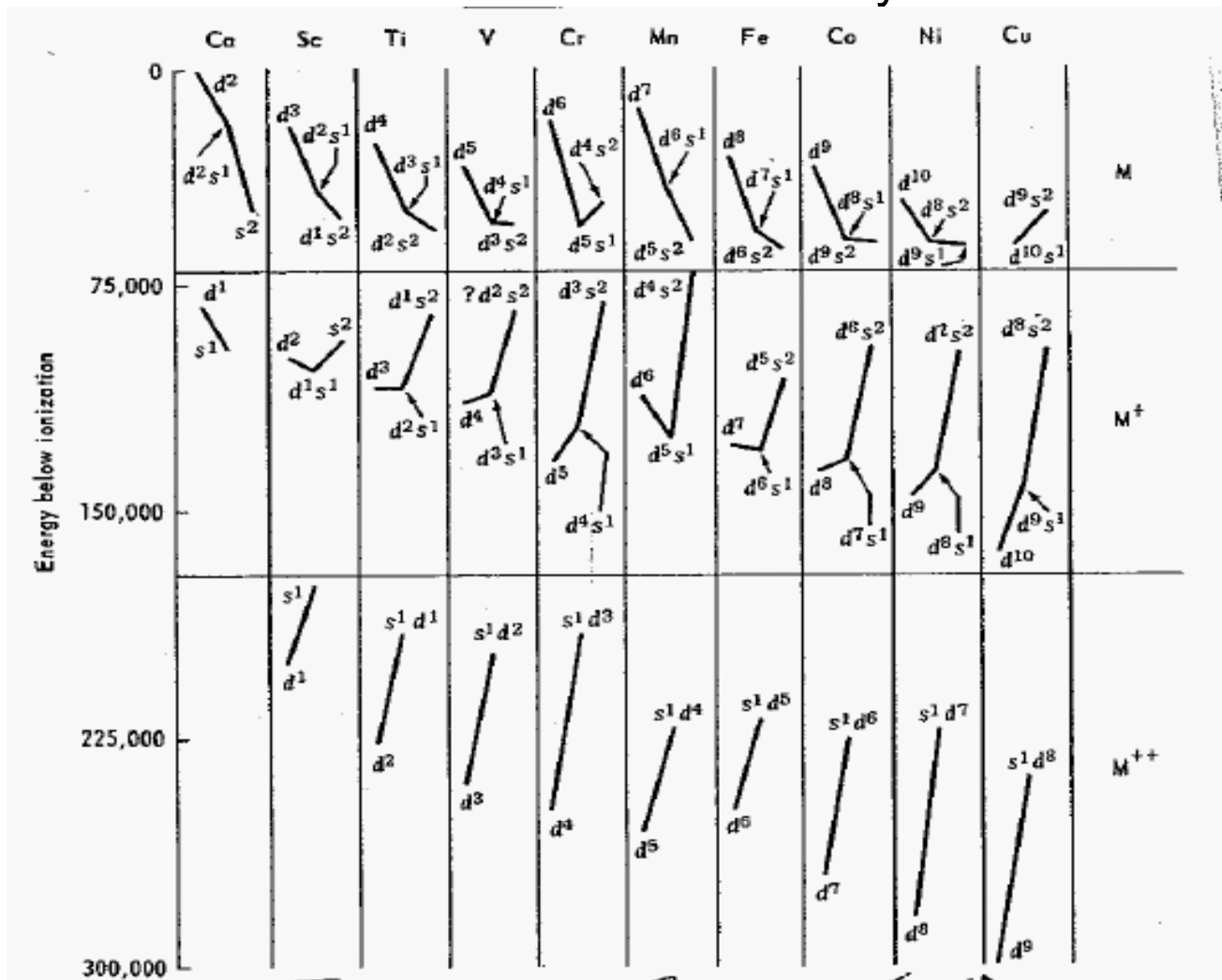
This is **configuration** - Represents $\psi^0 = \prod_{i=1}^N \phi_{n_i \ell_i m_i} (r_i)$

Solution to $H_0 = \sum h_i(r_i)$ -- Product w/f \rightarrow sum E: $E = \sum_{i=1}^N \epsilon_i$

Recall: $h(r_i) \phi_i(r_i) = \epsilon_i \phi_i(r_i)$

Variation – get extra stability by **half-filled shell** –
balanced by split of s, p – effect bigger for d,f electrons

Transition (3d, 4d, 5d series, and 4f, 5f) get $ns^1(n-1)d^5$
Transition metal ions a bit different yet



Ion pattern implies that **fill 3d last but lose 4s first**
inner orbitals (d) stabilize by increasing effective charge

Orbital Prod.-configuration-Represent $\psi^0 = \prod_{i=1}^N \phi_{n_i \ell_i m_i} (r_i)$

Product w/f \rightarrow sum Energy $E = \sum_{i=1}^N \epsilon_i$

Approximation -- Where does this come from?

these orbitals for multielectron atoms must adjust H-atom like solution to account for $\sum_{ij} e^2/r_{ij}$

recall: book uses SI units: $e^2/4\pi\epsilon_0 r_{ij}$



Central field approximation:

$$V(r) = \sum_i [-Ze^2/r_i + V(r_i)] + \sum_{i,j} \underbrace{[e^2/r_{ij} - V(r_i)]}$$

Not separable - pull out of repulsion - part depends on r_i
Solve problem for just the left hand \sum_i term

Think of it as: average potential for electron i

a) attracted to nucleus

b) repelled by all other electron j (average)

Result: Still a problem with central force,

now separable and include average repulsion

\rightarrow Misses out on "correlation" -

instantaneous e-e motion/interaction (keep apart)

Solution - $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots) = \prod_{i=1}^N \phi_{r_i \ell_i m_i} (r_i, \theta_i, \phi_i)$

get product wavefunction

get summed energy (orbitals): $E = \sum_{i=1}^N \epsilon_i$

Method – underlying this approach: Variation Principle
(go for getting the idea, if not the details)

if use **exact H**, **approximate** (guess) a w/fct: ψ_a
 then compute **expectation value of energy** in ψ_a

$$\langle H \rangle = \int \psi_a^* H \psi_a d\tau / \int \psi_a^* \psi_a d\tau \geq E_0$$

{where E_0 is true ground state energy -- $\langle H \rangle > E_{\text{exp}}$ }

guess w/fct $\psi(\lambda)$ with a parameter $\lambda \Rightarrow$ chooses form
 then $\partial \langle H \rangle / \partial \lambda = 0$ will give **best value** λ (minimum E)
 improvement in $\psi(\lambda, \mu)$ – alter form, add parameter μ

Example: He-atom 2 electrons $\psi \sim \phi_{1s}(r_1) \phi_{1s}(r_2)$
 if e^- shield then $Z \rightarrow Z'$ (less attraction to nucleus)
 $\psi_a \sim e^{-Z'r_1/a_0} e^{-Z'r_2/a_0}$ -- here, Z' is variation parameter

$$E_0 = 2 \langle 4 E_H \rangle = 8 E_H \sim -108.8 \text{ eV}$$

\rightarrow but $E_{\text{exp}} \sim -78.9 \text{ eV}$ big error! for $Z = 2$

solve $\partial \langle H \rangle / \partial Z' = 0 \Rightarrow Z' = Z - 5/16 = 27/16$ for best fct

\rightarrow variation improvement: $E' = -77.4 \text{ eV}$

To get better – add more variation

$$\text{e.g. } \psi'' = (1 + br_{12}) e^{-Z'r_1/a_0} e^{-Z'r_2/a_0}$$

get: $Z' \sim 1.85$ $E'' \sim -78.6 \text{ eV}$

$b \sim 0.364/a_0$ error $\sim 0.5\%$

\Rightarrow could go on and get E^{calc} more precise than $E_{\text{exp}}!!$

For **atoms** – represent orbital as sum of functions

$$\phi_{nl}(r_i) = \sum_k c_k f_k(r_i)$$

f_k could be various exponentials
or other forms (like Gaussians)

Variation: do **optimization**: $\partial\langle H \rangle / \partial c_k = 0$

find best c_k → linear combination solve problem

Actual modern research uses **Hartree-Fock method**
underlying Variation Principle is same but optimize
 $V(r_i)$ to calculate average repulsion then solve for
improved orbitals until self-consistent

Hartree-Fock – conventional method

Self-consistent approach, means cycle

⇒ Approximate set of ϕ^0 orbitals ⇒ compute $V(r_i)$
then insert $V(r_i)$ ⇒ into H → solve for improved ϕ'
then, use ϕ' - average potential $V'(r_i)$ - all electrons

cycle through: $V'(r) \rightarrow \phi'' \rightarrow V'' \dots$ until no change
(Approximate ψ_{HF} + Approximate H_{SCF})
→ misses Configuration Interaction (CI) again

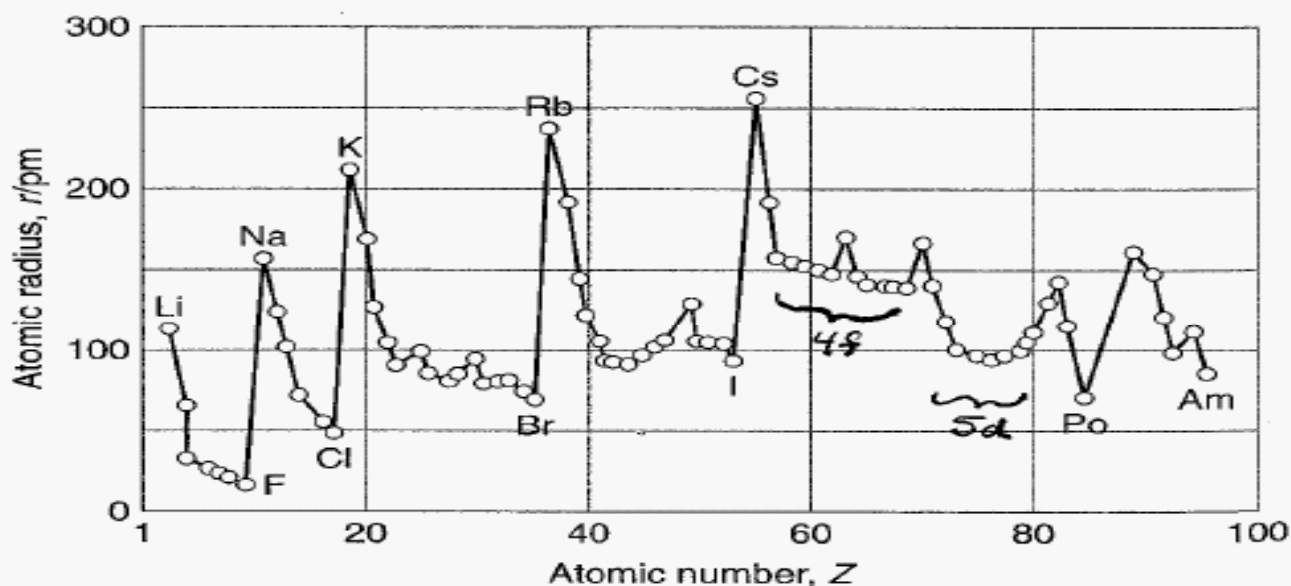
Other approaches called CI, perturbation methods,
excited configurations (empty orbitals) also included

Alternative is **Density Functional Theory** (DFT)

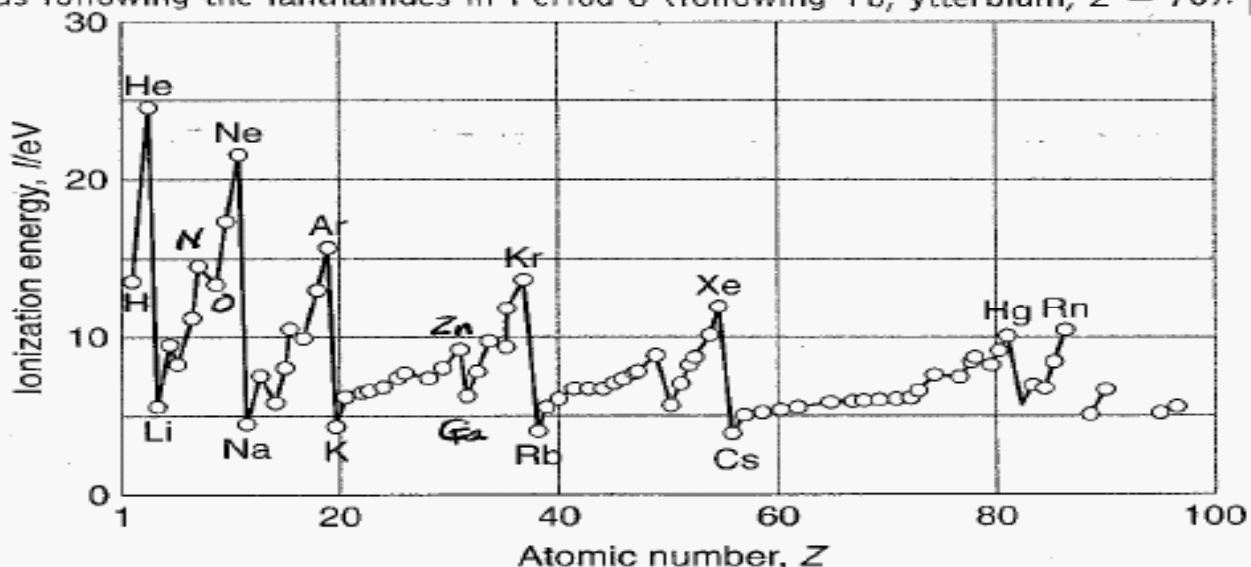
expression for electron density is optimized to give
lowest energy, then best wave function

these methods have parameters but otherwise are
comparable, but more accurate, than Hartree Fock

Atomic Radius - Increase down col., dec. across period
 Ln (4f) contract - cause 5d transition metals very dense



g. 9.51 The variation of atomic radius through the periodic table. Note the contraction following the lanthanides in Period 6 (following Yb, ytterbium, $Z = 70$).



g. 9.53 The periodic variation of the first ionization energies of the elements.

Ionization potential – Periodic table orientation

Left side – ns and np outside of rare gas core

– high shielding gives easy ionization

Right side – filling p-orbital—less shielded, attracts e^-

Half-filled - gives singularity: $N \rightarrow O : (2p)^3 \rightarrow (2p)^4$

Transition series - favor $(3d)^m (4s)^1$ for $m=5$ (Cr, Mo, W)

KEY

- ATOMIC NUMBER: 30
- BOILING POINT, °C: 100
- MELTING POINT, °C: 100
- OXIDATION STATES: (bold most stable)

Shells - if in these models: $H_0 = \sum_i h_i(r_i)$ summed

then $\psi_0 = \prod_i \phi_i(r_i)$ product

and $E = \sum_i \epsilon_i$ sum of orbital energies

Orbital – 1 electron wavefunction – “fiction”- not molec.
 State – multi electron w/f describe atom or molecule

Each orbital is a solution to H-atom—exact potential
 all have $Y_{lm}(\theta, \phi) \rightarrow$ eigenfunction L^2, L_z
 or ℓ_i^2 and ℓ_{iz} for electron i

Potential still central \rightarrow Angular Momentum conserved

- total w/f also eigenfunction angular momentum

$L = \sum_i \ell_i \rightarrow$ vector sum, need be careful

$L_z = \sum_i \ell_{zi} \rightarrow$ scalar sum – easier

Closed shells – maximum number electrons in orbital

$$M = \sum_{\text{shell}} m_i = 0 \quad (\text{since for each } m_i \text{ there is } -m_i \text{ up to } \pm \ell)$$

since only possible $M = 0$, then $L = 0$ (tot. ang. mom.)
Called 1S state (total $L=0$, also: all spins paired $2S+1=1$)

Open shells – ex. $(2p)^2$, $(3d)^4$, $(4f)^9$, ...

These can rearrange many ways—different ang. mom.

$$\left. \begin{array}{l} M_L = \sum m_{\ell_i} \\ M_S = \sum_{\text{shell}} m_{s_i} \end{array} \right\} \begin{array}{l} \text{scalar sum over electrons in open shell} \\ \text{same over spin,} \end{array}$$

called Russell-Saunders picture

L – more complex – **Vector sum**

$$2e^-: L_{\max} = |\ell_1 + \ell_2| \quad \text{since angular mom, steps of 1}$$

$$L_{\min} = |\ell_1 - \ell_2| \quad (S = 1, 0)$$

higher – use Pauli and M_i to work out

Rules: still eigenfunction: $\mathbf{L}^2 \psi_{LM} = L(L+1)\hbar^2 \psi_{LM}$
 $\mathbf{L}_z \psi_{LM} = M\hbar \psi_{LM}$

Term symbol $\psi_{LM} \sim {}^{2S+1}L_J$ $J = L+S, L+S-1, \dots, |L-S|$

$2S + 1$ – multiplicity (number M_S values)

– also indicates number of J values (if $L > S$)

J – total angular momentum – spin and orbit combine

Pauli is critical on what allowed—gets tricky

But to determine ground state – i.e. lowest energy state
there are simple rules for open shells, lowest term

Hund's Rules: Maximum S – lowest E_{LS}

Maximum L – of these is lowest

Minimum J – less half /

or Maximum J – more than half-filled shell

Total number of states in term: $(2S + 1)(2L + 1)$

in shell: $\sum_{L,S} (2S + 1)(2L + 1)$

ground state easy:

eg $(2p)^2$ – e.g. C atom

$\downarrow\uparrow$			vs.	\uparrow	\uparrow		Max S = 1	<u>3P_0</u>
+1	0	-1		+1	0	-1	Max L = 1	
							Min J = 0	

$(4d)^3$ – e.g. Nb⁺² ion or V⁺ $(4s)^1(3d)^3$

\uparrow	\uparrow	\uparrow			Max S = 3/2	<u>${}^4F_{3/2}$</u>
2	1	0	-1	-2	Max L = 3	

$(3d)^8$ – e.g. Ni⁺² ion or Co⁺ $(3d)^8$

$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	\uparrow	\uparrow	Max S = 1	3F_4
2	1	0	-1	-2	Max L = 3	
					Max J = 4	

Picture: same spin \Rightarrow different orbitals

keeps electron further apart on average

maximum orbital angular momentum – more spatial variation