

Multi-electron atoms (Notes 11) – 2014

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

Approximation: n-elect., assume prod. wavefct. of H-atom sol'n

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

$\phi_{n_i \ell_i m_i}$ – one electron w/fct – i.e. assume separable \neq

First idea: might expect the lowest energy state to be 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 **or**

b. For electrons in atoms using H-atom sol'n this turns out as – each electron has *different set of quantum numbers*

But we must add a **spin quantum number**, $m_s = \pm 1/2$, so for each $n \ell m_\ell$ – 2 electrons maximum -- (Stern-Gerlach)

“Spin” – intrinsic magnetic moment or angular momentum – *no physical picture* or *functional form*, despite the term - represent spin w/f as (note no coordinates!): α, β

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

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

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

where \mathbf{S}_z spin angular momentum operator about z

and \mathbf{S}^2 square total angular mom.

Multi-electron Atoms -- Simplest idea

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

Problem – potential now has electron-electron repulsion

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

$$r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2} \quad \text{note } ij \text{ two subscript}$$

distance between electrons (but $r_i \rightarrow e - \text{nucl. dist.}$, one i)

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

assume C of M

if ignore 3rd term $\rightarrow \mathcal{H}_0 \sim \sum_{i=1}^n h_i(r_i)$ - become separable

Note: this is big approx, since e^2/r_{ij} is same order as Ze^2/r_i

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 fill? (approximation: configuration/shell)

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

$$1s \rightarrow 2s - 2p \rightarrow 3s - 3p \rightarrow 4s - 3d - 4p \rightarrow$$

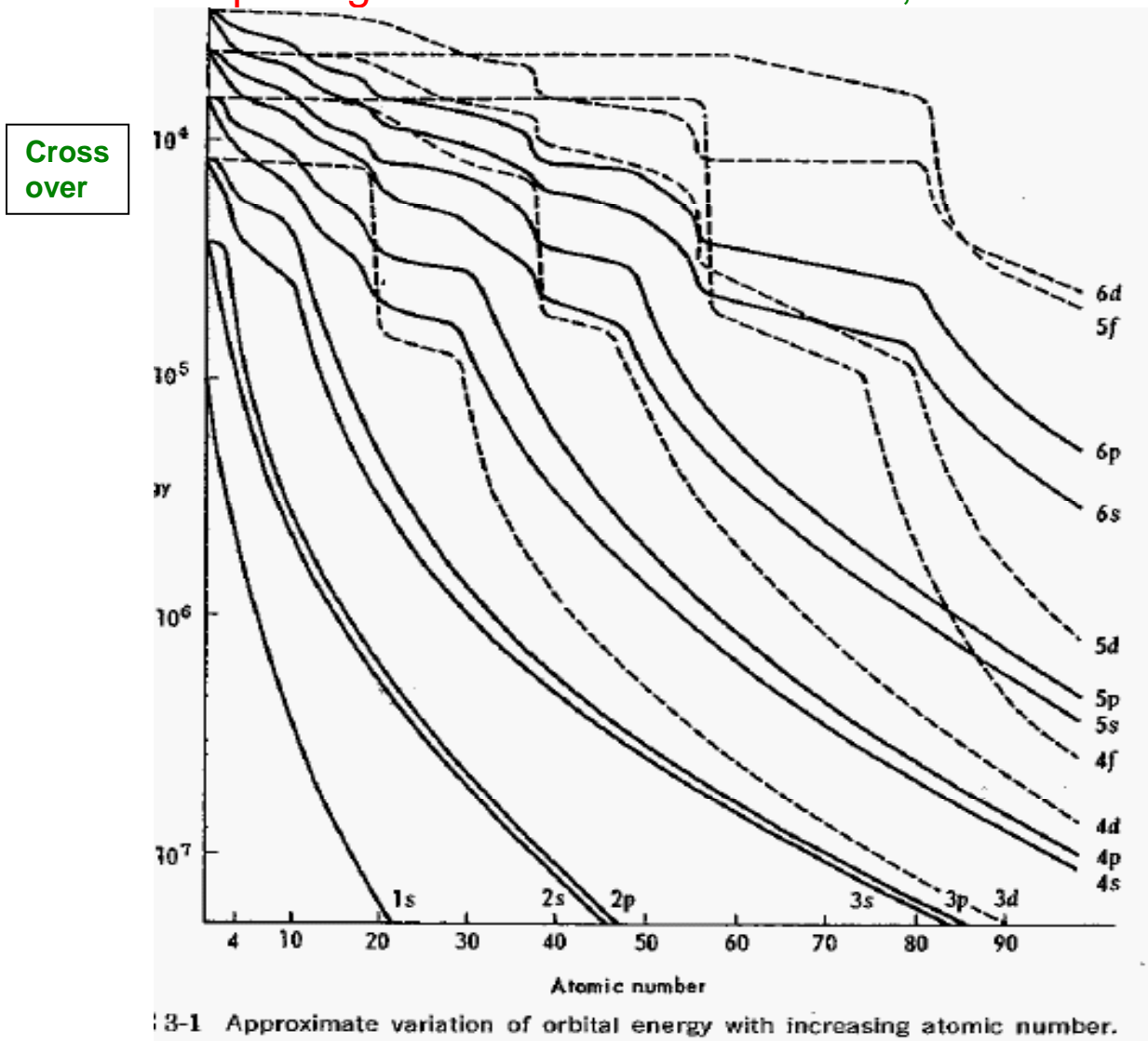
$$5s - 4d - 5p \rightarrow 6s - 4f - 5d - 6p \rightarrow 7s - 5f \dots$$

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, also transition elements, slip series, i.e. 4s before 3d, 4f before 5d, etc.

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_i) vs. Atomic Number (Z)

Why this order? → relates back to the d and f orbitals

being smaller because fewer nodes

but complex, (n+1)-s fill before n-d – inside node, feels nucleus

Added electrons shield outer electron from attraction to nucleus

(must account for 3rd term, e^2/r_{ij} , that we left out)

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

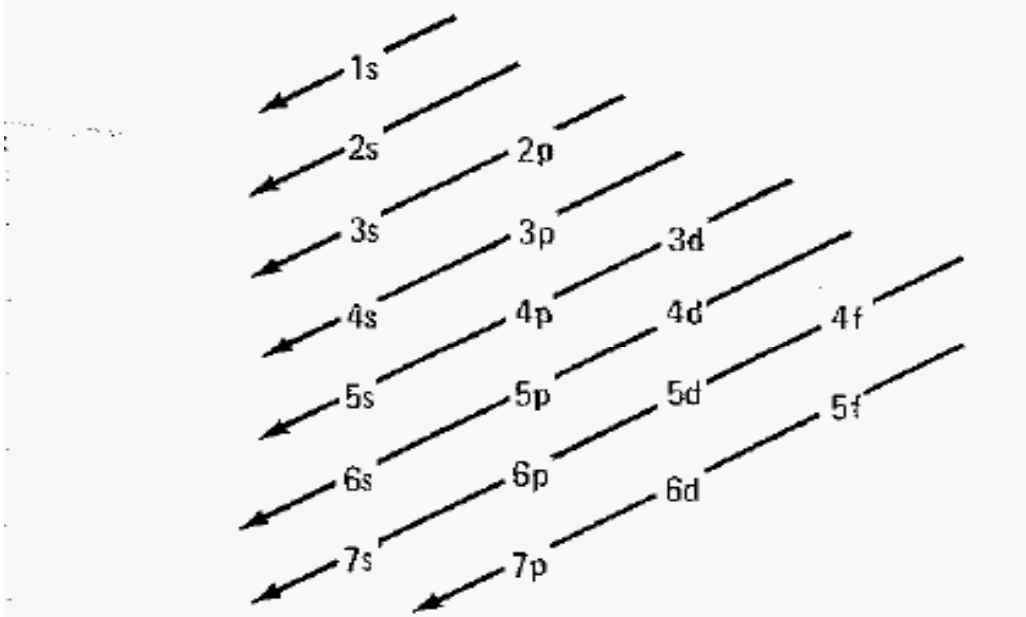
Same for n = 2 etc. but each shielded by $2e^-$ in 1s

and $2e^-$ in 2s, 6 in 2p, etc.

Different s & p radii cause: E_n -level split with l , i.e.: $E_n \rightarrow E_{nl}$

But *d, f abnormal* – do not fill until first fill higher *n* s-orbital
 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:

$$\sim (1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^2 (3d)^{10} (4p)^6 (5s)^2 (4d)^{10} (5p)^6 \dots$$

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

- **configuration (orbital occupation)** - represents $\psi^0 = \prod_{i=1}^n \phi_{n_i \ell_i m_i}(r_i)$

Solution to $\mathcal{H}_0 = \sum_{i=1}^n h_i(r_i)$ – **summed Hamiltonian**

$$\text{Product w/f} \rightarrow \psi^0 = \prod_{i=1}^n \phi_{n_i \ell_i m_i}(r_i) \quad \text{Recall: } h(r_i) \phi_i(r_i) = \varepsilon_i \phi_i(r_i)$$

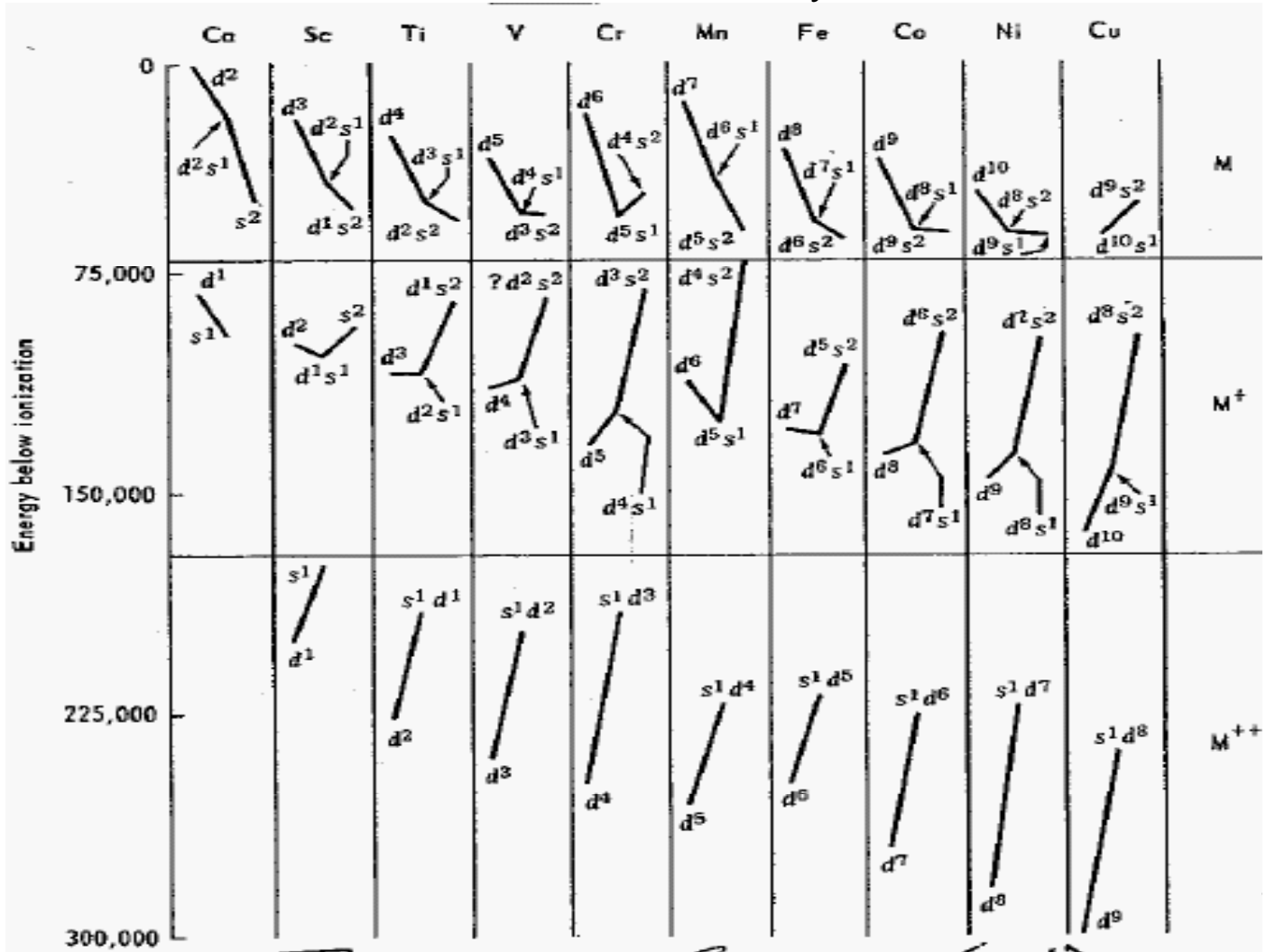
$$\text{Yields a summed E: } E = \sum_{i=1}^n \varepsilon_i$$

Exception – get extra stability by **half-filled shell** –

balance by split of s, p – effect bigger for d, f electrons

Transition elements (3d, 4d, 5d series, and 4f, 5f) get $ns^1(n-1)d^5$

Transition metal ions a bit different yet



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

Orbital Product – configuration – Rep. as: $\psi^0 = \prod_{i=1}^n \phi_{n_i \ell_i m_i}(\mathbf{r}_i)$

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

Approximation -- How does this work, since dropped e^- repulsion?
 these orbitals for multielectron atoms must

adjust H-atom like solution to account for $V_{ee} = \sum_{ij} e^2/r_{ij}$

Warning: some books use SI units: $e^2/4\pi\epsilon_0 r_{ij}$



Central field approximation:

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

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

Think of $[-Ze^2/r_i + V(r_i)]$ as: **average potential** for electron i

a) attraction to nucleus

b) repulsion by all other electron j (*average, time indep.*)

Result: Still a problem with **central force**, *if drop*: $\sum_{i,j} [e^2/r_{ij} - V(r_i)]$

now separable and include **average repulsion**, $V(r_i)$

→ **Misses out on “correlation”** –

instantaneous e–e motion/interaction (favor **keep e⁻ 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): $E = \sum_{i=1}^n \varepsilon_i$

since only change potential, **angular part same**: $Y_{LM}(\theta, \phi)$

Method – underlying this approach: **Variation Principle**

(go for getting the idea, if not the details)

if use *exact* \neq , approximate (guess) a w/fct: ψ_a

then compute **expectation value of energy** in ψ_a

$$\langle \mathcal{H} \rangle = \int \psi_a^* H \psi_a d\tau / \int \psi_a^* \psi_a d\tau \geq E_0 \quad \text{approx. } \psi \rightarrow \text{inc. } E$$

{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 $\partial \langle \mathcal{H} \rangle / \partial \lambda = 0$ 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*

$E_0 = 2 \langle 4 E_H \rangle = 8 E_H \sim -108.8 \text{ eV}$ ($8 E_H$ since $2 e^-$ & $Z^2=4$, for $Z=2$)

\rightarrow but $E_{\text{exp}} \sim -78.9 \text{ eV}$ so E_0 , no correction, big error (~28%)!

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

\rightarrow variation improvement: $E' = -77.4 \text{ eV}$ (error ~1.5 eV ~1.4%)

To get better – add more variation -*mix in correlated character*

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 ~ 0.5%

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

For **atoms** – rep. *orbital as sum of functions (linear comb.)*

$$\phi_{nl}(r_i) = \sum_k c_k f_k(r_i) \quad f_k \text{ could be various exponentials, } e^{-Z'r_i/a_0}$$

or other forms, e.g. Gaussians, $\exp(-\alpha'r_i^2)$

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

find best $c_k \rightarrow$ 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 → *cycle/repeat until no change*

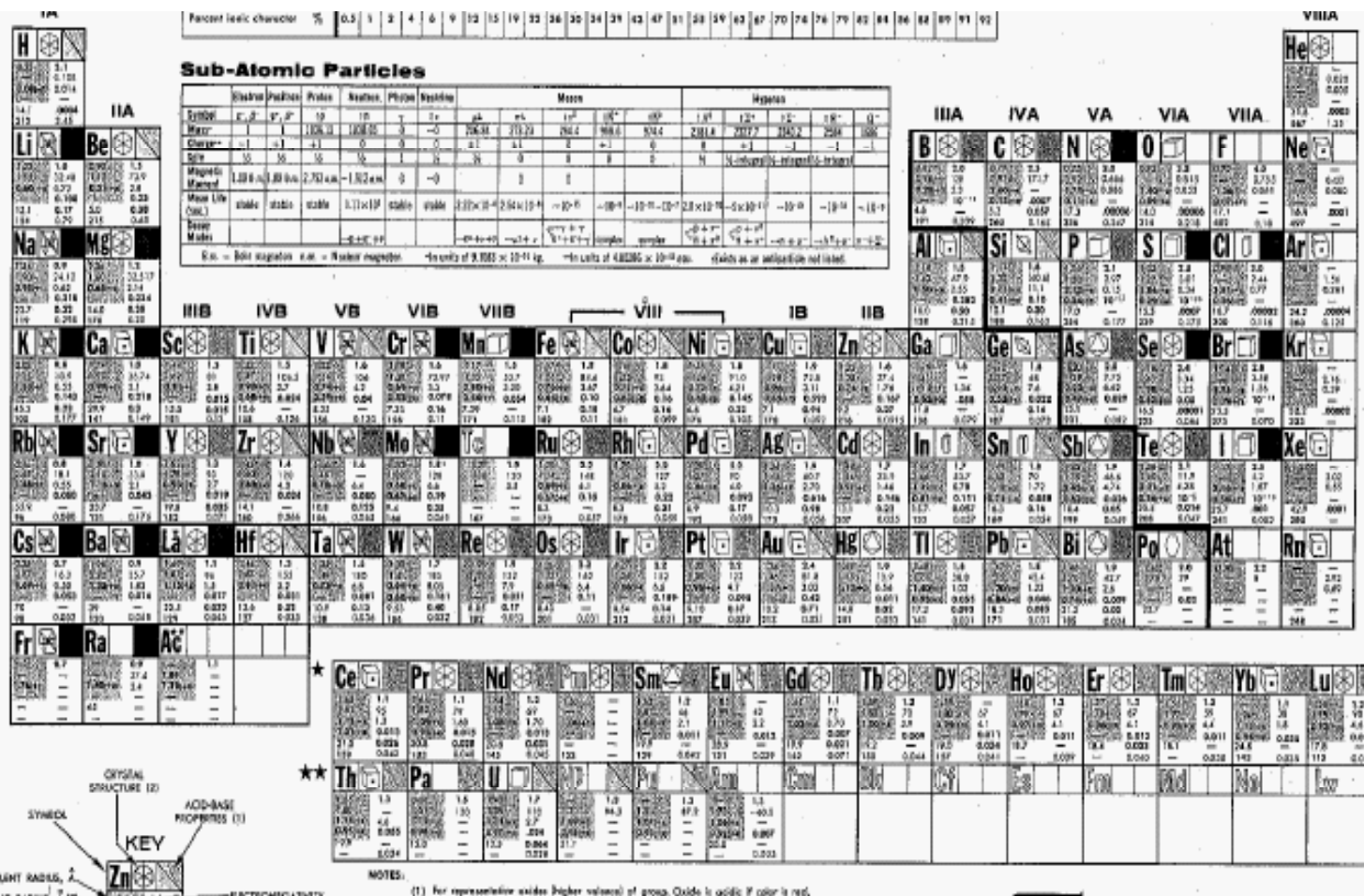
⇒ Approximate set of ϕ^0 orbitals ⇒ compute $V(r_i)$
 then insert $V(r_i)$ ⇒ into \mathcal{H} → solve for improved ϕ'
 then, use ϕ' - average potential $V'(r_i)$ - all electrons

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

Other approaches add CI, perturbation methods,
effect, 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

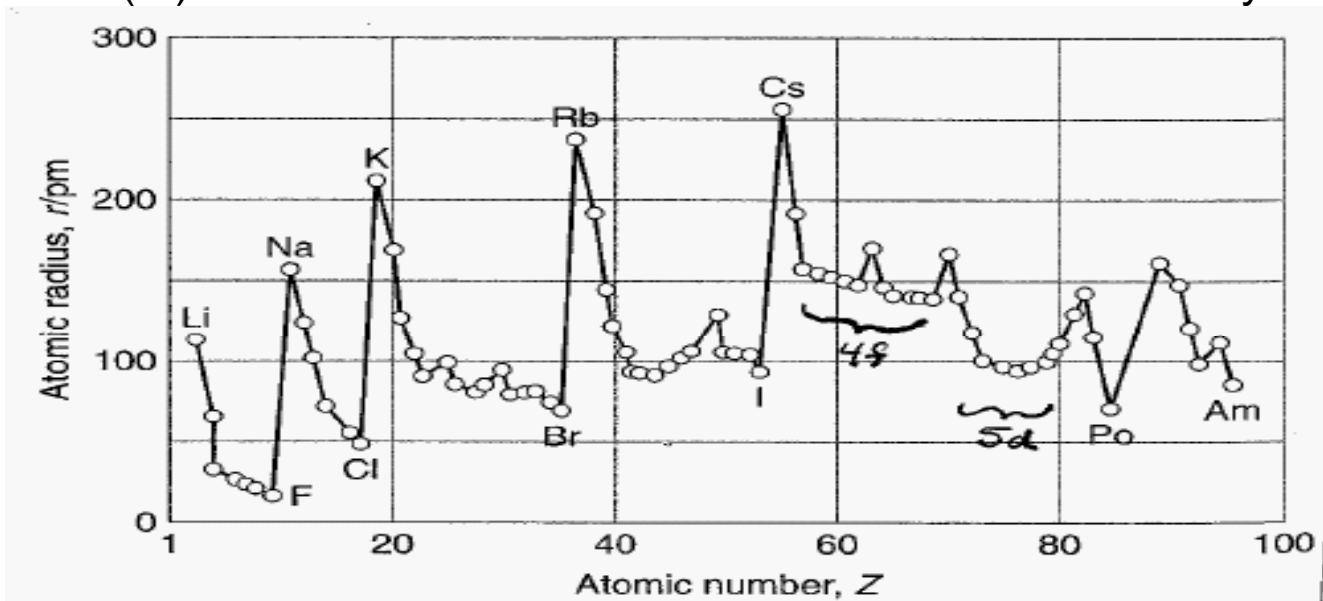
Periodicity and the buildup – gradual filling orbitals appreciate its origins in quantum mechanics – look, see trends



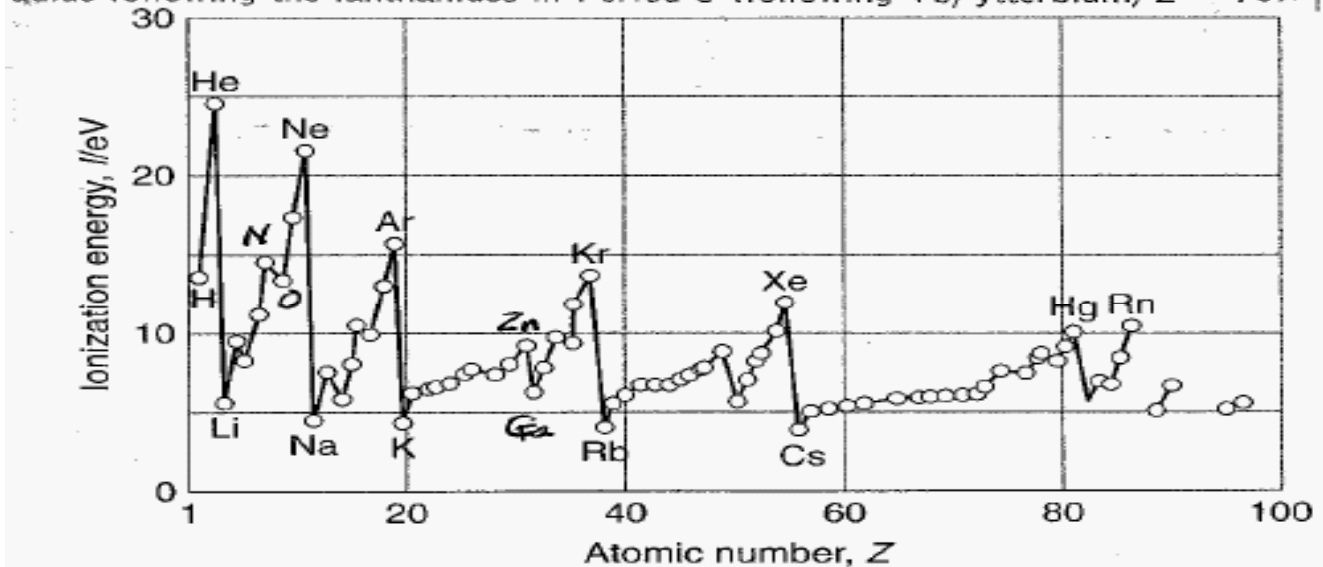
Shape of table reflects the filling sequence, Aufbau concept number of electrons in each type of orbital and the skipping of 3d and 4f in sequence

Atomic Radius - Increase down col., dec. across period

Ln (4f) contract - cause 5d transition metals become 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)

Shells - if in these models: $\Psi_0 = \prod_i h_i(r_i)$ *summed/separate*

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

and $E = \sum_i \varepsilon_i$ *sum of orbital energies*

Orbital – 1 electron wavefunction – “fiction”- *approx. for us*
State – multi electron wave fct. describe atom or molecule

Each orbital - *solution in θ, ϕ same as H-atom — central potential*
all have $Y_{lm}(\theta, \phi) \rightarrow$ eigenfunction L^2, L_z
 or ℓ_i^2 and ℓ_{iz} for each one-electron operator 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, add graphically*

$L_z = \sum_i \ell_{zi} \rightarrow$ *scalar sum – easier, normal addition*

Closed shells – maximum number electrons in orbital

$M = \sum_{\text{shell}} m_i = 0$ (for each $+m_i$ there is $-m_i$ up to $\pm\ell$, $2\ell+1$ values)

for $M = 0$ only one possible value, then $L = 0$ (total ang. mom.)

Called 1S state (total $L=0 \rightarrow S$, also: all spins must pair - $2S+1=1$)

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

These can rearrange many ways—different angular momentum

$M_L = \sum m_{\ell_i}$ } *scalar sum over electrons in open shell*

$M_S = \sum_{\text{shell}} m_{s_i}$ } *same over spin, can find max M_L lead to L*

called **Russell-Saunders** picture

L – more complex – *Vector sum*

$2e^-$: $L_{\max} = |\ell_1 + \ell_2|$ *angular momentum vary in steps of \hbar*

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

Higher # e^- – use Pauli principle and $M_{L,S} = \sum m_{\ell_i, s_i}$ to work out

Rules: still angular mom., eigenfunction: $L^2 \psi_{LM} = L(L+1) \hbar^2 \psi_{LM}$
 $L_z \psi_{LM} = M \hbar \psi_{LM}$

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 princ. - critical as what allowed—gets tricky—use M_L to find L

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

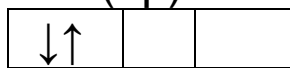
Total number of states in term: $(2S + 1)(2L + 1)$

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

For term symbols use: S,P,D,F,G,H,I for $L = 0,1,2,3,4,5,6,7$

ground state easy, just consider open shells:

ex.1: $(2p)^2$ – e.g. C atom



+1 0 -1

+1 0 -1

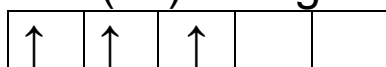
Max S = 1; $2S+1=3$

Max L = 1 → P

Min J = 0

3P_0

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



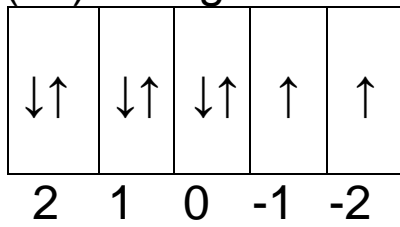
Max S = 3/2; $2S+1=4$

Max L = 3; → F

Min J = 3/2

${}^4F_{3/2}$

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



Max S = 1; $2S+1=3$

Max L = 3; $\rightarrow F$

Max J = 4

3F_4

Picture: same spin \Rightarrow different orbitals
 keeps electron further apart on average
 maximum orbital angular momentum – more spatial variation

A detailed periodic table of elements showing atomic numbers, symbols, names, and oxidation states. It includes a key for oxidation states and a box for element 30 (Zinc).