Electronic Configurations

Electronic Configurations of atom - there are sets of "rules" that dictate how e^-s populate AOs

Interactions between electrons can perturb the energies of AOs to which they belong

Consider He: 3 principal interactions

① Interaction $e^-(1)$ w/ the nucleus
② Interaction of $e^-(2)$ w/ the nucleus
③ Interaction of $e^-(1)$ w/ $e^-(2)$

Aufbaus Principle - "The Building up" principle

Atoms are "built" from lowest energy AOs → AOs
Starting from lowest principle QNs (n, ℓ, m_ℓ, m_s)

① **Pauli Exclusion principle** — Each e^- in an atom must be described by a unique set of QNs (n, ℓ, m_ℓ, m_s)

② **Hunds Rule** — e^- must placed into AOs such that the multiplicity of the species is maximized
↳ Maximize the # of unpaired spins (parallel)

$\uparrow\downarrow$ — — $\uparrow$ $\downarrow$ — $\uparrow$ $\uparrow$ —

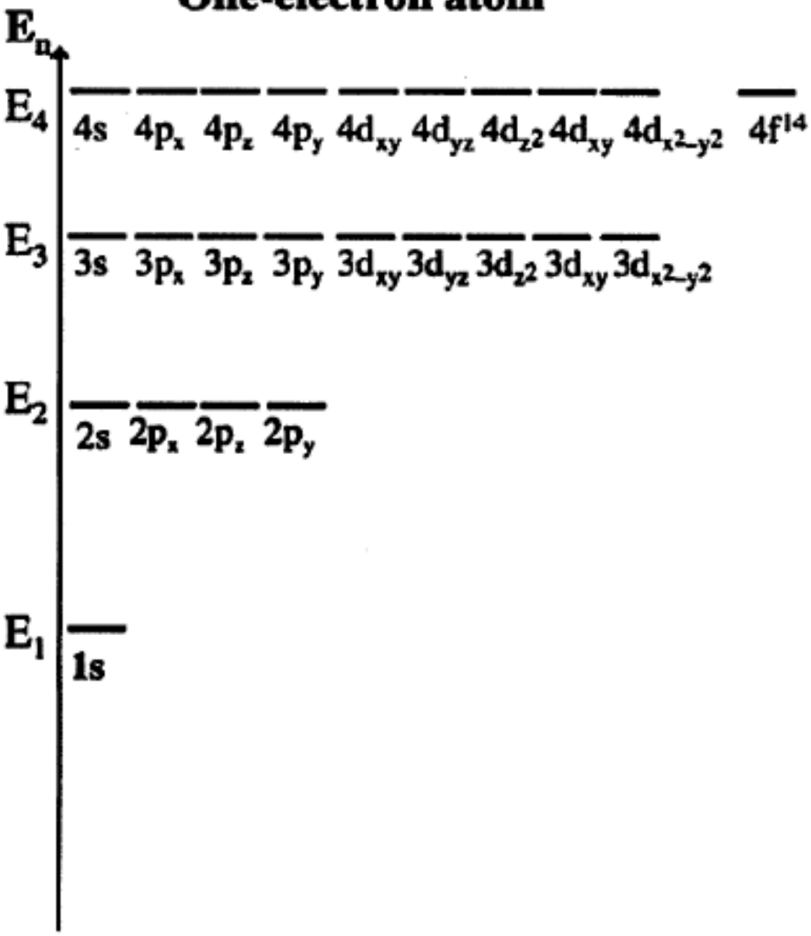
Multiplicity = # of unpaired unpaired e^- +1 $(2S+1)$
$S = \Sigma$ of unpaired half spins

	1S	2S	2P	Multiplicity $2S+1 = ?$	
Li	⇅	↑		$2S+1 = 2$	"Doublet"
Be	⇅	⇅		$2S+1 = 1$	"Singlet"
B	⇅	⇅	↑	$2S+1 = 2$	"Doublet"
C	⇅	⇅	↑ ↑	$2S+1 = 3$	"triplet"
N	⇅	⇅	↑ ↑ ↑	$2S+1 = 4$	"Quartet"

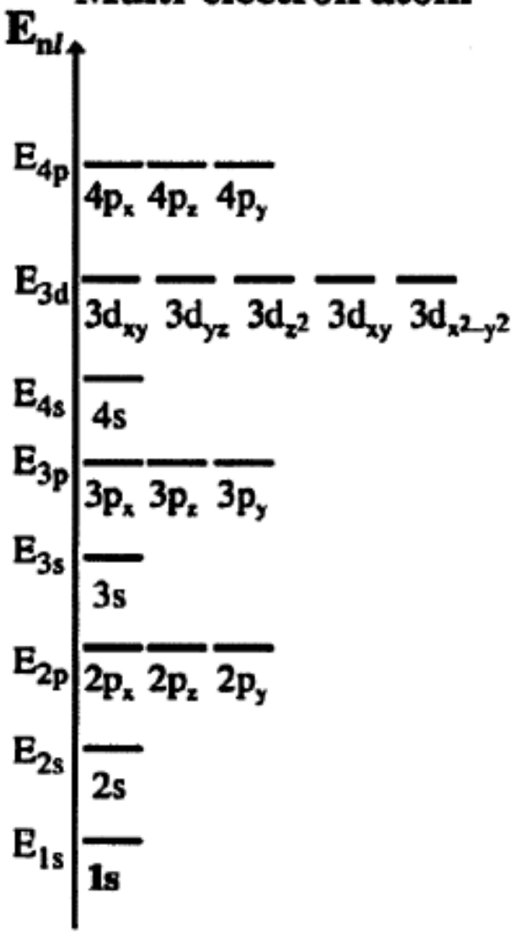
Diamagnetic – $S=0$ (singlet) Repelled by a magnetic field.

Paramagnetic – $S>0$ Attracted by a magnetic field.

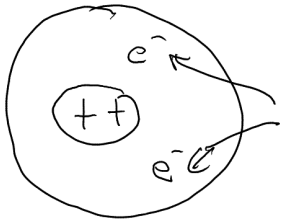
One-electron atom



Multi-electron atom



Hunds Rule is a consequence of 2 factors



$2e^-$ share the same orbital (Ψ) they repel each other (coulombic)

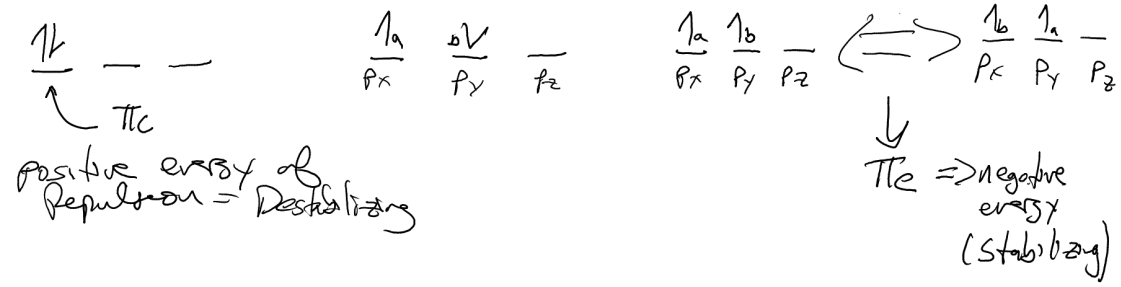
↳ Coulombic Energy of Repulsion (J_{rc})

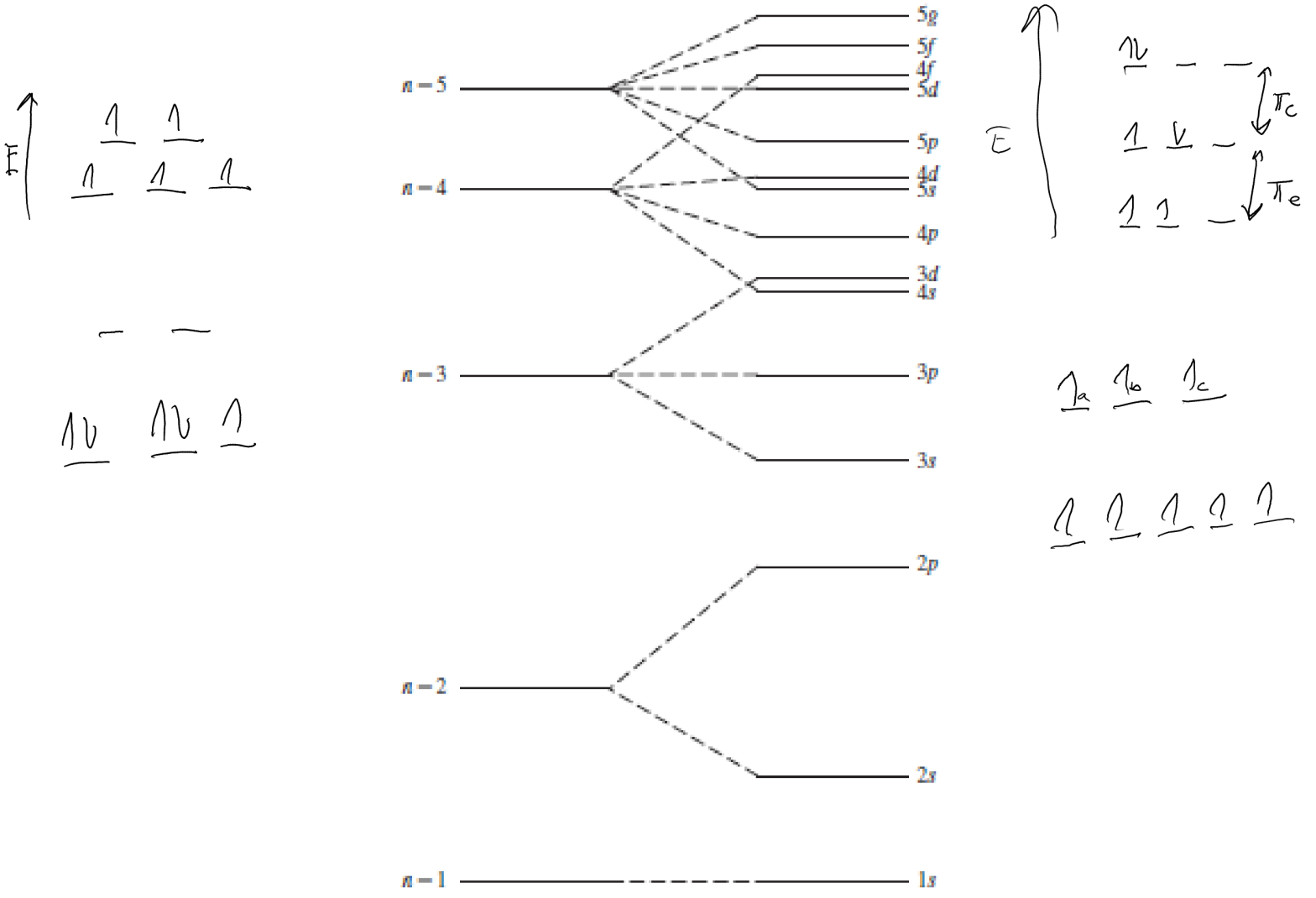
There is an additional energy term:

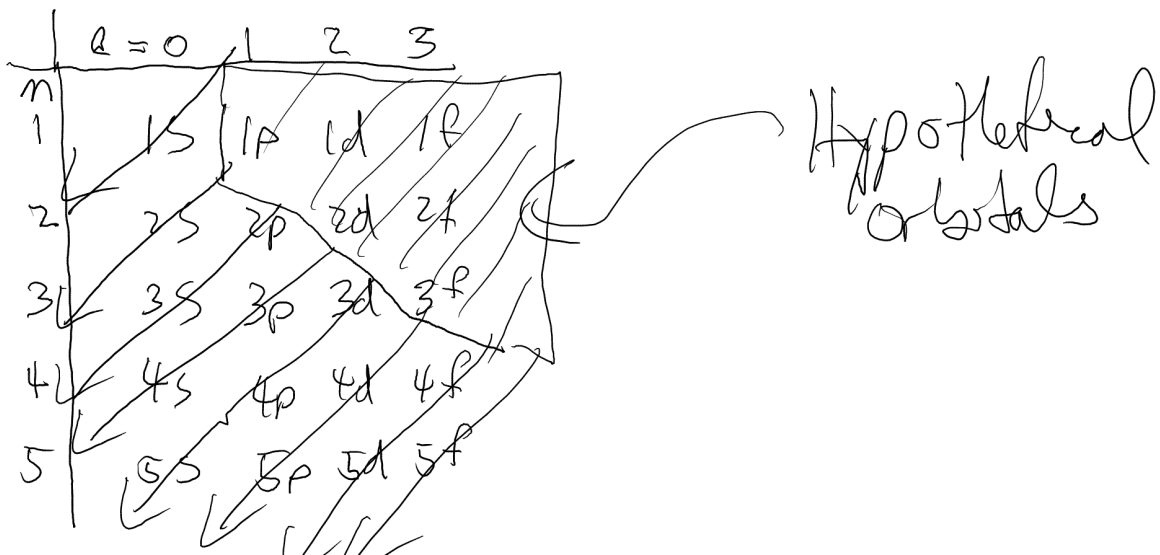
Exchange Energy (π_e)

↳ dictated by the number of possible exchanges between e⁻s w/ the same energy + spin

Carbon ($1s^2 2s^2 2p^2$)







Consider Rhenium (Re) — He Ne Ar Kr Xe

75 total e⁻ : $1s^2 | 2s^2 2p^6 | 3s^2 3p^6 | 4s^2 3d^{10} 4p^6 | 5s^2 4d^{10} 5p^6$

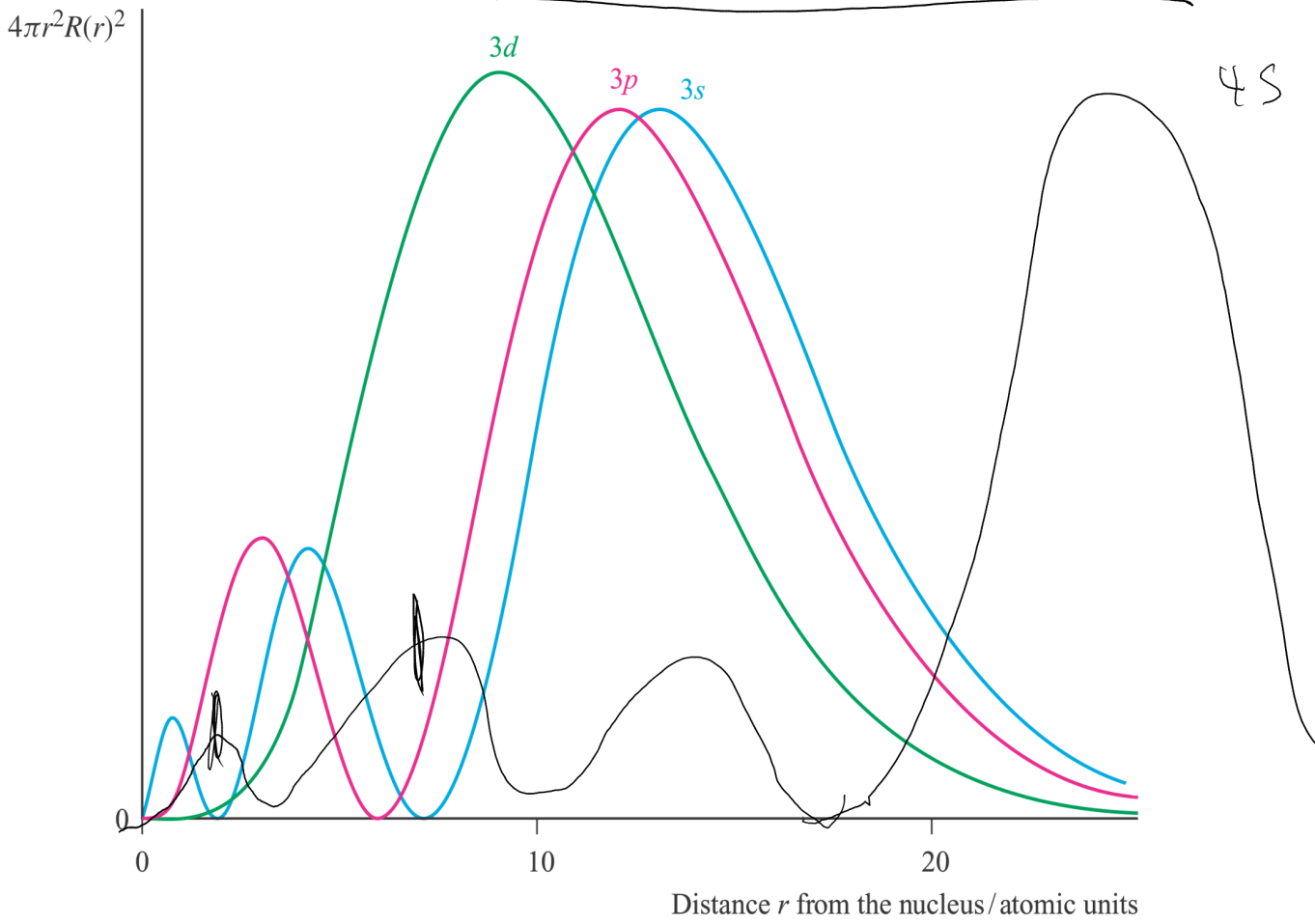
$6s^2 4f^{14} 5d^5 \Rightarrow [Xe]\, 6s^2 4f^{14} 5d^5$

Shielding - Every e^- acts to shield other e^- further out from the nucleus

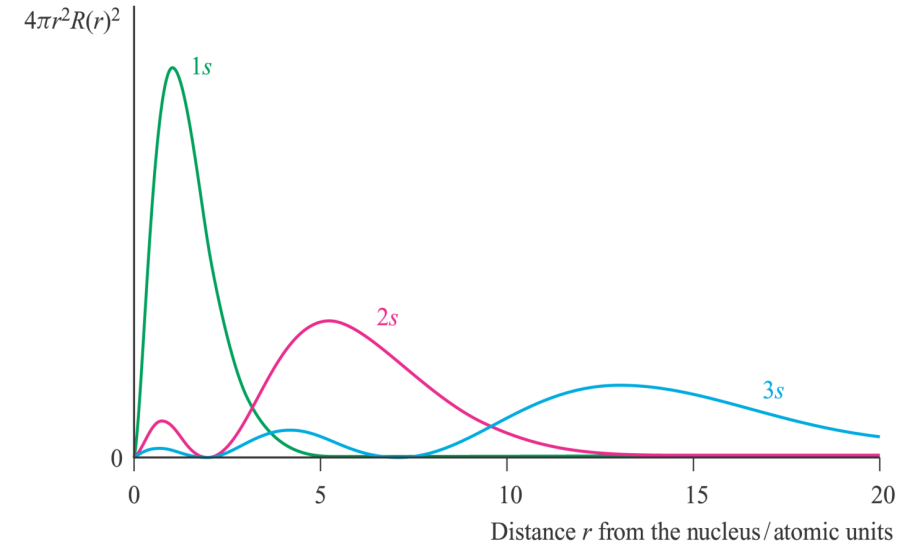
↳ Reduced attraction between the shielded e^- + the nucleus

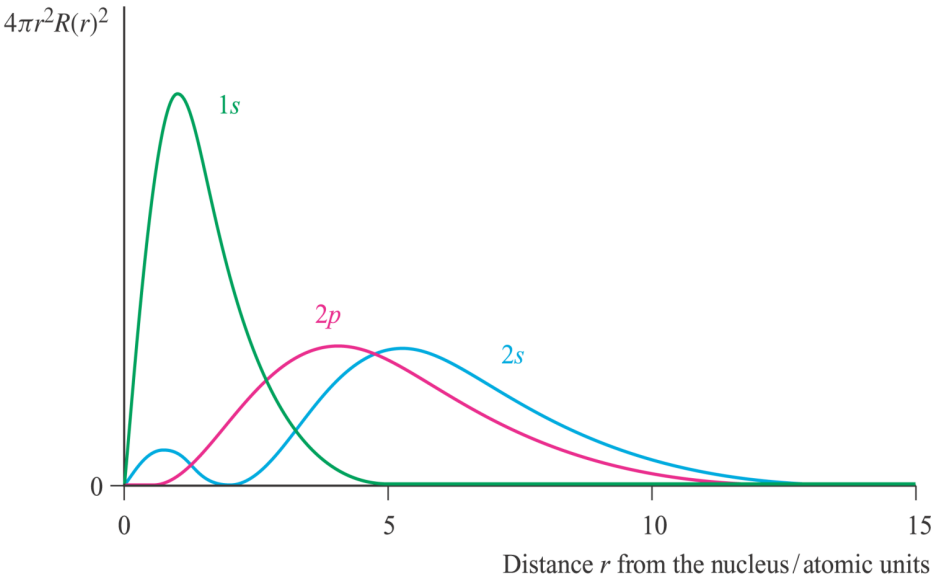
Screen Ability: $n_s > n_p > n_d > n_f$

← orbital penetration



For outer AOs, the increasing energy levels between AOs w/ same value of n but different values for l forces the energetic overlap of AOs w/ $n = 3, 4, 5 \ldots$


$4\pi r^2 R(r)^2$
1s
2s
3s
0
0
5
10
15
20
Distance r from the nucleus / atomic units


$4\pi r^2 R(r)^2$
1s
2p
2s
0
0
5
10
15
Distance r from the nucleus / atomic units

Configurations + Exceptions

For some TMs, the d-manifold will be populated before the valence S-orbital is completely filled.

Cr ($Z = 24$) $\Rightarrow$ $[Ar]\,4s^1 3d^5$ NOT $[Ar]\,4s^2 3d^4$

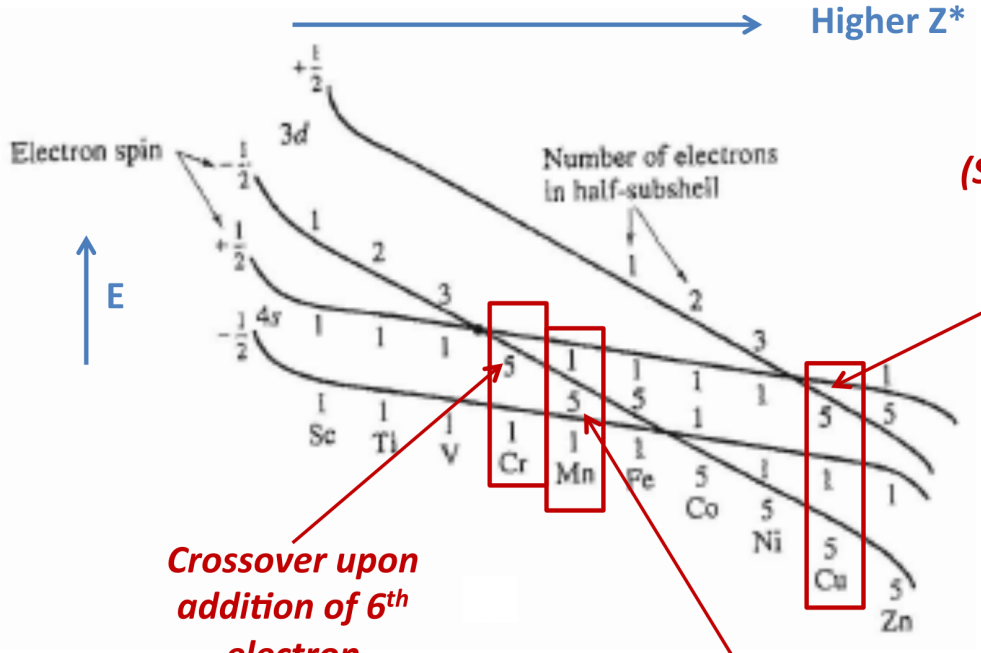
Cu ($Z = 29$) $\Rightarrow$ $[Ar]\,4s^1 3d^{10}$ NOT $[Ar]\,4s^2 3d^9$

Cr: 4s ↑ ; 3d ↑ ↑ ↑ ↑ ↑ — Maximize π

More stable than: 4s ↑↓ ; 3d ↑ ↑ ↑ ↑ — ↖ Destabilizing π

Cu: Energy of d-orbitals is not linear

Na	Mg				Half-filled *d*						Filled *d*		Al	Si	P	S	Cl	Ar
K	Ca	Sc $3d^1$		Ti $3d^2$	V $3d^3$	Cr $3d^5 4s^1$	Mn $3d^5 4s^2$	Fe $3d^6$	Co $3d^7$	Ni $3d^8$	Cu $3d^{10} 4s^1$	Zn $3d^{10} 4s^2$	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y $4d^1$		Zr $4d^2$	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc $4d^5 5s^2$	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10}$	Ag $4d^{10} 5s^1$	Cd $4d^{10} 5s^2$	In	Sn	Sb	Te	I	Xe
Cs	Ba	La $5d^1$	*	Hf $4f^{14} 5d^2$	Ta $4f^{14} 5d^3$	W $4f^{14} 5d^4$	Re $5d^5 6s^2$	Os $5d^6$	Ir $5d^7$	Pt $5d^9 6s^1$	Au $5d^{10} 6s^1$	Hg $5d^{10} 6s^2$	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac $6d^1$	**	Rf $5f^{14} 6d^2$	Db $5f^{14} 6d^3$	Sg $5f^{14} 6d^4$	Bh $5f^{14} 6d^5$	Hs $5f^{14} 6d^6$	Mt $5f^{14} 6d^7$	Ds $6d^9$	Rg $6d^{10} 7s^1$	Cn $6d^{10} 7s^2$		Uuq		Uuh		Uuo


Higher Z*
Electron spin
E
3d
4s
Number of electrons in half-subshell
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
11th electron into 3d not 4s (Shielding is less for d than for s)
Crossover upon addition of 6th electron
7th electron goes into 4s to maximize Πe from the 3d set