AUFBAU PRINCIPLE AND MANY ELECTRON ATOMS

Major Points:

(1) Order of energy for “screened” orbitals

$$E = -\frac{1}{n^2}\frac{Z_f e^2}{8\pi\varepsilon_0 (a_0 / Z_f)} = -\frac{1}{n^2}\frac{Z_f^2}{2}$$

$$\langle r \rangle = \frac{n^2}{Z_f} a_0 \left\{ \frac{3}{2} - \frac{\ell(\ell+1)}{n^2} \right\}$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z_f}{a_0 n^2}$$

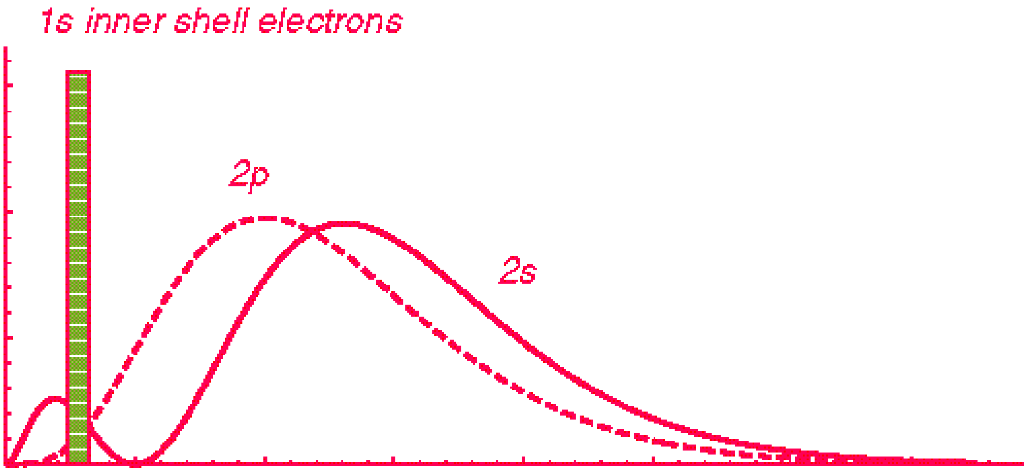
$$r_{Bohr} = \frac{n^2 a_0}{Z_f}$$

(2) Total nodes $(n - 1)$

angular nodes ℓ

radial nodes $(n - \ell - 1)$

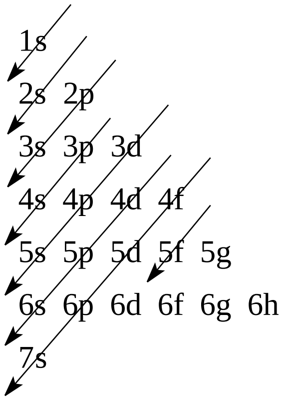
(3) Why is Z_f for 2p < Z_f for 2s?



Penetration of 2s inside of inner shell 1s increases Z_f for this relative to 2p.

(4) Competition between the n^2 (higher n ⇒ higher energy) and Z_f (higher Z_f ⇒ lower energy) contributions to E determines the energy ordering of the orbitals.

(5) For neutral species this competition yields the “usual” order with the following mnemonic [note that for $E_{4s} < E_{3d}$ one would argue that the increase of Z_f for 4s, mucho “inner maxima,” relative to Z_f for 3d more than compensates for $n = 4$ vs. $n=3$].



(6) Periodic structure relates to groups of orbitals with nearby energies, “magic” numbers

orbitals	1s	2s, 2p	3s, 3p	4s, 3d, 4p	5s, 4d, 5p	6s, 4f, 5d, 6p
electrons (total)	2	8 (10)	8 (18)	18 (36)	18 (54)	32 (86)

(7) Similar outer electronic structure for atoms in the same column.

(8) How do Z_f and n change as one goes across a row? down a column? How do the ionization potential (I.P.) and $\langle r \rangle$ change as one goes across a row? down a column?

(9) Elements within the Actinide and Lanthanide series have similar chemical behavior (added electrons do no change electronic distribution for larger r where “chemistry” occurs).

(10) Note added stability of half-filled and filled d and f shells:

Cr: [Ar] 4s $3d^5$	[“explained” by reduction of electron-electron repulsion]
Cu: [Ar] 4s $3d^{10}$	[“explained” by the Z_f for these d-electrons is relatively high (9 others in *same* shell) and orbital ordering is positive-ion like, see (11)]

(11) For positive ions the order of orbital energies is more hydrogen-like (depends more on *n* and less on Z_f variations; shielding less important)

Co^0: [Ar] $4s^2\ 3d^7$ but Cu^{+2}: [Ar] $3d^9$

$E_{4s} < E_{3d}$ $E^{+}_{3d} < E^{+}_{4s}$

note:

$$\left.\begin{aligned} \left(\frac{\partial E}{\partial n}\right)_{Z_f} &= \frac{1}{n^3} Z_f^2 \\ \left(\frac{\partial E}{\partial Z_f}\right)_{n} &= -\frac{Z_f}{n^2} \end{aligned}\right]$$

for large Z_f, energy changes are relative more sensitive to change in $n \Rightarrow$ hydrogen-like.