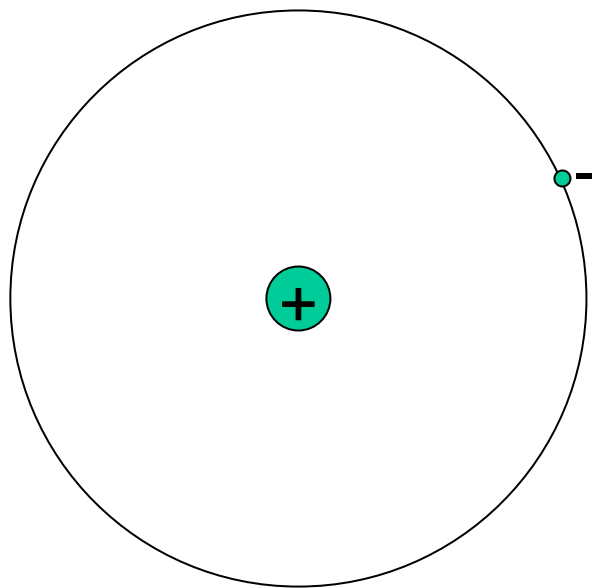


# The Electronic Structure of Atoms

Classical Hydrogen-like atoms:



Atomic Scale:  $10^{-10}$  m or 1 Å

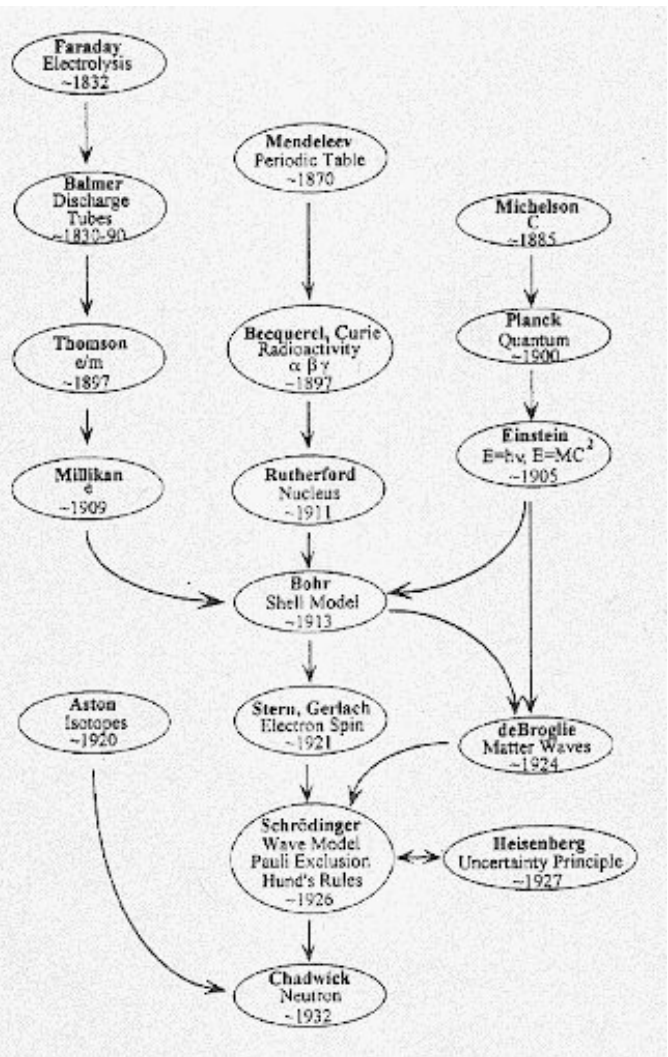
Proton mass : Electron mass  
1836 : 1

Problems with classical interpretation:

- Should not be stable  
(electron should spiral into nucleus)
- Atomic spectra wrong  
(discrete lines instead of continuum)

# Quantum Chemical Interpretation:

$e^-$  are best described by wave functions and quantum numbers.



“Quantum” means not continuous.

## Quantum numbers for electrons:

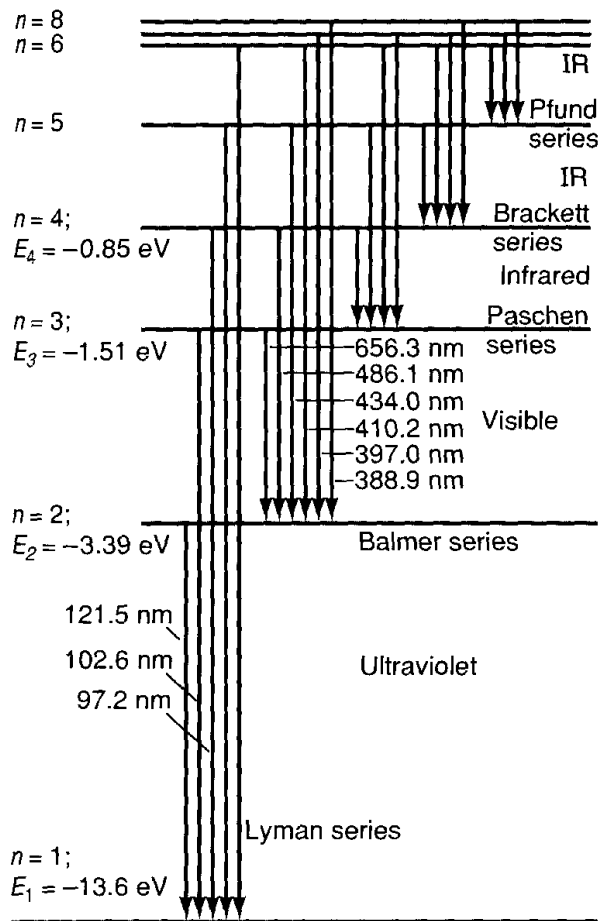
$n$  = principal quantum number

$l$  = azimuthal quantum number  
(orbital angular momentum)

$m_l$  = magnetic quantum number

$m_s$  = spin magnetic quantum number

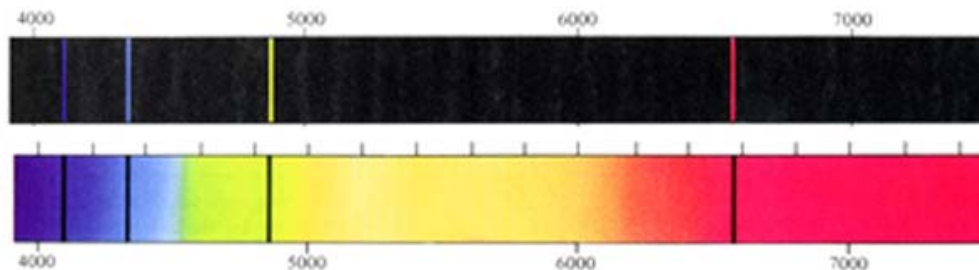
# Energy levels and $n$



Spectral transitions predicted by:

$$E = h\nu = \mathcal{R}_H \left( \frac{1}{n_l^2} - \frac{1}{n_h^2} \right)$$

where:  $n_l < n_h$



The Hydrogen Spectrum  
Above: Emission  
Below: Absorption

# Bohr Model of the H atom

$$E_n = -\mathcal{R} \left( \frac{Z^2}{n^2} \right) = -\mathcal{R} \left( \frac{1}{n^2} \right)$$

$$\mathcal{R} = \frac{2\pi^2\mu e^4}{(4\pi\epsilon_0)^2 h^2}$$

$$\mathcal{R} = 13.6 \text{ eV}$$

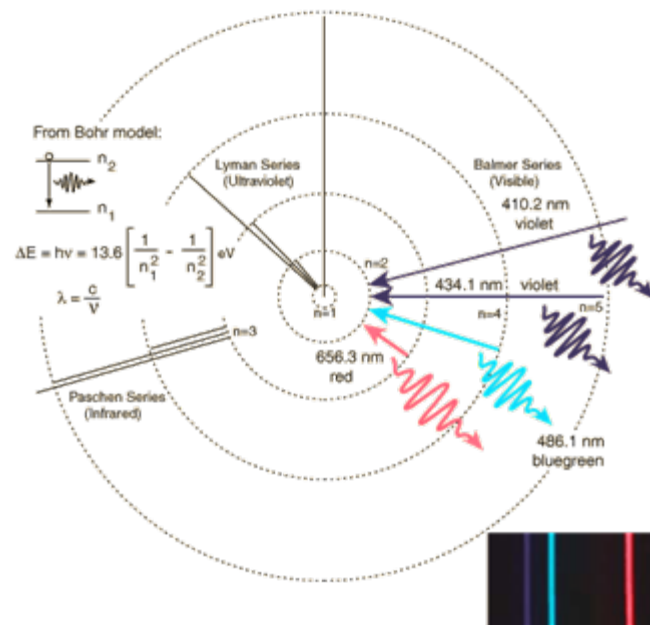
$\mu$  = reduced mass (nucleus and electron)

$Z$  = nuclear charge (1 for H)

$e$  = charge of electron

$\epsilon_0$  = permittivity of a vacuum

$h$  = Plank's constant



$$\text{radius}(n) = n^2 a_0$$

$$a_0 = \text{Bohr radius} = 0.529 \text{ \AA}$$

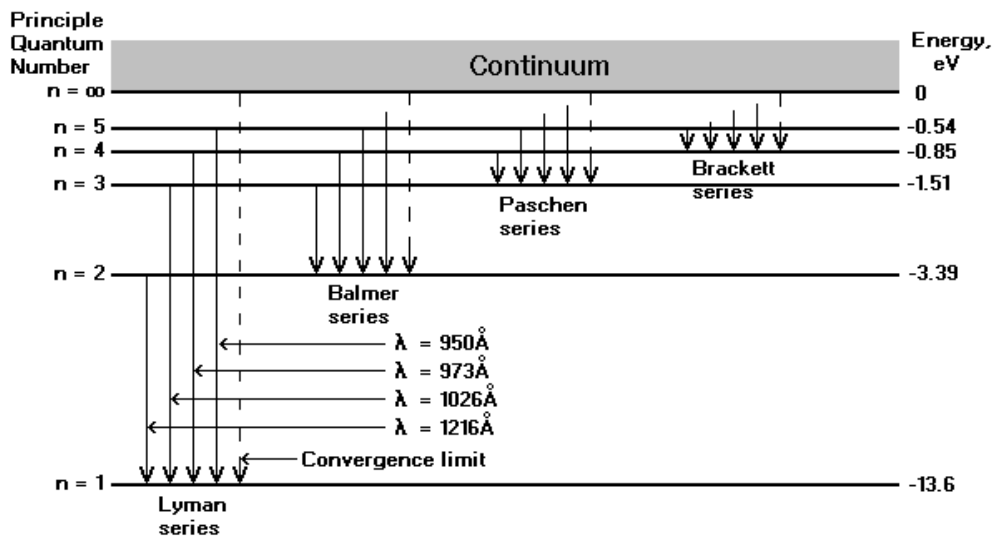
$n = principal \rightarrow$  Energy, Size  $\rightarrow$  SHELL

$n = 1, 2, 3 \dots \infty$

$n = 1$  : ground state

$n = 2$  : first excited state

$n = 3$  : second excited state



$$E_n = -13.6 \left( \frac{1}{n^2} \right)$$

$$E_1 = -13.6 \text{ eV}$$

$$E_2 = -3.40 \text{ eV}$$

$$E_3 = -1.51 \text{ eV}$$

$$E_4 = -0.85 \text{ eV}$$

$$E_5 = -0.54 \text{ eV}$$

•

•

•

$$E_\infty = 0 \text{ eV}$$

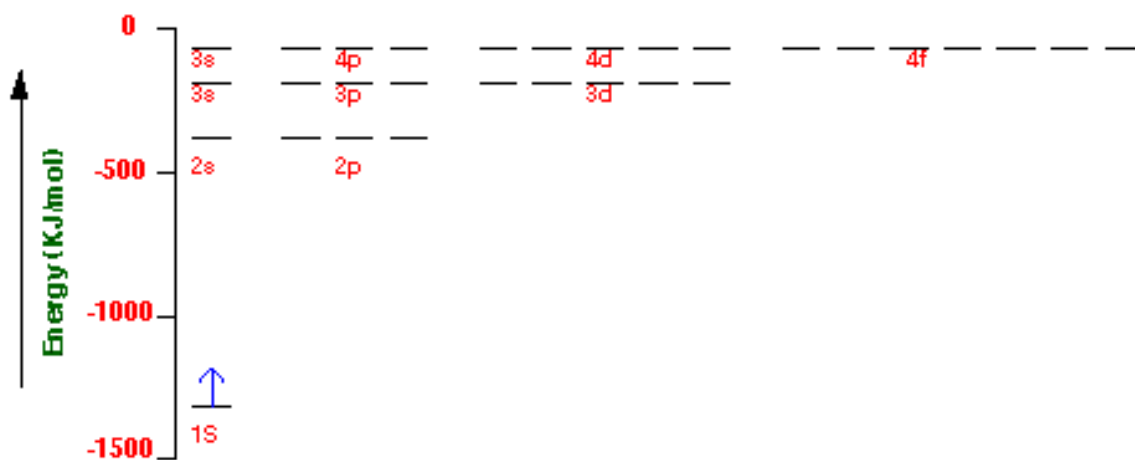
$l = azimuthal, orbital\ angular\ momentum$

→ degeneracy, shape → SUBSHELL

$$l = 0, 1, 2 \dots n - 1$$

$$degeneracy = 2l + 1$$

$l$	0	1	2	3	4, 5, 6 ...
type	s	p	d	f	g, h, i ...
degeneracy	1	3	5	7	9, 11, 13 ...

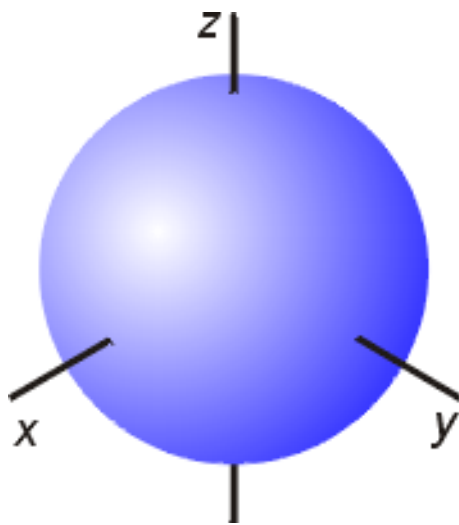


s = “sharp”  
 p = “principal”  
 d = “diffuse”

$m_\ell = \text{magnetic} \rightarrow$  type, “orientation in space”  $\rightarrow$  ORBITAL

$$m_\ell = 0, \pm 1, \pm 2 \dots \pm \ell$$

# of orbitals in a subshell =  $2\ell + 1$



1s orbital

$\ell$	$m_\ell$	orbital
0	0	s
1	0	$p_z$
	$\pm 1$	$p_x$
	$\pm 1$	$p_y$
2	0	$d_{2z^2-x^2-y^2} = d_{z^2}$
	$\pm 1$	$d_{xz}$
	$\pm 1$	$d_{yz}$
	$\pm 2$	$d_{x^2-y^2}$
	$\pm 2$	$d_{xy}$

# Wave functions and Orbitals

$\Psi$  = wave function

$\Psi^2$  = probability (electron) density

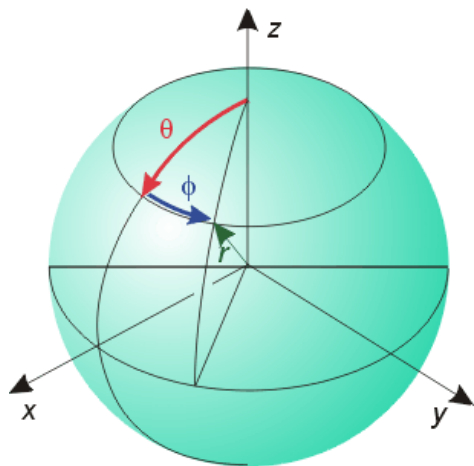
$4\pi r^2 \Psi^2$  = radial distribution function

$$\hat{H}\Psi = E\Psi$$

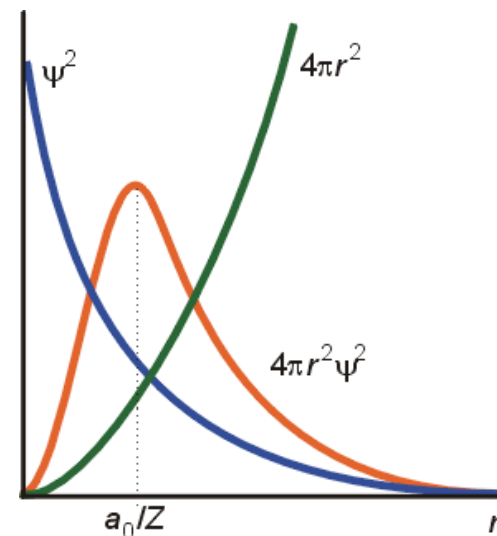
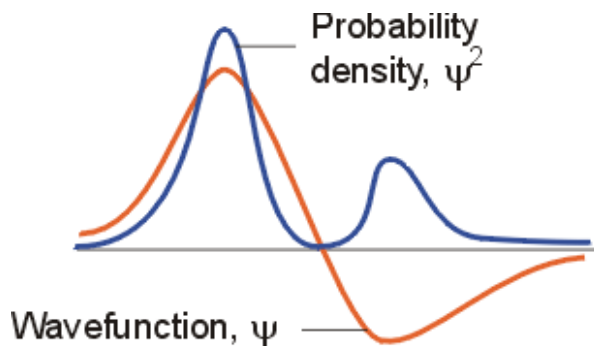
$$\Psi = R_{nl}(r) Y_{lm}(\theta, \phi)$$

$R_{nl}(r)$  – radial function

$Y_{lm}(\theta, \phi)$  – angular function



polar coordinates





Nodes: surfaces where there is 0 probability of finding an electron

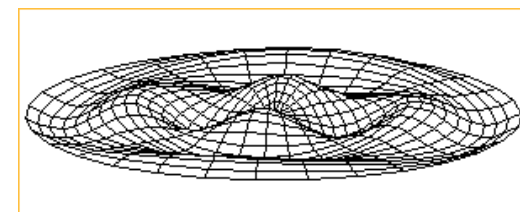
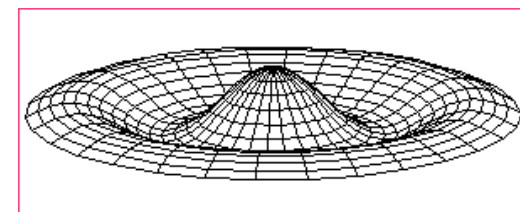
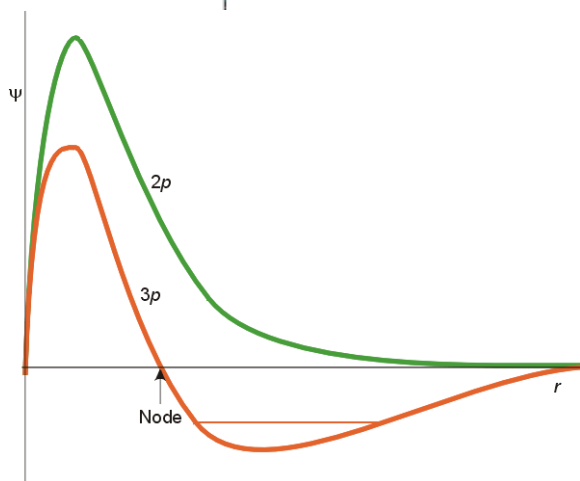
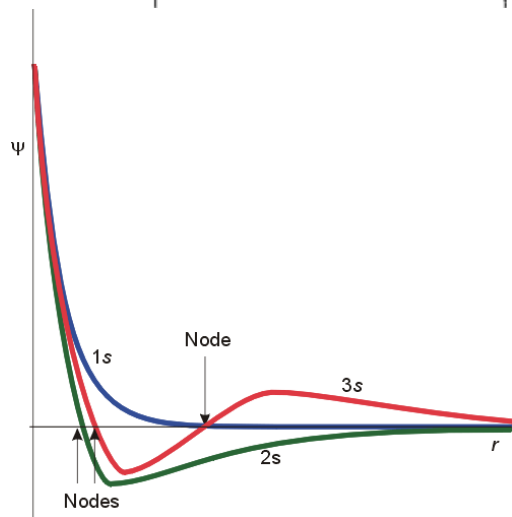
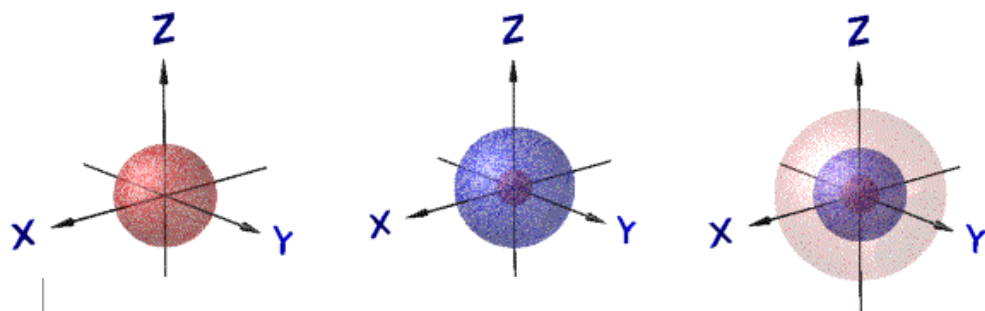
Number of nodes =  $n - 1$

Number of radial nodes =  $n - \ell - 1$

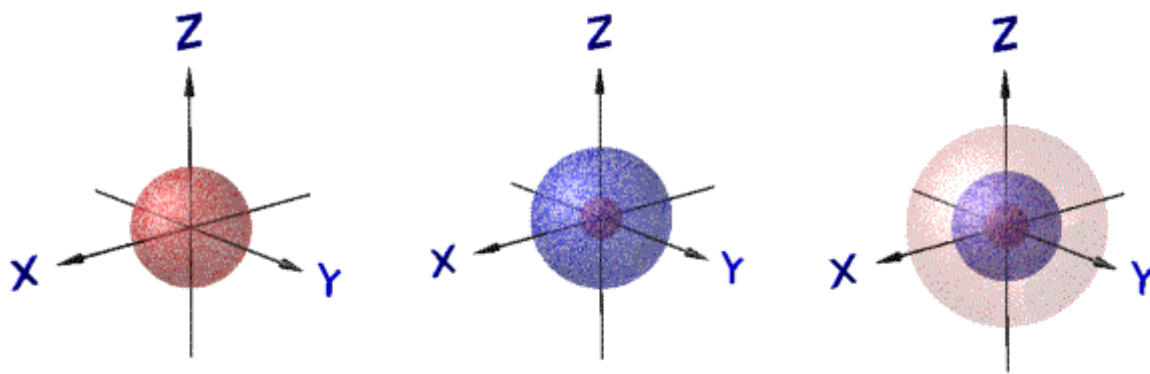
Number of angular nodes =  $\ell$       0 for s orbitals

1 for p orbitals

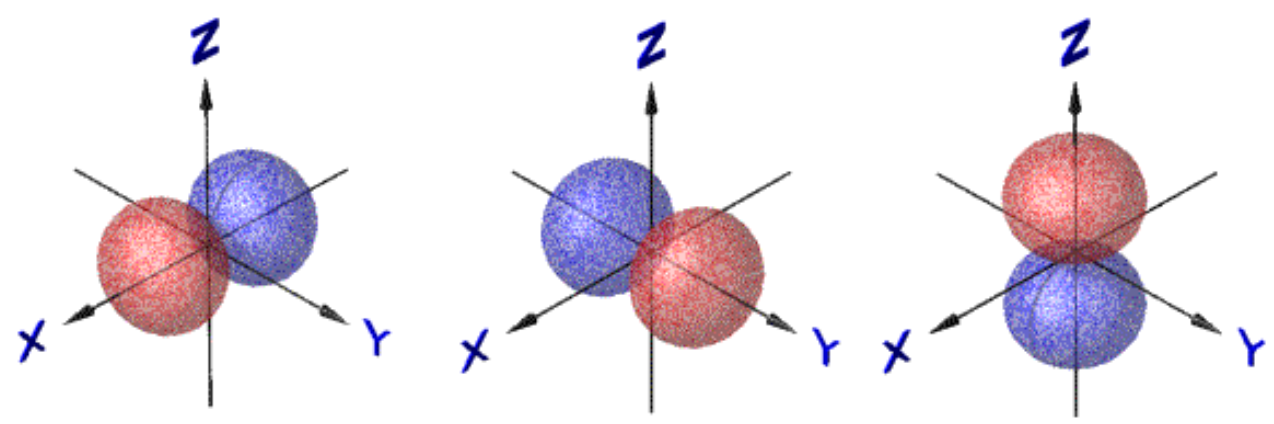
2 for d orbitals (except  $d_{z^2}$ )



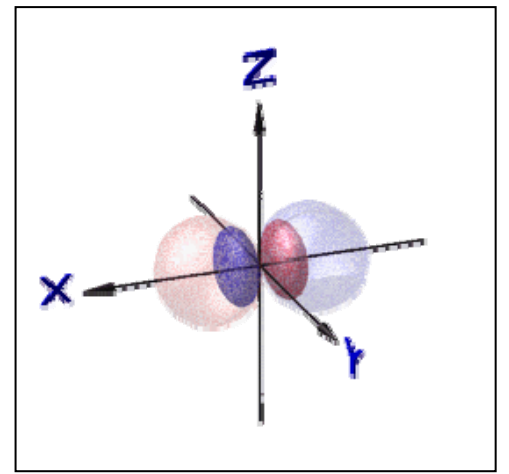
A website demonstrating nodes for 2D wavefunctions can be found at:  
<http://www.kettering.edu/~drussell/Demos/MembraneCircle/Circle.html>



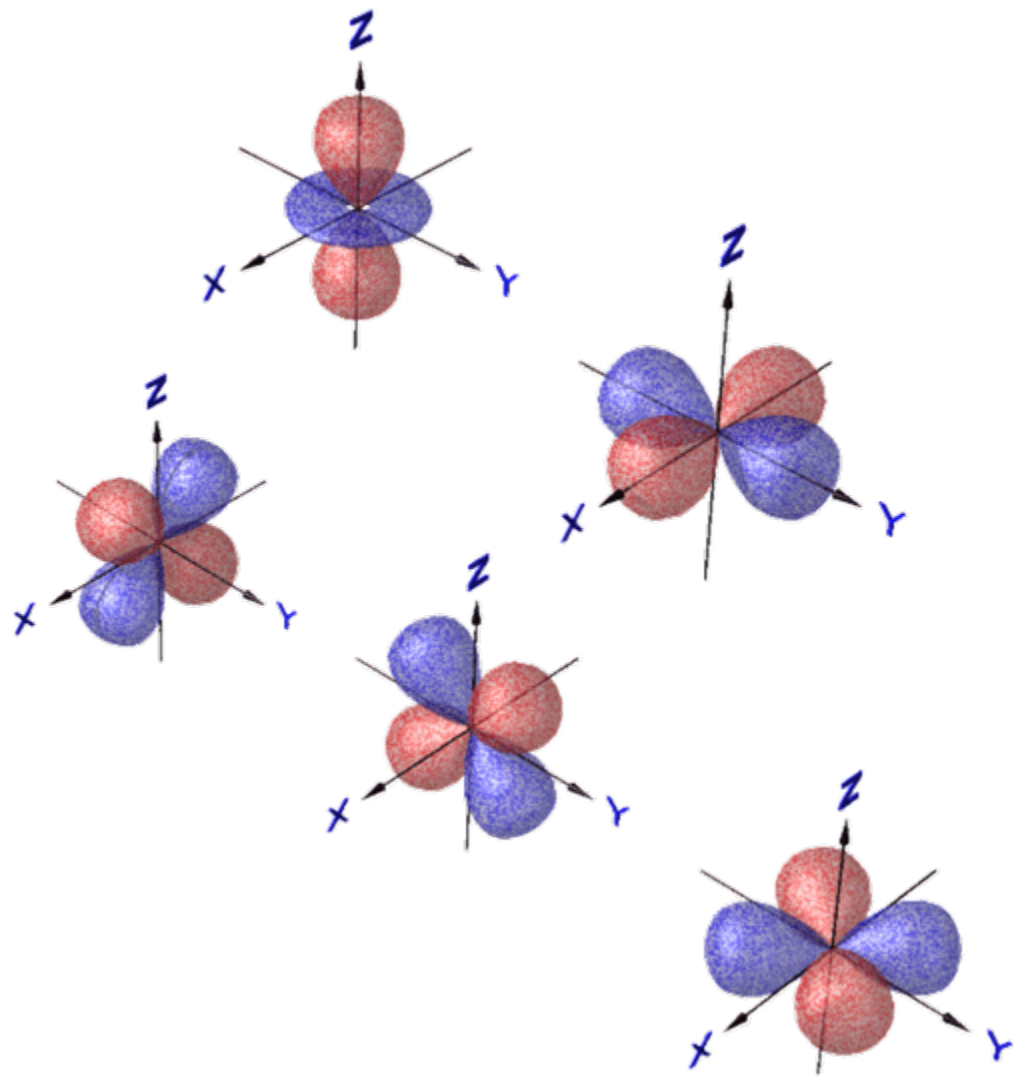
s orbitals



p orbitals



(the shading is backwards)



d orbitals

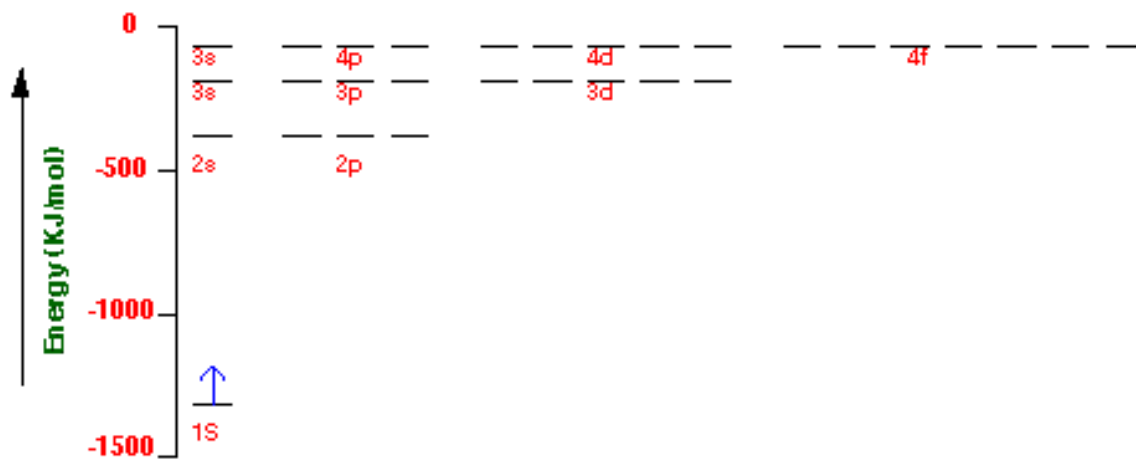
## Summary of quantum numbers needed for H:

$n \rightarrow$  **Energy** of shell:  $E_n = -\mathcal{R} \left( \frac{Z^2}{n^2} \right)$ , size:  $\text{radius}(n) = n^2 a_0$

$\ell \rightarrow$  type (degeneracy) of subshell: s(1), p(3), d(5), f(7) ....

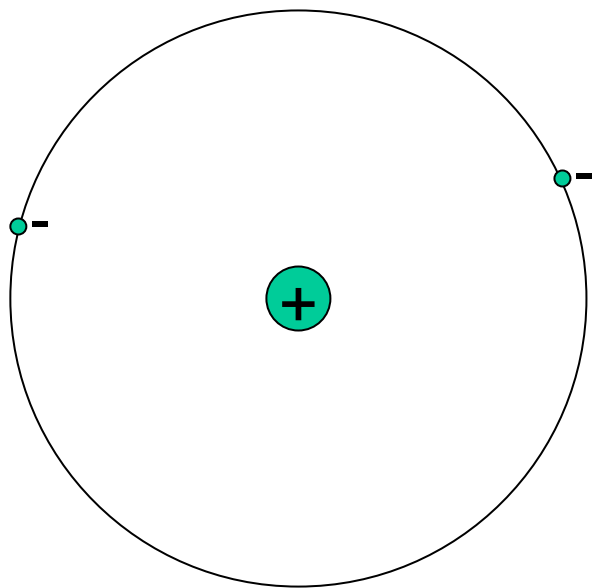
$m_\ell \rightarrow$  type and orientation of orbitals in a subshell

Energy level diagram:



## Many electron atoms

He,  $Z = 2$



$$E_n = -\mathcal{R} \left( \frac{Z^2}{n^2} \right)$$

$$E_1 = -\mathcal{R} \left( \frac{2^2}{1^2} \right)$$

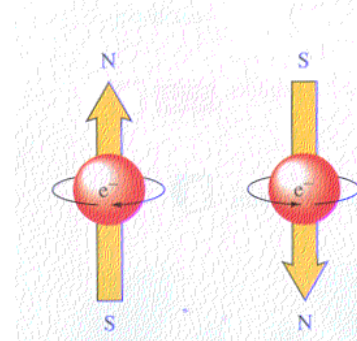
Predict:  $E_1 = -54.4 \text{ eV}$

Actual:  $E_1 = -24.6 \text{ eV}$

Something is wrong with the Bohr Model!

$m_s = \text{spin magnetic} \rightarrow \text{electron spin}$

$$m_s = \pm 1/2 \quad (-1/2 = \alpha) \quad (+1/2 = \beta)$$

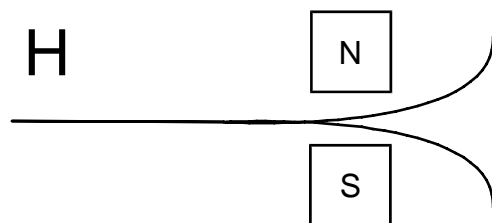


Pauli exclusion principle:

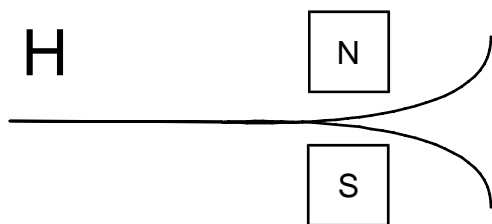
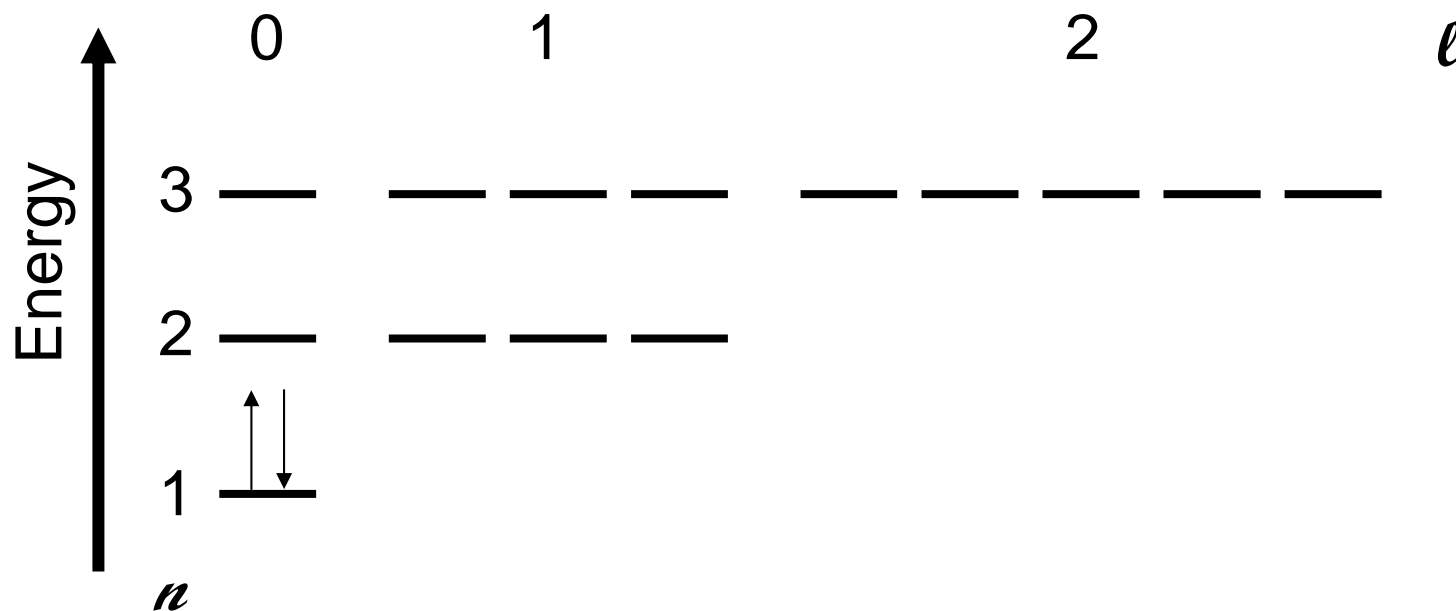
Each electron must have a unique set of quantum numbers.

*Two electrons in the same orbital must have opposite spins.*

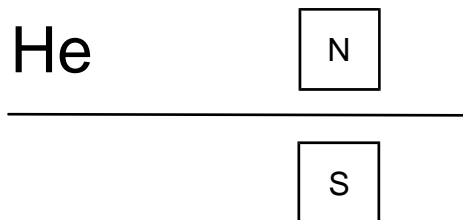
Electron spin is a purely quantum mechanical concept.



Energy level diagram for He. Electron configuration:  $1s^2$



paramagnetic – one (more) unpaired electrons



diamagnetic – all paired electrons

## Effective Nuclear Charge, $Z^*$

The presence of other electrons around a nucleus “screens” an electron from the full charge of the nucleus.

We can approximate the energy of the electrons by modifying the Bohr equation to account for the lower “effective” nuclear charge:

$$E_n = -\mathcal{R} \left( \frac{Z^{*2}}{n^2} \right)$$

$$Z^* = Z - \sigma$$

$Z^*$  is the effective nuclear charge

$Z$  is the atomic number

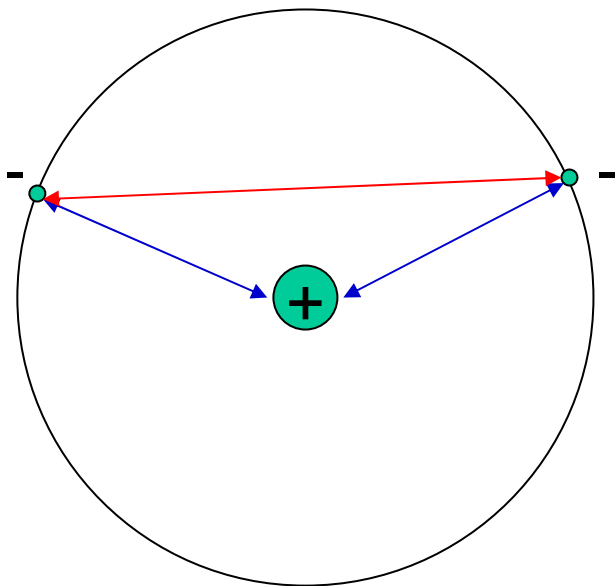
$\sigma$  is the shielding or screening constant



Helium ,  $Z = 2$

Predicted:  $E_1 = -54.4 \text{ eV}$

Actual:  $E_1 = -24.6 \text{ eV}$



$$E_n = -\mathcal{R} \left( \frac{Z^{*2}}{n^2} \right)$$

$$-24.6 = -13.6 \left( \frac{Z^{*2}}{1^2} \right)$$

$$Z^* = \sqrt{\frac{24.6 \times 1^2}{13.6}}$$

$$Z^* = 1.34$$

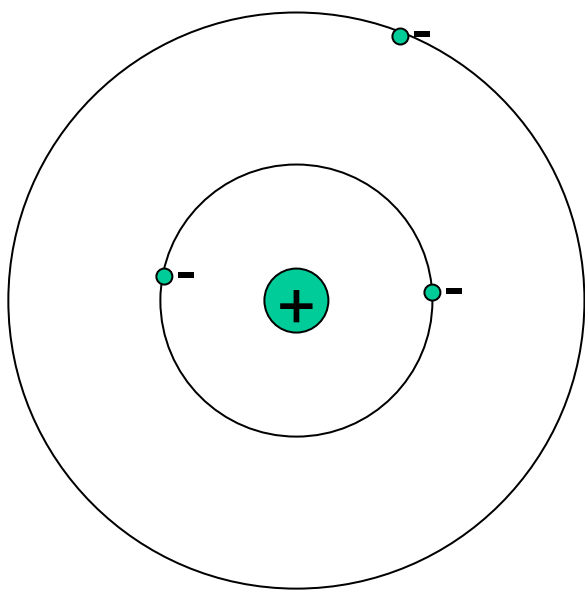
$$1.34 = 2 - \sigma$$

$$\sigma = 0.66$$

Lithium,  $Z = 3$

Predicted:  $E_2 = -30.6 \text{ eV}$

Actual:  $E_2 = -5.4 \text{ eV}$



$$E_n = -\mathcal{R} \left( \frac{Z^{*2}}{n^2} \right)$$

$$-5.4 = -13.6 \left( \frac{Z^{*2}}{2^2} \right)$$

$$Z^* = \sqrt{\frac{5.4 \times 2^2}{13.6}}$$

$$Z^* = 1.26$$

$$1.26 = 3 - \sigma$$

$$\sigma = 1.74$$

We want to be able to predict  $\sigma$  and  $Z^*$

Slater's rules for the prediction of  $\sigma$  for an electron:

1. Group electron configuration as follows:  
(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.
2. Electrons to the right (in higher subshells and shells) of an electron do not shield it.
3. If the electron of interest is an  $ns$  or  $np$  electron:
  - a) each other electron in the same group contributes 0.35 (0.30 for 1s)
  - b) each electron in an  $n-1$  group contributes 0.85
  - c) each electron in an  $n-2$  or lower group contributes 1.00
4. If the electron of interest is an  $nd$  or  $nf$  electron:
  - a) each other electron in the same group contributes 0.35
  - b) each electron in a lower group (to the left) contributes 1.00

Example with a valence electron on oxygen: O,  $Z = 8$

Electron configuration:  $1s^2 2s^2 2p^4$

a)  $(1s^2) (2s^2 2p^4)$

$$Z^* = Z - \sigma$$

b)  $\sigma = (2 * 0.85) + (5 * 0.35) = 3.45$

1s

2s,2p

$$Z^* = Z - \sigma$$

$$Z^* = 8 - 3.45 = 4.55$$

This electron is actually held with about 57% of the force that one would expect for a +8 nucleus.

Example with two electrons for nickel: Ni,  $Z = 28$

Electron configuration:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$

$(1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^8) (4s^2)$

$$Z^* = Z - \sigma$$

For a 3d electron:

$$\sigma = (18 * 1.00) + (7 * 0.35) = 20.45$$

$1s, 2s, 2p, 3s, 3p$ 
 $3d$

$$Z^* = Z - \sigma \quad Z^* = 28 - 20.45 = 7.55$$

For a 4s electron:

$$\sigma = (10 * 1.00) + (16 * 0.85) + (1 * 0.35) = 23.95$$

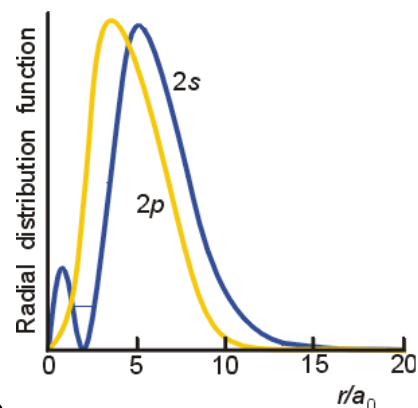
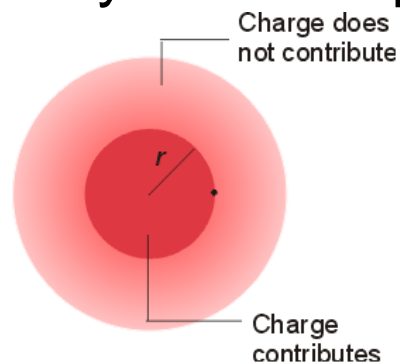
$1s, 2s, 2p$ 
 $3s, 3p, 3d$ 
 $4s$

$$Z^* = Z - \sigma \quad Z^* = 28 - 23.95 = 4.05$$

The basis of Slater's rules for  $\sigma$

s and p orbitals have better "penetration" to the nucleus than d (or f) orbitals for any given value of  $n$

i.e. there is a greater probability of s and p electrons being near the nucleus

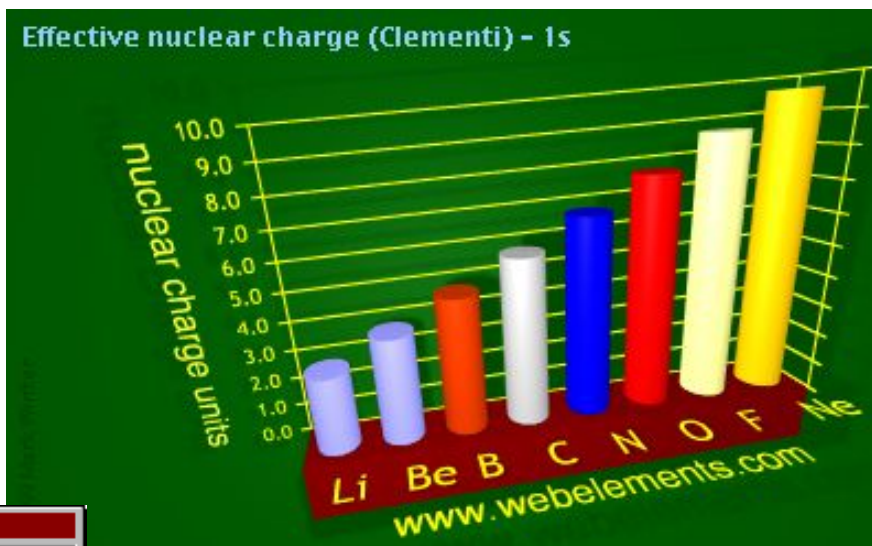
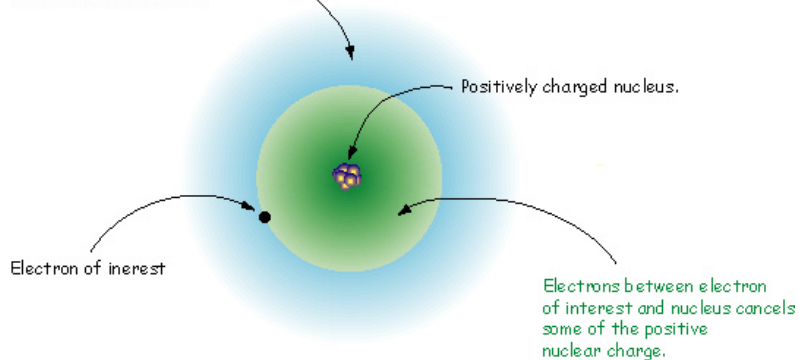


This means:

1.  $ns$  and  $np$  orbitals completely shield  $nd$  orbitals
2.  $(n-1)$  s and p orbitals don't completely shield  $n$  s and p orbitals

# Chem 59-250 Periodicity of Effective Nuclear Charge

Electrons outside have no effect on effective nuclear charge for electron of interest.



**WebElements**

**Effective nuclear charge (Clementi) - 1s [nuclear charge units] coded by intensity of red**

H																	He																												
Li	Be											B	C	N	O	F	Ne																												
Na	Mg											Al	Si	P	S	Cl	Ar																												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																												
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																												
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo																												
<table border="1"> <tr> <td>La</td><td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td> </tr> <tr> <td>Ac</td><td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td> </tr> </table>																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																																
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																																

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## Z\* on valence electrons

K 4133		Kh 4198
Ol 4163	Eh 41<8	Qh 81;8
Qd 5153	Pj 51;8	Du 91:8
N 5153	Fd 51;8	Nu ;158
Ue 5153	Vu 51;8	[h ;158
Fv 5153	Ed 51;8	Uq ;158

E 5193	F 6158	Q 61<3	R 7188	I 8153	Qh 81;8
Do 6183	Vl 7148	S 71;3	V 8178	Fo 9143	Du 91:8
Jd 8133	Jh 8198	Dv 9163	Vh 91<8	Eu :193	Nu ;158
Iq 8133	Vq 8198	Ve 9163	Wh 91<8	L :193	[h ;158
Wo 8133	Se 8198	El 9163	Sr 91<8	Dw :193	Uq ;158

## Shielding and Effective Nuclear Charge

**The energy of valence electrons in an atom/ion changes with the loss or addition of an electron.**

Slater's rules are only approximate and can give poor predictions. For example:

They ignore the differences in penetration between s and p orbitals. Real s and p orbitals do not have the same energy.

They assume that all electrons in lower shells shield outer electrons equally effectively.

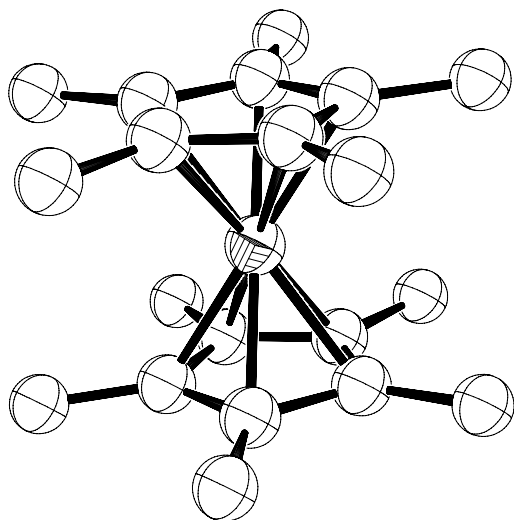
$Z^*$  can be used to estimate ionization energy:

$$\Delta H_{ie} = 13.6 \left( \frac{Z^{*2}}{n^2} \right)$$

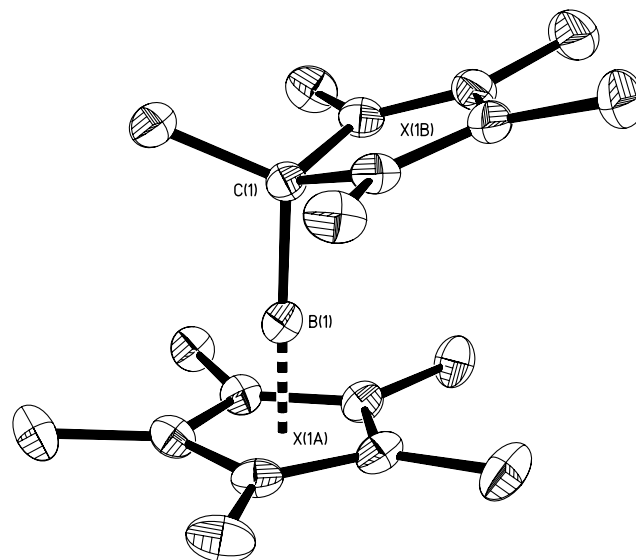


## Shielding and Effective Nuclear Charge

Effective nuclear charge can be used to rationalize properties such as the size of atoms and ions.



$\text{Cp}^*_2\text{Be}$



$\text{Cp}^*_2\text{B}^+$

Be and  $\text{B}^+$  are *isoelectronic* ( $1s^2 2s^2$ ) but very different because of effective nuclear charge.