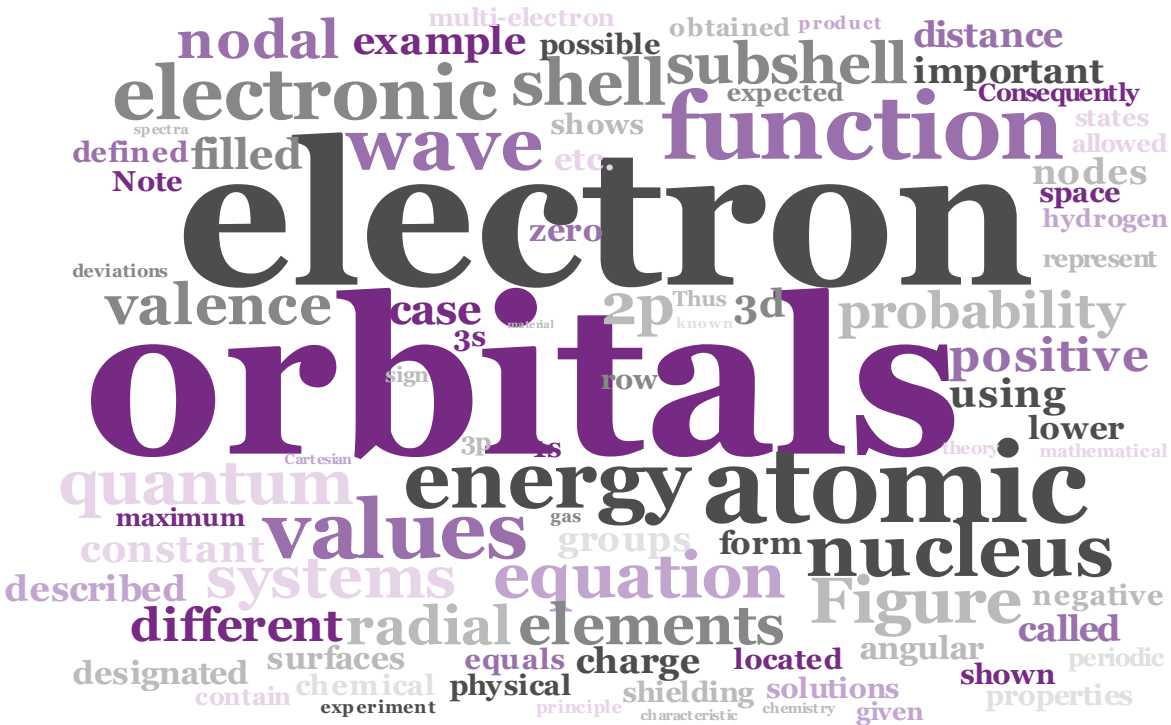


# Electronic structure of atoms



# Electronic Structure: Orbitals

- The atomic *orbitals* are wave functions (a mathematical expressions or functions describing a wave,  $\Psi$ ) obtained as solutions of the Schrödinger equation ( $\hat{H}\Psi = E\Psi$ )
- Each orbital has three quantum numbers associated with it:

- **Principal ( $n$ )**: determines the allowed orbital energy:

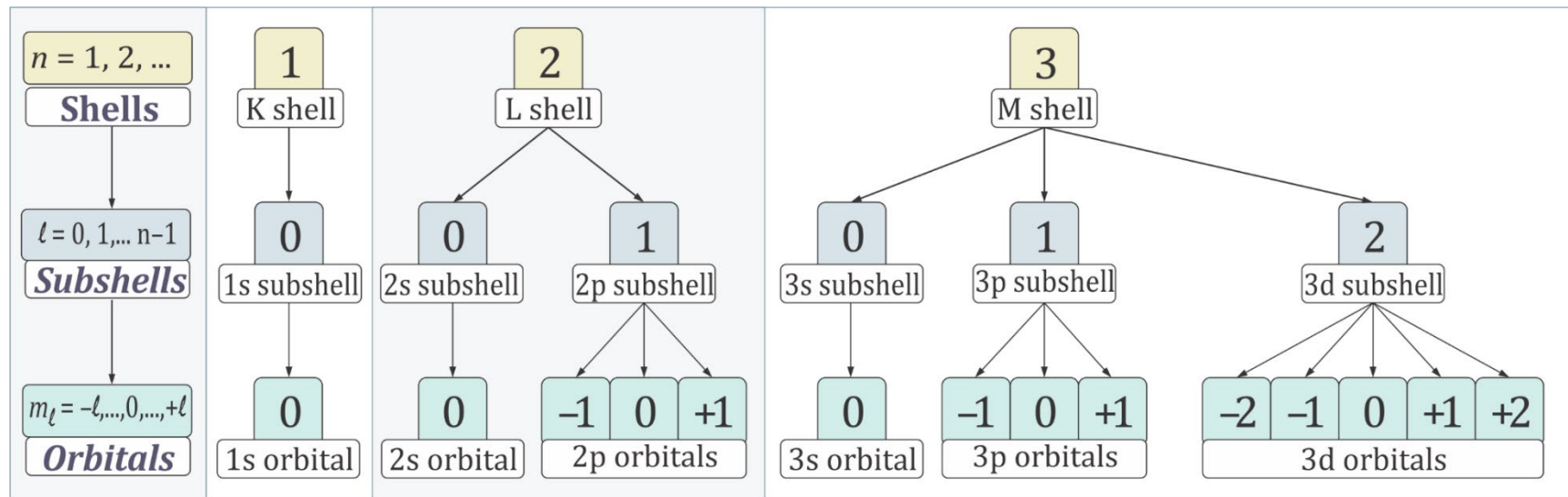
$$E_n = -\frac{hcRZ^2}{n^2} \quad \text{where } h - \text{Planck constant, } c - \text{speed of light in vacuum and } R - \text{Rydberg constant}$$

- **Orbital angular momentum ( $\ell$ )**: determines the orbital shape and total angular momentum
- **Magnetic ( $m_\ell$ )**: determines the number of orbitals for each  $\ell$ , and provides the information about the directionality (orientation) of an atomic orbital

- The relationship between quantum numbers:

$$n > 1; \ell = 0, \dots, n - 1; -\ell \leq m_\ell \leq +\ell$$

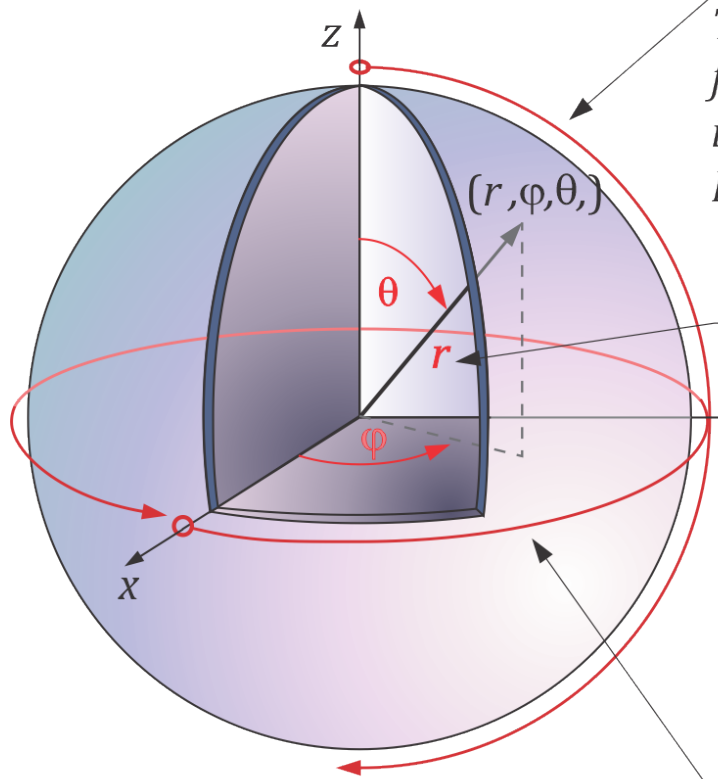
# Shells, subshells and orbitals



- The orbitals with the same quantum number  $n$  belong to the same *shell*.
  - In hydrogen-like systems (have only one electron) all orbitals with the same  $n$  (in the same shell) have the same energy.
- Each shell can have one or more *subshells* distinguished by quantum number  $\ell$ 
  - Subshells are designated by letters  $s$  ( $\ell = 0$ ),  $p$ , ( $\ell = 1$ ),  $d$  ( $\ell = 2$ ) etc.
- A subshell with quantum number  $\ell$  consists of  $2\ell + 1$  *orbitals*

# Cartesian vs. spherical coordinates

- For practical reasons,  $\Psi$  is expressed as a function of spherical coordinates:



The polar angle ( $\theta$ ) is measured from the positive end of the z-axis ; it can have values from 0 to  $\pi$ . Every point on z axis has  $\theta = 0$ .

Radial distance ( $r$ ) is the distance from the origin

The azimuth angle ( $\phi$ ) is measured counterclockwise along the sphere's equator starting from the x-axis; it can have values from 0 to  $2\pi$ . Each point on x-axis has  $\phi = 0$ .

$$r^2 = x^2 + y^2 + z^2$$

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

# Orbitals as wave -functions

The wave functions ( $\Psi$ , the solutions of the Schrödinger equation) can be written as products of a radial function (component) and angular function (component):

$$\underbrace{\Psi_{nlm_\ell}}_{\text{a wave function}} = \underbrace{R_{nl}(r)}_{\substack{\text{a radial component} \\ \text{(f-tion of } r \text{ only)}}} \times \underbrace{Y_{\ell m_\ell}(\theta, \phi)}_{\substack{\text{an angular component} \\ \text{(f-tion of 2 angles)}}$$

The regions where wave functions have zero value ( $\Psi = 0$ ) are called *nodes*:

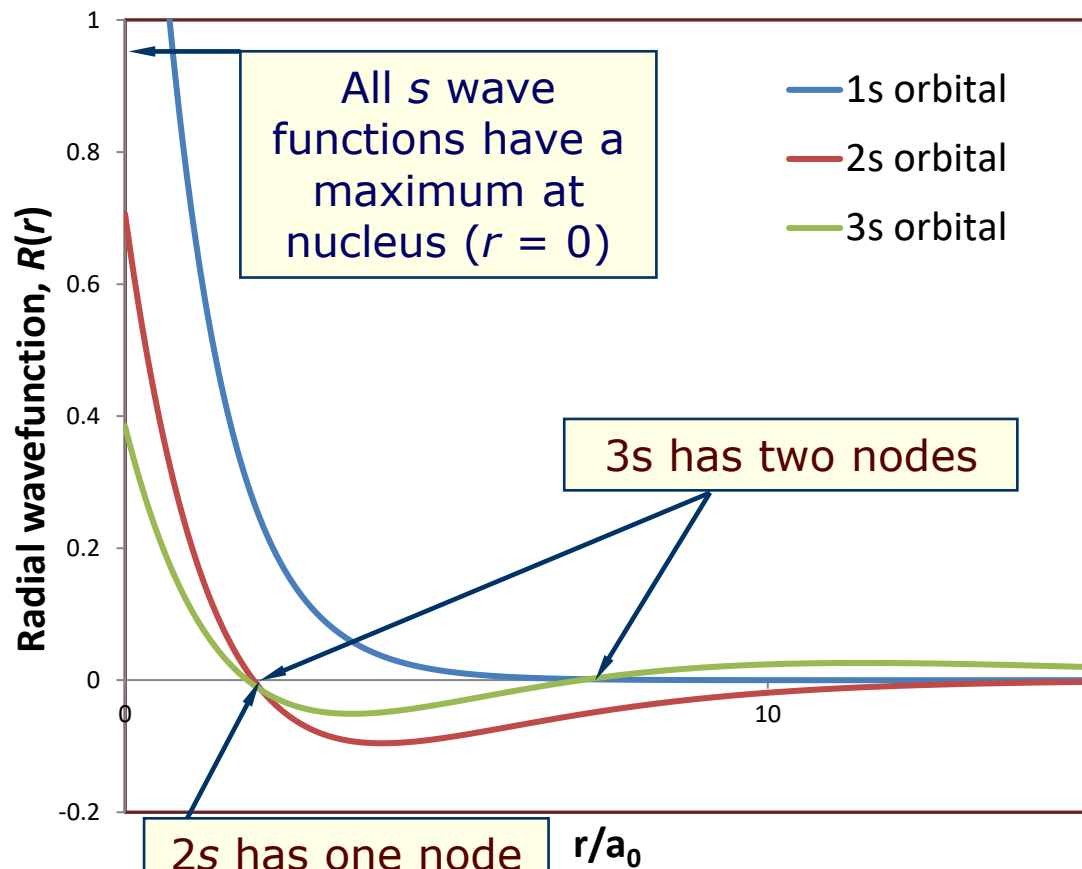
- When the radial component equals zero ( $R_{nl}(r) = 0$ ), the wave function has a *radial node* (radial nodes are spherical in shape)
- When the angular component equals zero ( $Y_{\ell m_\ell}(\theta, \phi) = 0$ ), the wave function has an *angular node* (angular nodes are planes or cones).

# Graphical representation of orbitals

- A wave function has no physical meaning, but the square of wave function ( $\Psi^2$ ) has: it represents a probability of finding an electron inside any given volume.
- The orbitals are graphically represented with *boundary surfaces*:
  - Boundary surfaces define a region of space within which there is a high probability (usually 90% or 95%) of finding the electron.
  - Keep in mind that *theoretically* an electron can be anywhere between the atomic nucleus and infinity!
- The overall orbital shape is in function of quantum number  $\ell$ .
- Nodes can further ‘cut’ each orbital into lobes:
  - Total number of nodes =  $n - 1$
  - Number of angular nodes =  $\ell$
  - Number of radial nodes =  $n - 1 - \ell$ .

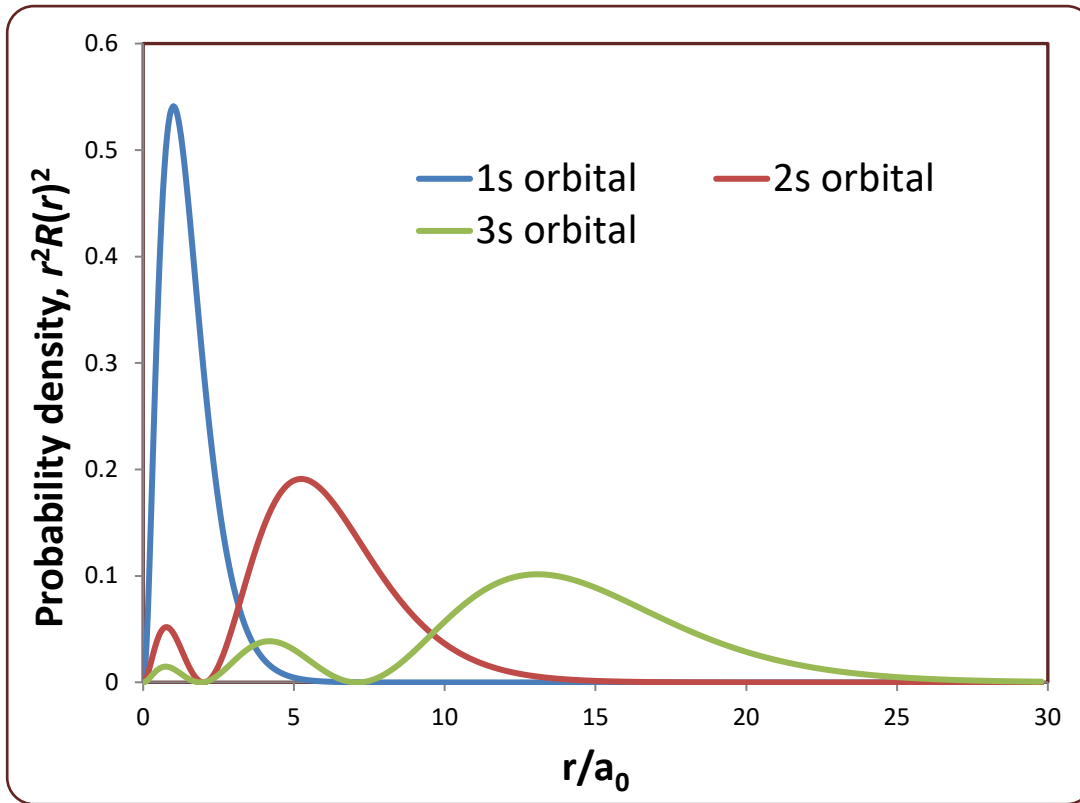
# A look at s orbitals

- All s orbitals have angular component equal to 1 (they are not in function of angles, just on  $r$ ): they are spherically symmetric
- The s orbitals have no angular nodes (since  $\ell = 0$ ) but have radial nodes for  $n > 1$

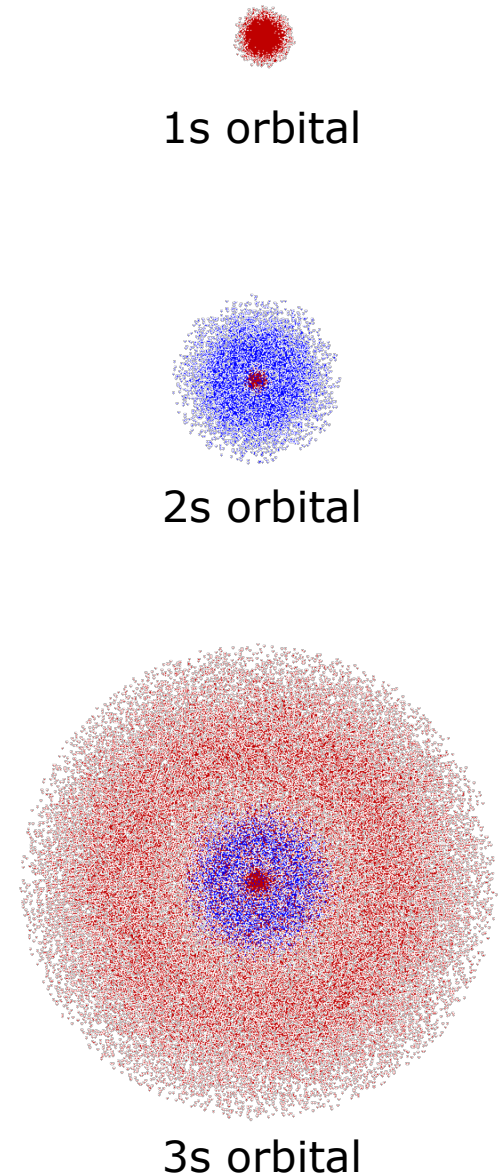


$$a_0 = 5.292 \times 10^{-11} \text{ m}$$

# A look at s orbitals (cont.)



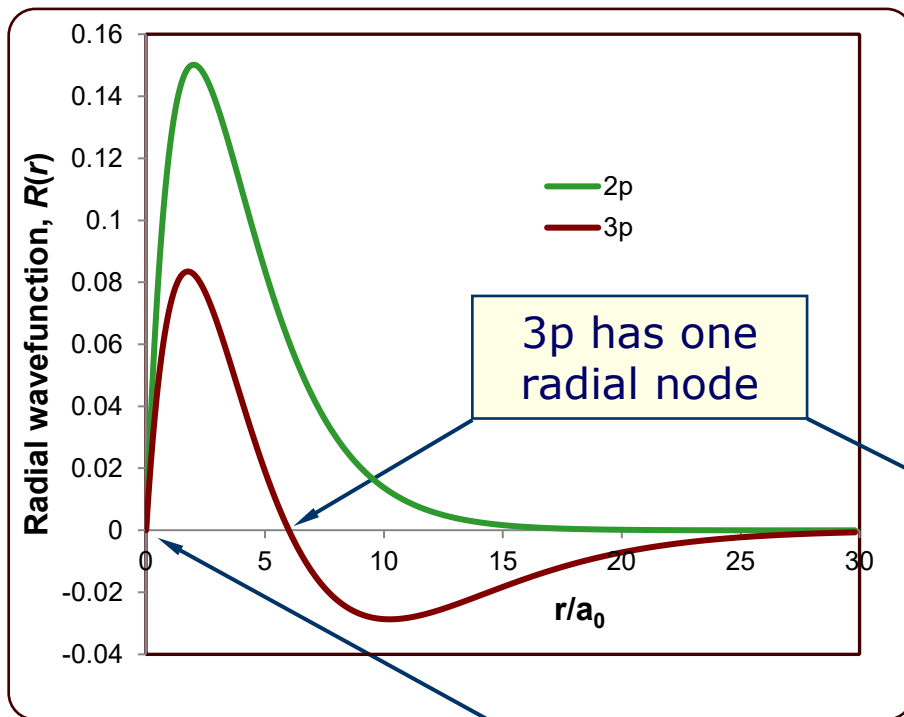
One way of graphically representing the orbitals is shown on the left: the number of dots is proportional to the probability.



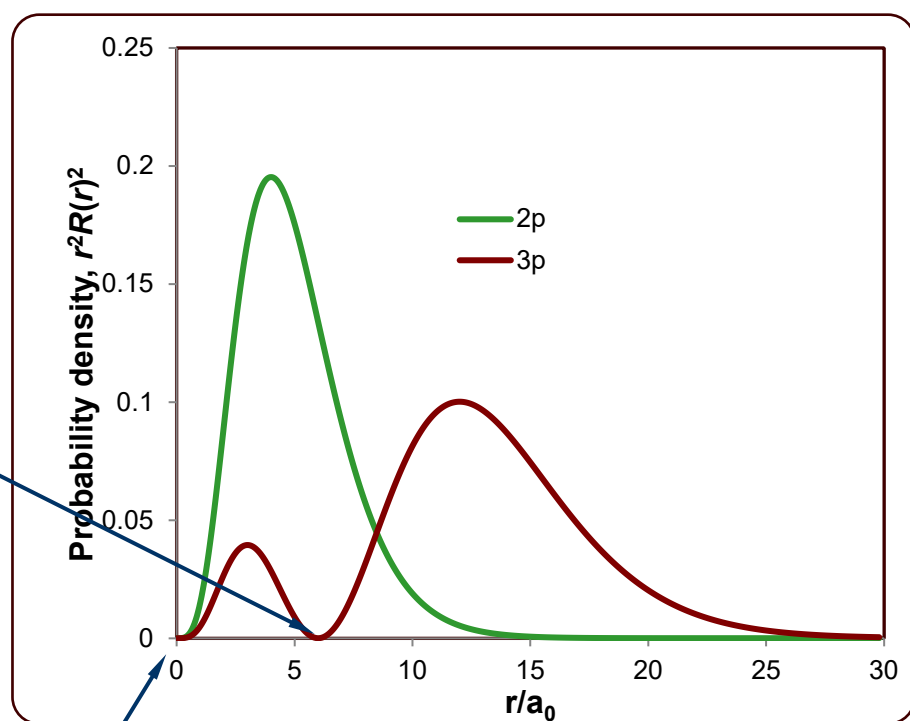


# A look at p orbitals

## Radial wavefunctions

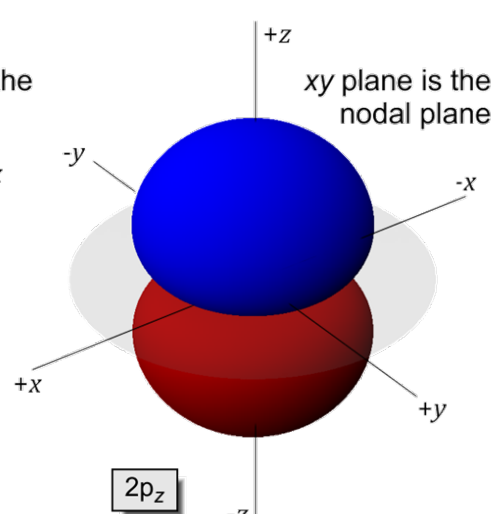
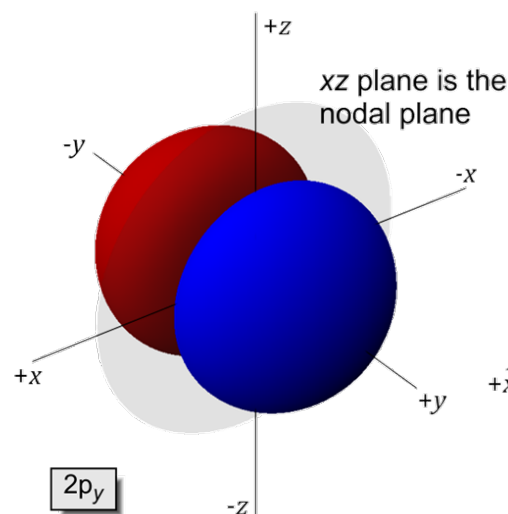
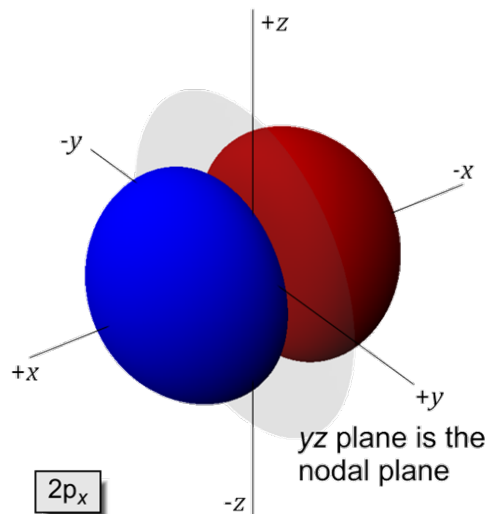


## Probability density

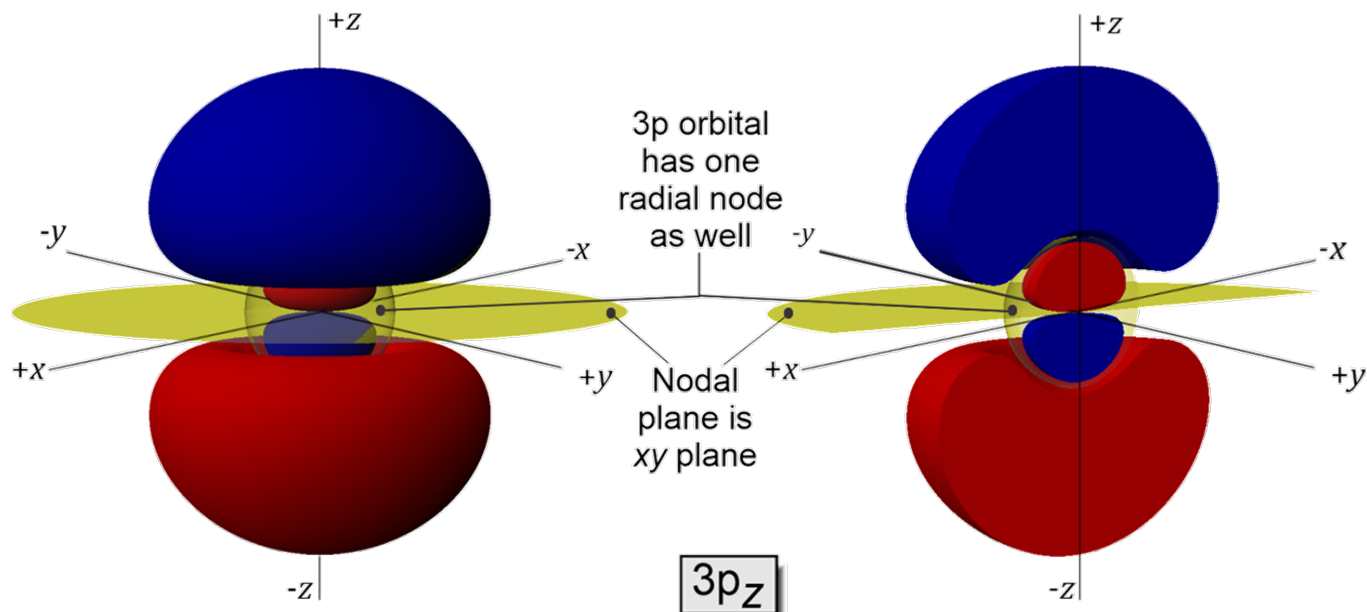


# A look at p orbitals (cont.)

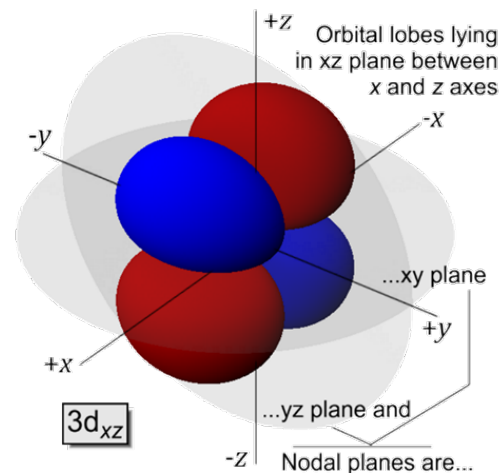
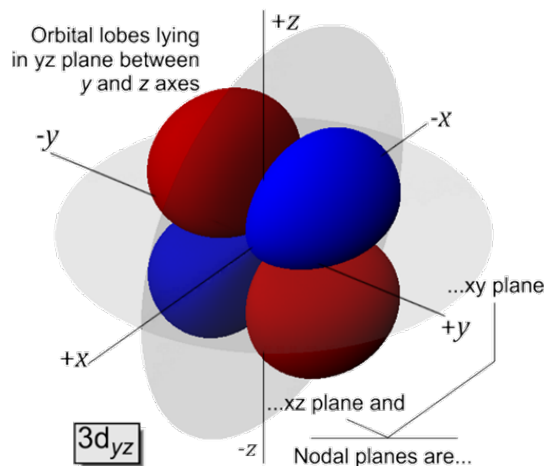
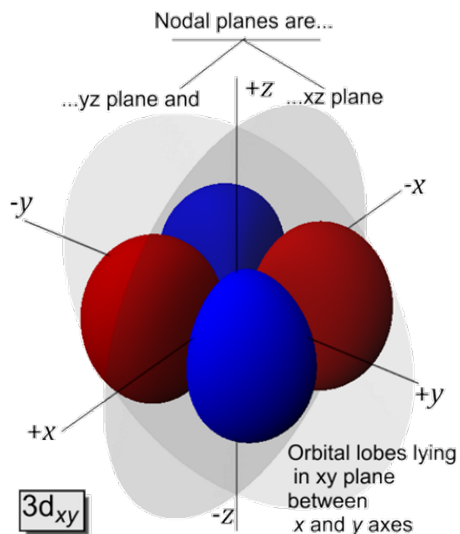
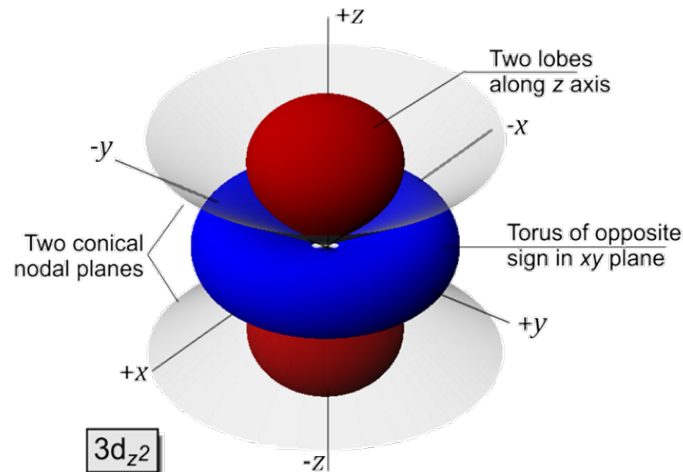
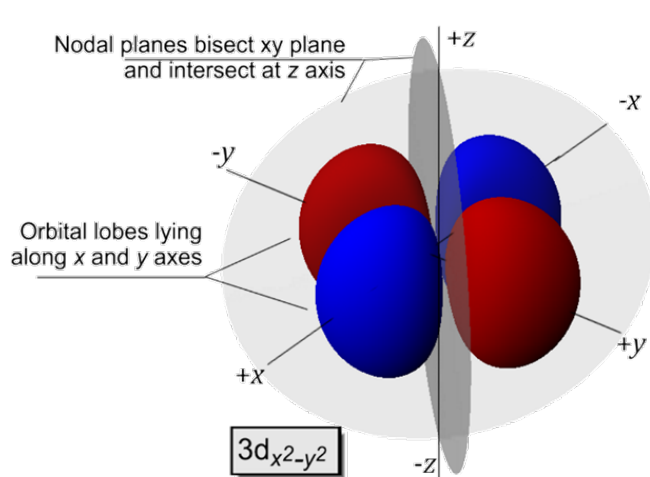
Boundary surfaces and angular node for  $2p$  atomic orbitals



Boundary surface and nodes for  $3p_z$  atomic orbital



# A (quick) look at d orbitals



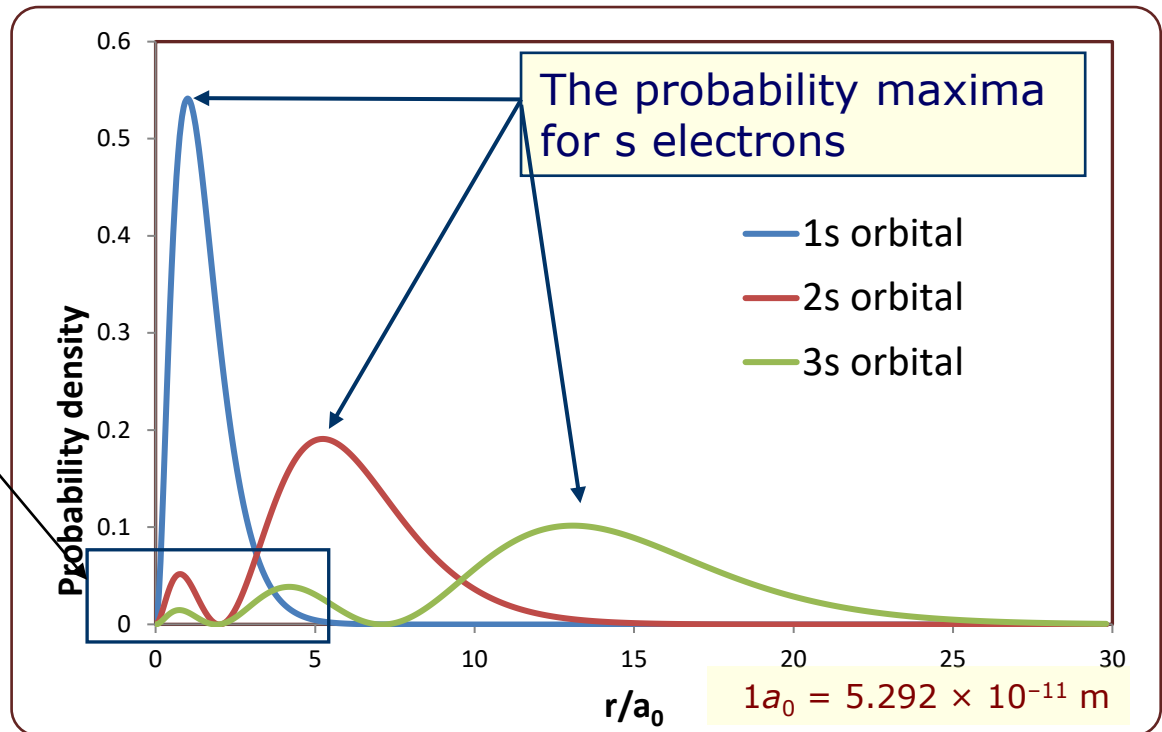
# The electron spin

- Spin is a propriety of an electron (i.e. an electron always has spin regardless whether it is free, or placed in an atom):
  - Spin quantum number ( $s$ ): dictates the magnitude of the spin angular momentum vector and has a value of  $\frac{1}{2}$ .
  - Magnetic spin quantum number ( $m_s$ ): determines the direction of the spin angular momentum vector;  $m_s$  has values of  $-\frac{1}{2}$  (spin vector 'down') and  $+\frac{1}{2}$  (spin vector 'up').
- The electron in an atomic orbital is defined by a unique set of four quantum numbers:  $n$ ,  $\ell$ ,  $m_\ell$  and  $m_s$ .

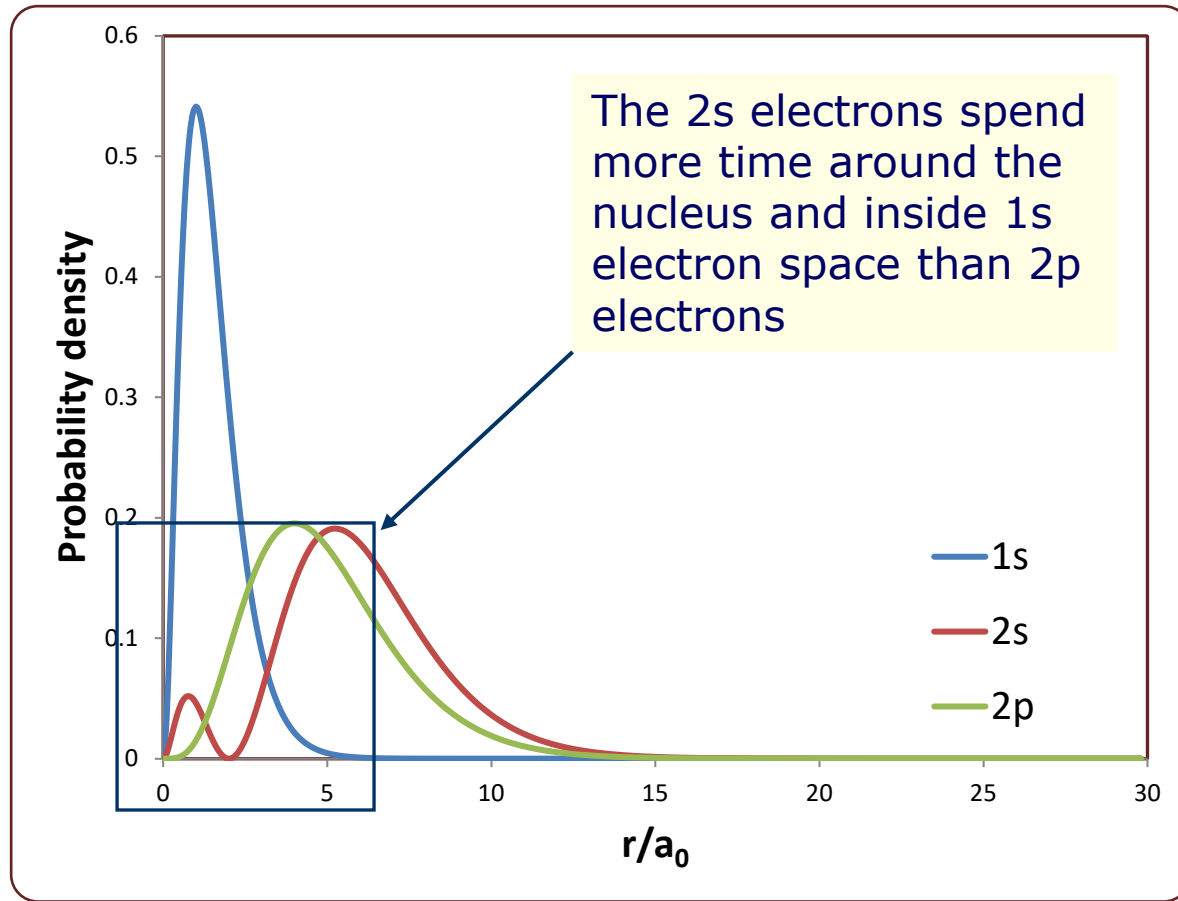
# Many-electron atoms: Penetration

- We cannot exactly solve the Schrödinger equation for many-electron atoms (not even for He atom with only two electrons!).
- What we know is based mostly on experimental data and significant approximations in calculations: these show that it is reasonable to approximate many-electron atomic orbitals (their shapes, nodes energies, etc.) with hydrogen orbitals.

**Penetration:** The presence of an electron(s) inside orbitals of other electrons (i.e. 3s electrons inside 2s and 1s; 2s inside 1s).



# Many-electron atoms: Penetration (cont.)



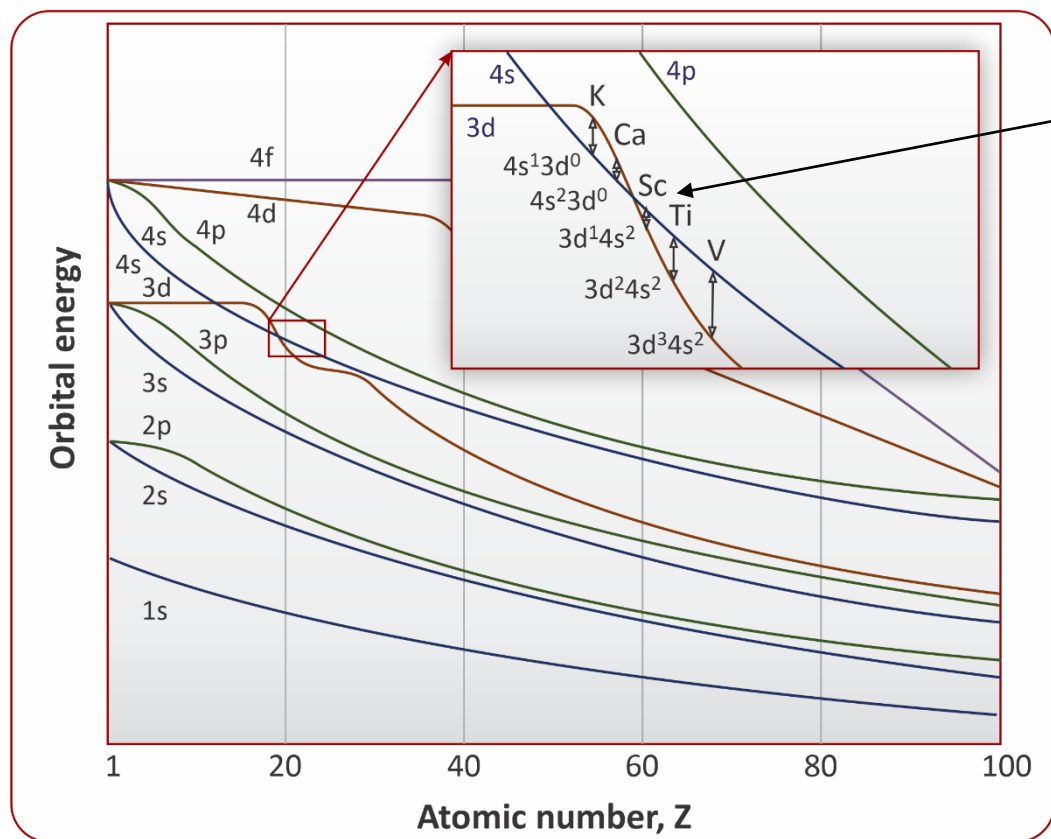
- As a consequence 2s electrons are more stable than 2p electrons (lower in energy!)

# Many-electron atoms: Filling the orbitals

- Only two electrons can be placed in one orbital (**Pauli exclusion principle**)
- The shell  $n = 1$  has only one orbital (1s) and thus can accommodate only two electrons (H and He)
- Lithium has one electron more which has to go in shell with  $n = 2$ ; but where: 2s or 2p?
- As we have seen electrons in 2s orbitals can get closer to the nucleus than electrons in 2p orbitals:
  - ☛ *Consequence:* 2s orbital is lower in energy than 2p and the third electron in Li atom occupies 2s *not* 2p
- The order of filling is:  $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p$
- Everything seems fine until we reach...

## ...potassium

- The 19<sup>th</sup> electron in potassium atom 'unexpectedly' occupies 4s orbital instead of the 'expected' 3d orbital because for K and Ca, 3d orbitals (red line on the plot below) is higher in energy than 4s (blue line).



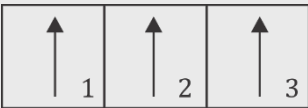
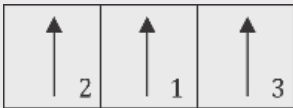


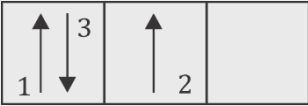
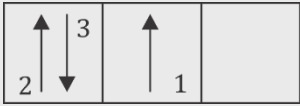
After Ca 3d 'goes' below 4s!

4s orbital is more stable (= lower in energy) than 3d orbital because 4s electrons spend significant time around the nucleus and experience higher effective nuclear charge.



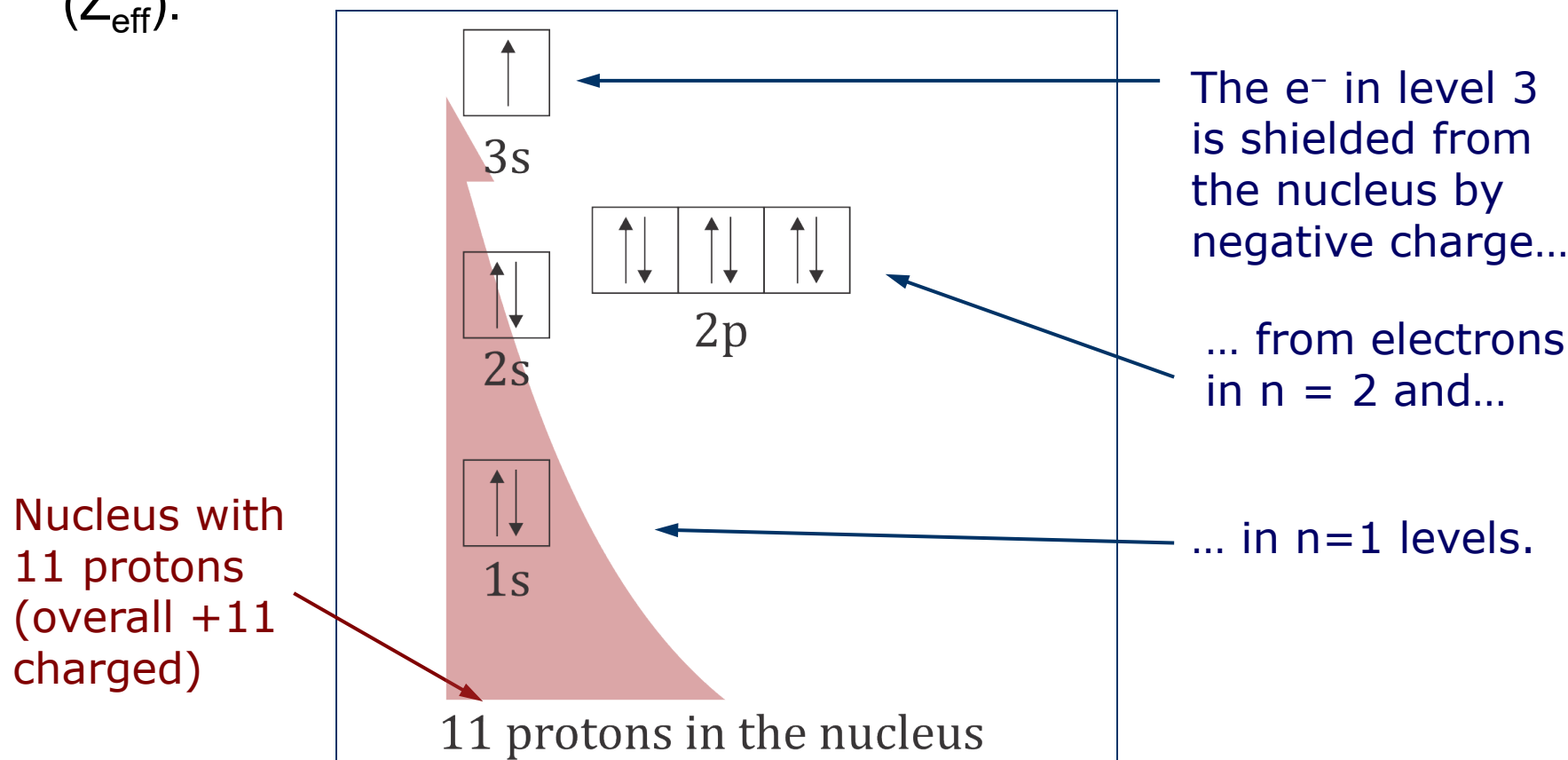
# Many-electron atoms: Hund's rule

- **Hund's rule:** One of the most stable distributions of electrons among degenerate orbitals is obtained if each orbital is initially occupied with one electron and the spins are kept parallel. Once when each orbital contains one electron, the electrons can be paired with antiparallel spins.
- The reason behind this rule is **exchange energy ( $K$ )**: stabilizing energy gained whenever we can exchange two electrons with *parallel* spins.
  - For example, N has three unpaired electrons in p orbitals (i.e.  $2p_x^1 2p_y^1 2p_z^1$ ) because this configuration is more stable than one electron pair and one unpaired electron ( $2p_x^2 2p_y^1 2p_z^0$ ) for  $2K$ :

Starting point	1 ↔ 2	1 ↔ 3	2 ↔ 3	Total
				-3K
				-K

# Many-electron atoms: Shielding

- The electrons in upper energy levels are *shielded* from the nucleus by electrons in lower energy levels.
- Because of this shielding, the electrons in levels  $n > 1$  experience a decreased nuclear charge called the *effective nuclear charge* ( $Z_{\text{eff}}$ ).



# Slater's Rules

- Slater's rules are used to approximate  $Z_{\text{eff}}$ :  $Z_{\text{eff}} = Z - \sigma$  ( $Z_{\text{eff}}$  = effective nuclear charge,  $Z$  = atomic number [number of protons],  $\sigma$  = screening, Slater or shielding constant).

## Determining $\sigma$ :

- Write the electron configuration of the element and group the subshells as follows:  
(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p),...
- Electrons in the groups on the right from the designated electron contribute nothing to the shielding constant.
- If the designated electron is in one of the ( $ns$ ,  $np$ ) groups, then other electrons in the *same* group contribute 0.35 each to the  $\sigma$  value, all electrons in  $n - 1$  shell contribute 0.85 each while those in  $n - 2$  contribute 1 each.
- If the designated electron is in one of the  $nd$  or  $nf$  groups, then each electron on the left side of the group contributes 1.00 to the shielding constant.

# Slater rules and potassium's 19<sup>th</sup> electron

- Calculate the  $Z_{\text{eff}}$  for the 4s electron (= the designated electron) in potassium atom!
- **Step 1:** write down full electronic configuration:
- **Step 2:** Group the subshells in (ns np), (nd) & (nf) groups:
- **Step 3<sub>a</sub>:** Calculate  $\sigma$ :
  - ▶ Ignore all electrons on the right side of the designated electron (*there are none here*)
  - ▶ Other electrons in the same group contribute 0.35 to  $\sigma$  (*there are no other electrons in this group = contribution 0*)
  - ▶ All electrons in the  $n - 1$  group contribute 0.85 to  $\sigma$  (*there are 8 electrons in  $4 - 1 = 3$  group contributing  $8 \times 0.85 = 6.8$* ):

# Slater Rules and Potassium's 19<sup>th</sup> Electron (cont.)

- ▶▶ All electrons in the  $n - 2$  group and below contribute 1.00 to  $\sigma$   
(*there are 10 such electrons contributing  $10 \times 1.00 = 10.00$  to  $\sigma$* )

- **Step 4:** Sum the contributions to obtain  $\sigma$ :

$$\sigma = 0 + 6.8 + 10.00 = \mathbf{16.80}$$

- **Step 5:** Calculate  $Z_{\text{eff}}$

$$Z_{\text{eff}} = Z - \sigma = 19 - 16.80 = \mathbf{2.20}$$

- In other words, the charge experienced by a 4s electron in potassium atom is about +2 and *not* +19 (full nuclear charge).
- What happens if....

# Slater rules and potassium's 19<sup>th</sup> electron (cont.)

- ...we place the 19<sup>th</sup> electron in 3d not in 4s?
- **Step 1:** write down full electronic configuration:
- **Step 2:** Group the subshells in (*ns np*), (*nd*) & (*nf*) groups:
- **Step 3b:** Calculate  $\sigma$ :
  - ▶ Ignore all electrons on the right side of the designated electron (*there are none here*)
  - ▶ Other electrons in the same group contribute 0.35 to  $\sigma$  (*there are no other electrons in this group = contribution 0*)
  - ▶ All electrons in the groups on the left side contribute 1.00 to  $\sigma$  (*there are 18 such electrons:  $18 \times 1.00 = 18.00$* )
- **Steps 4 & 5:** Calculate  $\sigma$  and  $Z_{\text{eff}}$ :

$$\sigma = 0 + 18.00 = 18.00; Z_{\text{eff}} = 19 - 18.00 = \mathbf{1.00}$$

# Overview: Electronic structure of atoms

- Electrons:
  - Quantum numbers;
  - Nodes, penetration and orbital shapes;
  - Effective nuclear charge and the Slater rules (calculating  $Z_{\text{eff}}$ )
  - Orbital energies.

# Readings and problems

## ✓ Readings:

- If you have 6<sup>th</sup> ed. Chapter 1 “The structures of Hydrogenic Atoms” up to 1.7 Atomic properties (pp. 3 – 22)
- If you have 7<sup>th</sup> ed. Chapter 1 “The structures of Hydrogenic Atoms” up to 1.7 Atomic properties (pp. 7 – 23)
- Recommended: pdf file provided on Quercus

## ✓ Problems:

- For 6<sup>th</sup> ed:
  - In- text Examples and self-tests: 1.2 (p. 11), 1.3 (p. 12), 1.4 (p. 13), 1.5 (p. 19), 1.6 (p. 20) & 1.7 (p. 22).
  - End-of-chapter Exercises: 1.9 – 1.15, 1.18, 1.24 – 1.26
- For 7<sup>th</sup> ed:
  - In- text Examples and self-tests: 1.2 (p. 11), 1.3 (p. 13), 1.4 (p. 13), 1.5 (p. 16), 1.6 (p. 18), 1.7 (p. 20) & 1.8 (p. 23)
  - End-of-chapter Exercises: 1.9 – 1.15, 1.18, 1.24 – 1.26