

## Electron Configuration and Chemical Periodicity

### The Periodic Table

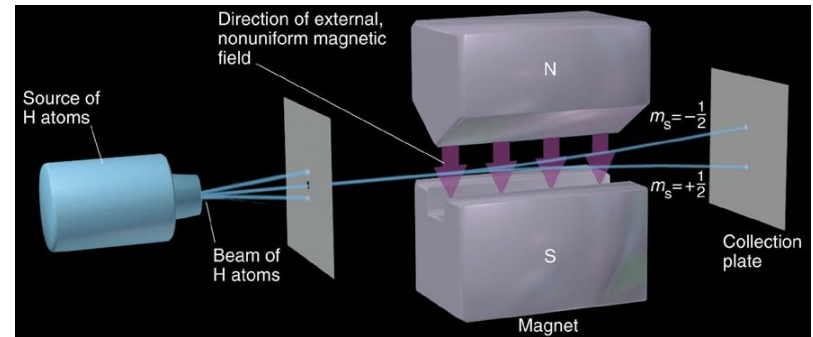
- **Periodic law (Mendeleev, Meyer, 1870)** – periodic reoccurrence of similar physical and chemical properties of the elements arranged by increasing **atomic mass**
  - Periodic table included the 65 known elements
  - Mendeleev left blank spaces for the undiscovered elements and was able to predict their properties
  - The true basis of periodicity is the **atomic number** not the atomic mass (Mosley, 1913)

### 8.1 Many-Electron Atoms

- Only approximate solutions of the Schrödinger equation are available
- Electron-electron interactions are important
- The same three quantum numbers ( $n$ ,  $l$  and  $m_l$ ) are used to describe the solutions (the orbitals are hydrogen-like)

#### The Electron Spin

- The electron can be viewed as a ball of spinning charge – has a magnetic moment
- The magnetic moment is quantized – only two orientations of the spin are allowed in a magnetic field



- ⇒ **Spin quantum number ( $m_s$ )** – two possible values of  $m_s$  ( $+1/2$  and  $-1/2$ )
- Each electron in an atom is described by four quantum numbers –  $n$ ,  $l$ ,  $m_l$ ,  $m_s$

- **The Pauli exclusion principle** – no two electrons in an atom can have the same set of four quantum numbers

⇒ Each orbital can hold no more than two electrons and they must have opposite spins (paired spins,  $\uparrow\downarrow$ )

### Orbital Energies

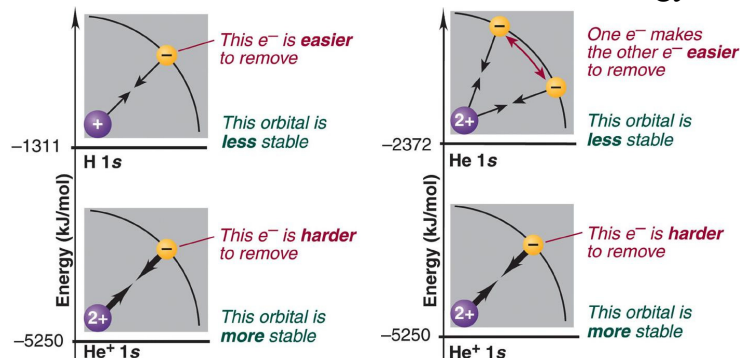
- Orbital energies depend on both  $n$  and  $l$

$$n \uparrow \rightarrow E \uparrow \quad l \uparrow \rightarrow E \uparrow$$

⇒ Orbitals in different subshells of a given principal shell have different energies

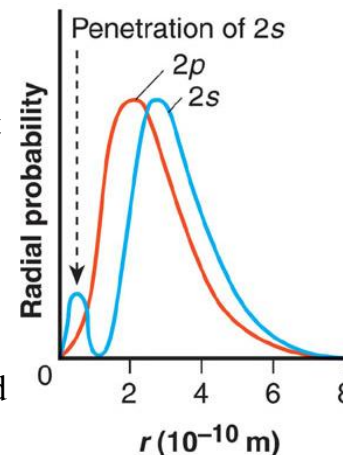
- Evidence – many-electron atoms have more complex atomic spectra (splitting of  $E$ -levels)

- Electrons are attracted by the nucleus and repelled by each other
  - **The effect of nuclear charge ( $Z$ )** – higher  $Z$  lowers the orbital energy
  - **The effect of electron repulsion** – an additional  $e^-$  in the same orbital raises the orbital energy



- **Electron shielding** – electrons shield each other from the nuclear charge
  - **Inner electrons shield outer electrons** more effectively than electrons in the same orbital or subshell
- **Effective nuclear charge ( $Z_{eff}$ )** – smaller than the actual nuclear charge ( $Z$ ) due to electron shielding
- **Penetration** – electrons on orbitals in different subshells of a given shell are shielded to a different extent depending on their penetration (closeness) to the nucleus
  - More penetration → less shielding → higher  $Z_{eff}$**

- The **s-orbitals** have the greatest penetration to the nucleus
  - Least shielded → highest  $Z_{eff}$  → lowest energy
- The **p-orbitals** have a node at the nucleus and lower penetration than the s-orbitals
  - More effectively shielded → lower  $Z_{eff}$  → higher energy



- Penetration decreases with increasing  $l$

More effective shielding  
→ lower  $Z_{eff}$  → higher energy

– Energy order of the subshells in a given shell:

$$\mathbf{s < p < d < f < g \dots}$$

– This leads to a much greater number of energy levels compared to one-electron species like H

