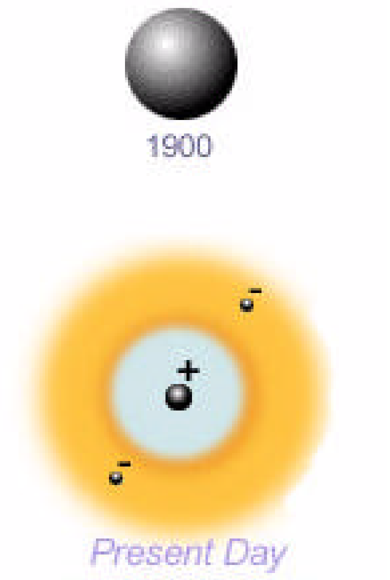
The atom



- Stationary states for central potentials
- Solutions for the hydrogen atom
- Magnetic dipole moment of hydrogen
- The independent electron model
- Ground state of atoms
- The Zeeman effect
- Spin-orbit coupling
- (X-rays and Auger electrons)
- (Fluorescence)

Spherically symmetric potentials

We will look for stationary states describing the 3d motion of an object in a central potential $V(r)$

- We will not consider the time dependence of the wavefunctions (measurements)

Our stationary states will be used to describe the electron states of the hydrogen atom.

They are also eigenstates of $\boldsymbol{L}^2$ and $\boldsymbol{L}_z$.

The Schrödinger equation

Stationary states: $\psi(r, \phi, \theta)$

$$-\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]\psi + \frac{1}{2m}\frac{1}{r^2}\boldsymbol{L}^2\psi + V(r)\psi = E\psi$$

but we already have the spherical harmonics

so we can write $\psi(r, \phi, \theta) = R(r)Y_{lm}(\theta, \phi)$

and solve the radial equation:

$$\left\{-\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{1}{r^2}l(l+1)\right] + V(r)\right\}R(r) = ER(r)$$

Application: the hydrogen atom

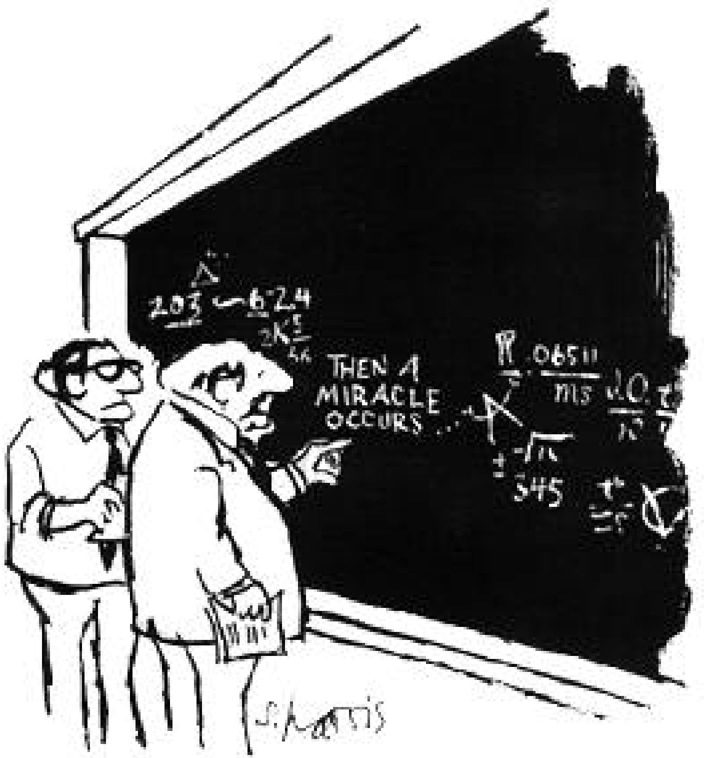
$$V_H(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

r = distance between the electron and the proton

The radial equation can be use for $V_H(r)$ provided that

$$m \rightarrow \mu = \frac{m_p m_e}{m_p + m_e}$$

The solution



"I think you should be more explicit here in step two."

Hydrogen atom: the results

1. The energy levels:

$$E_n = -\frac{1}{n^2} E_R, \quad E_R = 13.6 \ eV$$

where $n = 1, 2, \ldots$ is the principal quantum number

2. The radial wavefunction: $R_{nl}(r)$ depends on n, l

probability density for electron $P(r) = r^2 |R_{nl}(r)|^2$

average position varies roughly as n^2 (application: *shells*)

Hydrogen atom : the results (cont'd)

3. The spatial dependence of the wavefunction:

$\psi_{nlm}(r, \phi, \theta) = R_{nl}(r) Y_{lm}(\theta, \phi)$ but $\left|\psi_{nl}(r, \theta)\right|^2$

4. The parity of hydrogen: $\boldsymbol{P}\psi_{nlm} = (-1)^l \psi_{nlm}$

5. 'Orbitals' instead of 'orbits'

6. Spin: the complete wavefunction is $\psi_{nlm_l m_s}$

7. Degeneracy of energy levels: $2n^2$

Magnetic dipole moment of hydrogen

In general, μ *is due to angular momentum*

The hydrogen atom has:

(a) orbital angular momentum, l

(b) spin orbital momentum, s

We thus have 'two' magnetic dipole moments:

$$\mu_{L,z} = -\frac{eh}{4\pi m_e} m_l = -m_l \mu_B \text{ and } \mu_{S,z} = -\frac{eh}{2\pi m_e} m_s = -2 m_s \mu_B$$

The independent electron model

We describe many-electron atoms by using an 'effective potential' in the Schrödinger equation

- wavefunction: $\psi_{nlm_lm_s}$ as in hydrogen atom *but*

- energy levels: depend on n, l

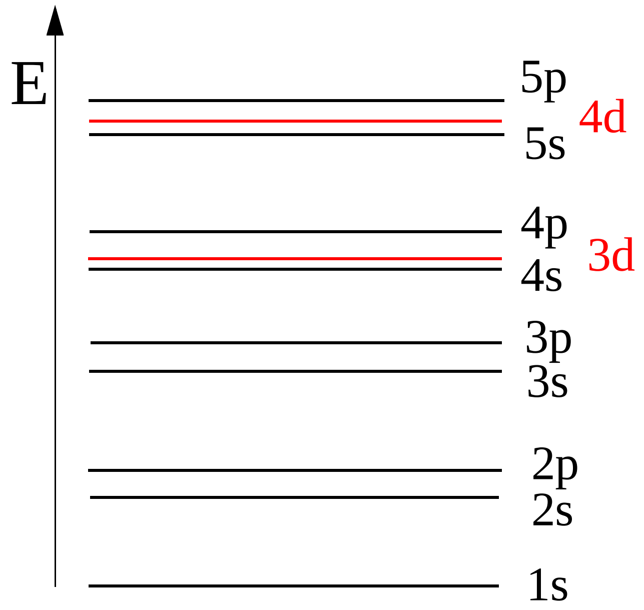
l = 0, 1, 2, 3, ...

name of the level: s, p, d, f, ...

- notation for electronic energy levels: n*l*, e.g. 1s
- energy ordering: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, ...

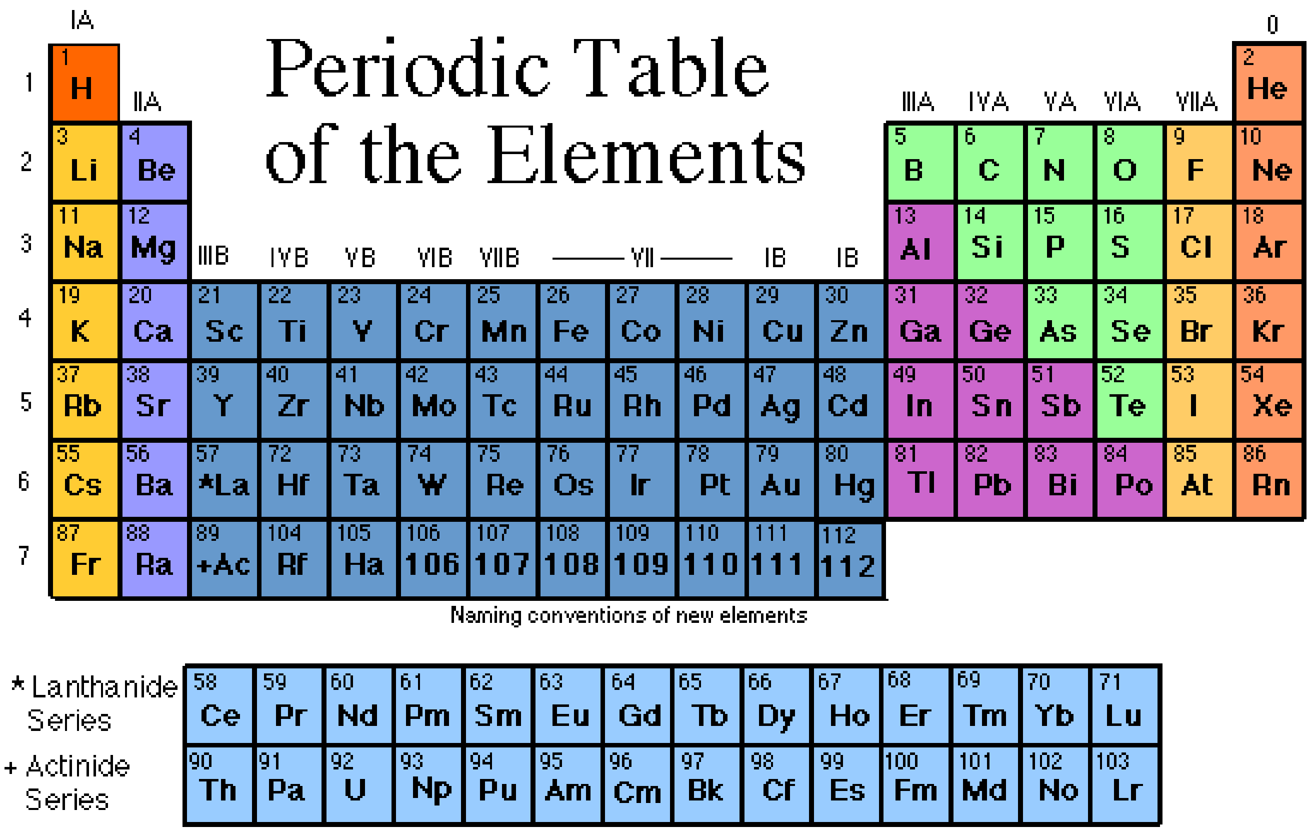
The independent electron model

Energy levels



s and p orbitals ‘go’ closer to the nucleus

Application of the independent electron model



The Pauli principle

'For each set of values for the quantum numbers n, l, m_l, m_s, we can have only one electron'

Applications of the model (i.e.m)

- electronic structure of atoms
- determine the chemical and electromagnetic properties of the atom
- calculate angular momentum of atom (L-S coupling)
- explain optical transitions
- ground state for light atoms

✗ cannot be used for the study of X-rays (heavy atoms)

(Optical) transitions

frequency of emitted/absorbed photon:

$$\nu = \frac{1}{h}(E_i - E_f)$$

selection rule:

$$\Delta l = \pm 1$$

The ground state of atoms

Hund's rules

1. add spins of valence electrons so that the total spin is maximized

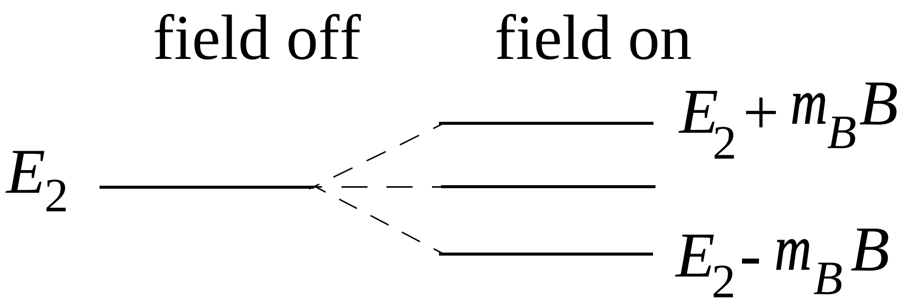
2. add the orbital angular momenta of valence electrons so that $L_z = \sum m_l \left(\frac{h}{2\pi}\right) = \left(\frac{h}{2\pi}\right) m_L$ is max.

3. S and J are added to calculate J

The Zeeman effect

Assume 'spinless' valence electron with *n*=2, *l*=1 in a magnetic field (along z-axis)

Interaction energy between the magnetic moment and the magnetic field: $U = -\mu_{L,z}B = m_l\mu_B B$



Spin-orbit coupling

The nucleus produces a magnetic field that interacts with the spin magnetic dipole moment of the electron

$$U = -\mu_{S,z}B = 2m_s\mu_B B = \pm\mu_B B$$

Electron states: eigenstates of $\boldsymbol{J}^2, \boldsymbol{L}^2, \boldsymbol{S}^2, \boldsymbol{J_z}$ ~~(i.e.m.)~~

notation: ${}^{2s+1}A_j$