Multi-electron Atom

The atomic orbitals of hydrogen-like atoms are solutions to the Schrödinger equation in a spherically symmetric potential. In this case, the potential term is the potential given by Coulomb's law:

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$$

where
- ε_0 is the permittivity of the vacuum,
- *Z* is the atomic number (number of protons in the nucleus),
- *e* is the elementary charge (charge of an electron),
- *r* is the distance of the electron from the nucleus.

After writing the wave function as a product of functions:

$$\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi)$$

(in spherical coordinates), where Y_{lm} are spherical harmonics, we arrive at the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)-\frac{l(l+1)R(r)}{r^2}\right)+V(r)R(r)\right]=ER(r),$$

where μ is, approximately, the mass of the electron. More accurately, it is the reduced mass of the system consisting of the electron and the nucleus.

$$\mu=\frac{m_N m_e}{m_N+m_e} \qquad \mu\approx m_e$$

Different values of *l* give solutions with different angular momentum, where *l* (a non-negative integer) is the quantum number of the orbital angular momentum. The magnetic quantum number *m* (satisfying $-l\leq m\leq l$) is the (quantized) projection of the orbital angular momentum on the *z*-axis.

Quantum numbers

The quantum numbers *n*, *l* and *m* are integers and can have the following values:

$$n = 1, 2, 3, 4, \ldots$$

$$l = 0, 1, 2, \ldots, n-1 \qquad l < n$$

$$m = -l, -l+1, \ldots, 0, \ldots, l-1, l$$
$$-l \leq m \leq l$$

n	1	2		3		
l	0	0	1	0	1	2
m	0	0	-1, 0, 1	0	-1, 0, 1	-2, -1, 0, 1, 2
# of degeneracy for *l*	1	1	3	1	3	5
# of degeneracy for *n*	1	4		9		

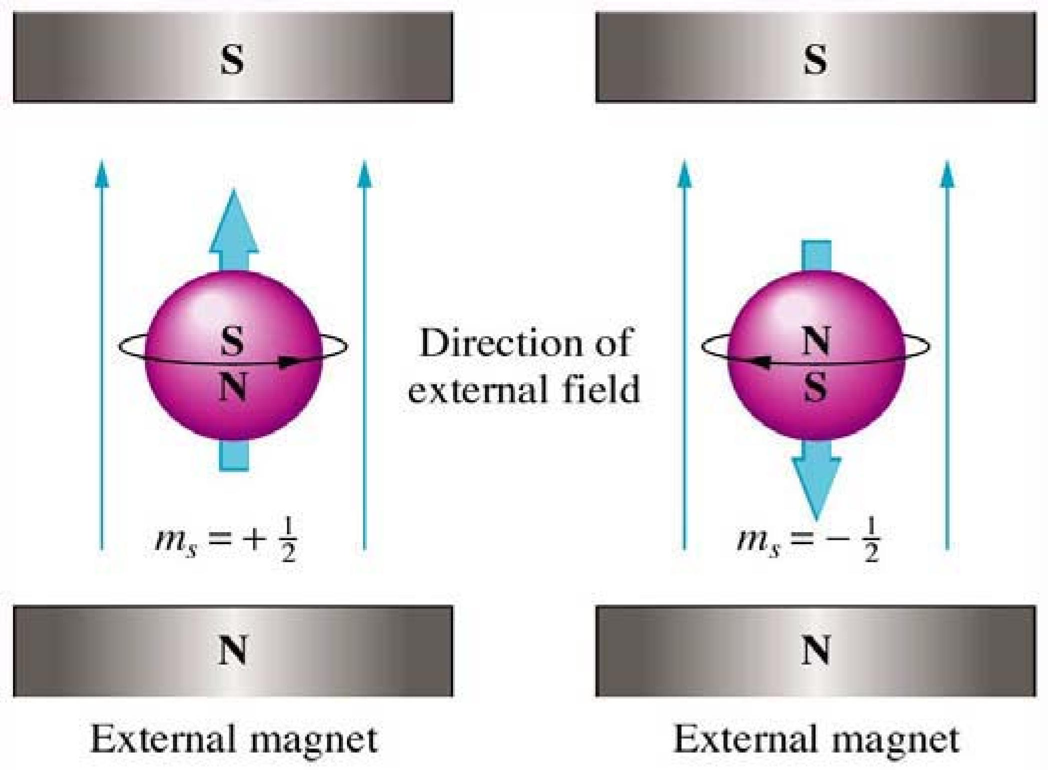
Energy

$$E_n = -\left(\frac{Z^2\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\right)\frac{1}{n^2} = -\left(\frac{Z^2\hbar^2}{2\mu a_\mu^2}\right)\frac{1}{n^2}$$

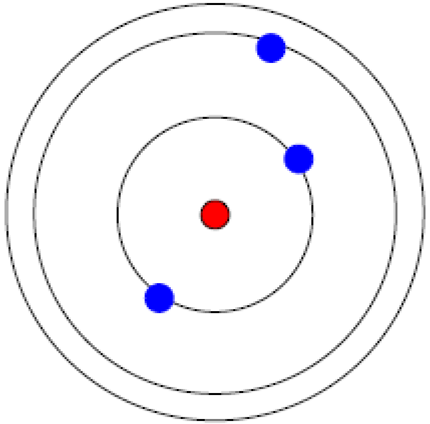
For Hydrogen atom

$$E_n = -13.6\ eV/n^2$$

Electron Spin



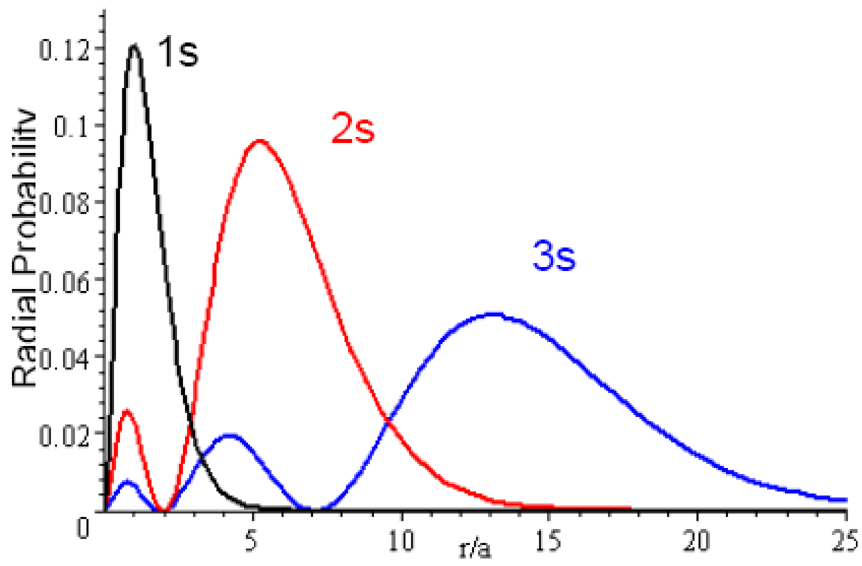
Screening (shielding) Effects



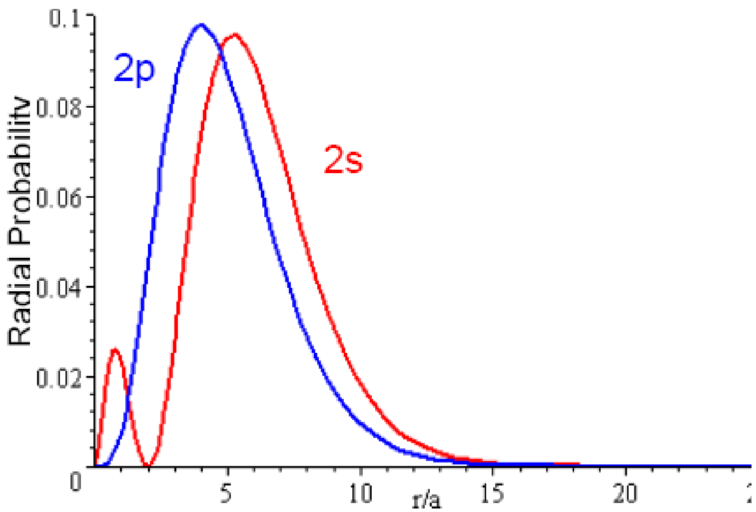
$$E_n = -RZ^2/n^2$$

$$E_n = -RZ_{eff}^2/n^2$$

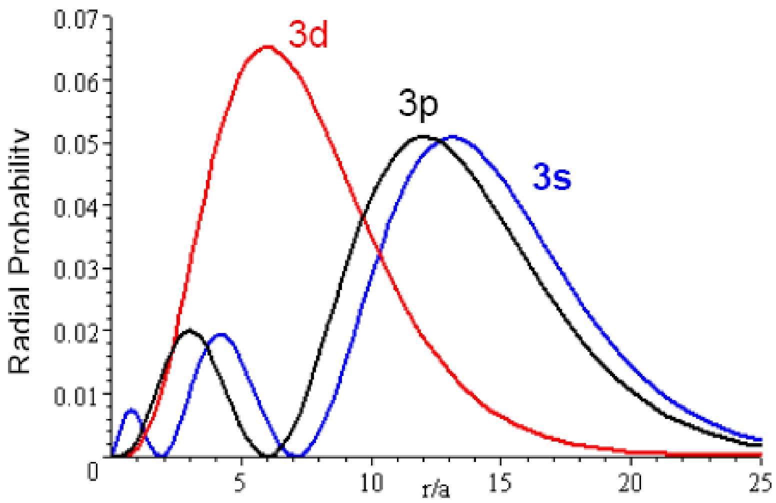
$$Z_{eff} = 1.3$$



1s
2s
3s
Radial Probability
0.12
0.1
0.08
0.06
0.04
0.02
0
5
10
r/a
15
20
25

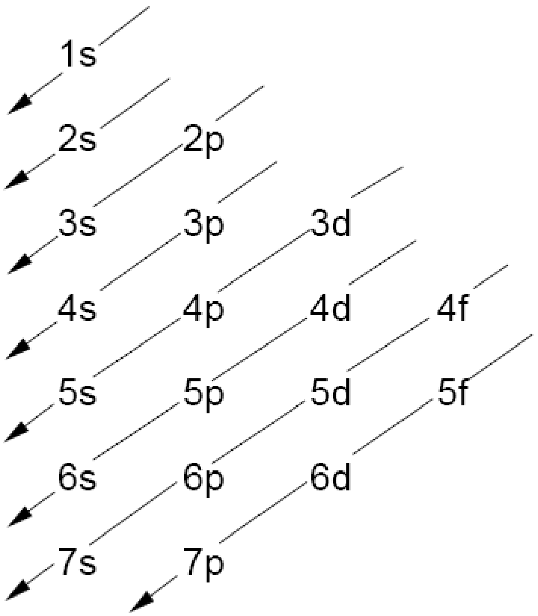


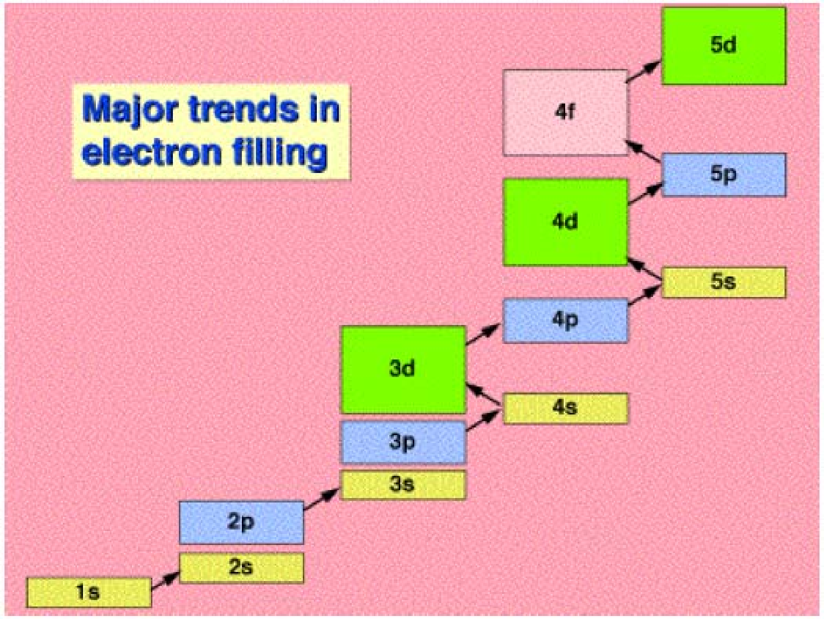
2p
2s
Radial Probability
0.1
0.08
0.06
0.04
0.02
0
5
10
r/a
15
20



3d
3p
3s
Radial Probability
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
5
10
r/a
15
20
25

Aufbau principle





SUMMARY

The energy eigenfunction for the state described by the quantum numbers (n,ℓ,m_ℓ) is of the form:

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = A_{n\ell m_\ell} R_{n\ell}(r) Y_\ell^{m_\ell}(\theta,\phi)$$

Table 7-2 in the book (pg. 243) lists the first ten eigenfunctions. The table is reproduced below.

There are three quantum numbers:

n = 1, 2 ,3,... (Principal quantum no.)

ℓ = 0, 1, 2,..., n-1 (Azimuthal quantum no.)

m_ℓ = -ℓ, -ℓ+1,..., 0,..., ℓ-1, ℓ (Magnetic quantum no.)

The energy of any state only depends on the principal quantum number (for now!) and is given by:

$$E_n = -\frac{Z^2}{n^2}(13.6 \text{ eV})$$