One-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 $-l \le m \le l$) is the (quantized) projection of the orbital angular momentum on the *z*-axis.

Wave function

In addition to *l* and *m*, a third integer *n* > 0, emerges from the boundary conditions placed on *R*. The functions *R* and *Y* that solve the equations above depend on the values of these integers, called *quantum numbers*. It is customary to subscript the wave functions with the values of the quantum numbers they depend on. The final expression for the normalized wave function is:

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

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-Zr/na_\mu} \left(\frac{2Zr}{na_\mu}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

where:

- L_{n-l-1}^{2l+1} are the generalized Laguerre polynomials in the definition given here.
- $a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = \frac{m_e}{\mu} a_0$

Here, μ is the reduced mass of the nucleus-electron system, where m_N is the mass of the nucleus. Typically, the nucleus is much more massive than the electron, so $\mu \approx m_e$.

- $Y_{lm}(\theta, \phi)$ function is a spherical harmonic.

It is customary to multiply the $\Phi(\phi)$ and $\Theta(\theta)$ functions to form the so-called *spherical harmonic functions* which can be written as:

$$Y_{\ell}^{m_\ell}(\theta,\phi) = \Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\phi)$$

The first few spherical harmonics are given below:

$Y^{0}_{0} = 1$

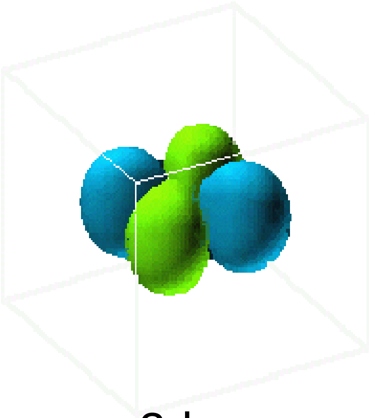
$Y^{0}_{1} = \cos\theta$

$Y^{\pm 1}_{1} = (1-\cos^2\theta)^{1/2}\, e^{\pm i\phi}$

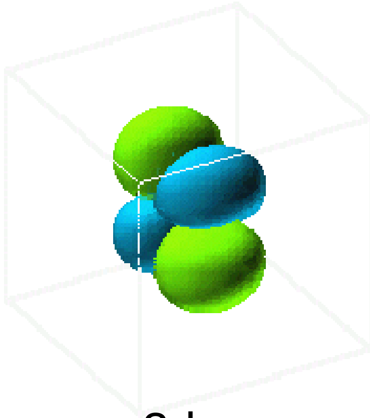
$Y^{0}_{2} = 1-3\cos^2\theta$

$Y^{\pm 1}_{2} = (1-\cos^2\theta)^{1/2}\cos\theta\, e^{\pm i\phi}$

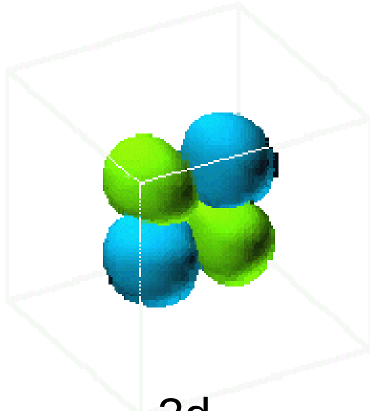
$Y^{\pm 2}_{2} = (1-\cos^2\theta)\, e^{\pm i\phi}$



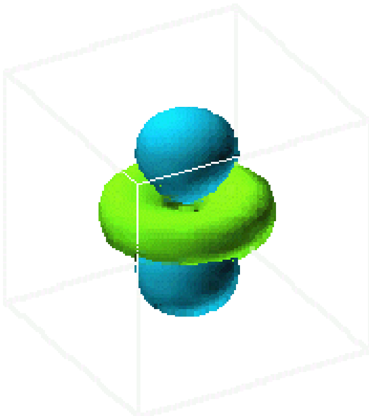
$3d_{xy}$



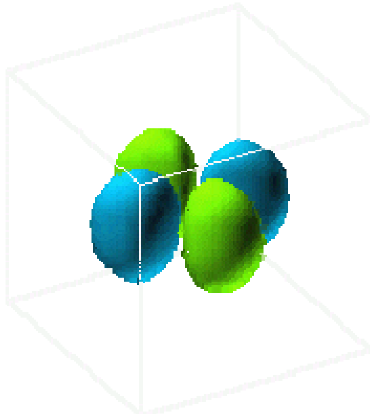
$3d_{yz}$



$3d_{xz}$



$3d_{z}{}^{2}$



$3d_{x}2_{-y}2$

Table 7-2 Some Eigenfunctions for the One-Electron Atom

Quantum Numbers n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta\, e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \sin\theta\, e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$
3	2	± 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta\cos\theta\, e^{\pm i\varphi}$
3	2	± 2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta\, e^{\pm 2i\varphi}$

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

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

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		

Angular momentum

Each atomic orbital is associated with an angular momentum ***l***. It is a vector operator, and the eigenvalues of its square $l^2 \equiv l_x^2 + l_y^2 + l_z^2$ are given by:

$$l^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

The projection of this vector onto an arbitrary direction is quantized. If the arbitrary direction is called *z*, the quantization is given by:

$$l_z Y_{lm} = \hbar m Y_{lm},$$

where *m* is restricted as described above. Note that l^2 and l_z commute and have a common eigenstate, which is in accordance with Heisenberg's uncertainty principle. Since l_x and l_y do not commute with l_z, it is not possible to find a state which is an eigenstate of all three components simultaneously. Hence the values of the *x* and *y* components are not sharp, but are given by a probability function of finite width. The fact that the *x* and *y* components are not well-determined, implies that the direction of the angular momentum vector is not well determined either, although its component along the *z*-axis is sharp.

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:

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

$\ell = 0, 1, 2, \ldots, n-1$ (Azimuthal quantum no.)

$m_\ell = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$ (Magnetic quantum no.)

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

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

Homework#2 (Oct. 12, 2009):

1.(a) Evaluate, in electron volts, the energies of the three levels of the hydrogen atom in the states for n = 1, 2, 3.
(b) Then calculate the frequency in hertz, and the wavelength in angstroms, of all the photons that can be emitted by the atom in transitions between these levels.

2. Verify by substitution that the ground state eigenfunction ψ_{310}, and the ground state eigenvalue E_3, satisfy the time-independent Schroedinger equation for the hydrogen atom.