# *Internal Energy and Structure of the Wave-functions*

The energy (in the SI system) associated with the internal motion is found by solving the eigenvalue equation

$$\hat{H}_{\text{int}}\psi = \left( -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \right)\psi = E_{\text{int}}\psi$$

Subject to the boundary conditions that $\psi$ be finite at the origin and vanish at $\infty$. This solution is developed in detail in many texts and we will simply sketch the procedure and discuss the results. Note that although the energy of the atom is the sum of the energy associated with the center of mass motion and the internal motion one usually assumes that the atom is at rest and the center of mass energy is zero. We will call the internal energy simply the energy.

The kinetic energy operator in spherical polar coordinates is

$$-\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2\mu r^2}\left( \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

And since the square of the orbital angular momentum operator $\hat{L}^2$ is given by

$$\hat{L}^2 = -\hbar^2\left( \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

the Hamiltonian may be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0}$$

The first term on the right is the radial kinetic energy operator while the second term is the angular kinetic energy operator. We show in appendix 1 that the eigenfunctions of $\hat{L}^2$ are the spherical harmonics, $Y_\ell^m(\theta,\phi)$ with eigenvalue $\ell(\ell+1)\hbar^2$

$$\hat{L}^2 Y_\ell^m(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\theta,\phi)$$

Where $\ell$ is the angular momentum quantum number and is a positive integer, $0 \le \ell < \infty$ and $m$ is the magnetic quantum number and for a given $\ell$ is an integer $-l \le m \le l$.

If we seek a solution to the equation

$$\left(-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{L}^2}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

and write $\psi$ as a product of a radial function and a spherical harmonic, as $\psi = R(r)Y_\ell^m(\theta,\phi)$ we find that the radial part of the wavefunction $R(r)\,\&\,E$ and the internal energy are determined by the differential equation

$$\left(-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)R(r) = ER(r)$$

***Angular Functions***

Lets first look at the spherical harmonics. The explicit form of $Y_\ell^m(\theta,\phi)$ is

$$Y_\ell^m(\theta,\phi) = \Theta_{\ell m}(\theta)\Phi_m(\phi)$$

with

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

and

$$\Theta_{\ell m}\left(\theta\right)=\delta_m\left\{\frac{\left(2\ell+1\right)\left(\ell-\left|m\right|\right)!}{2\left(\ell+\left|m\right|\right)!}\right\}^{\frac{1}{2}}P_\ell^{|m|}\left(\cos\theta\right)$$

$P_\ell^{|m|}\left(\cos\theta\right)$ is an associated Legendre polynomial which may be written in terms of the Legendre polynomials $P_\ell(x)$ as

$$P_\ell^{|m|}(x)=(1-x^2)^{|m|/2}\,\frac{d^{|m|}P_\ell(x)}{dx}$$

The first five Legendre polynomials are collected below.

$$\begin{aligned}
P_0(x)&=1\\
P_1(x)&=x\\
P_2(x)&=\frac{1}{2}(3x^2-1)\\
P_3(x)&=\frac{1}{2}(5x^3-3x)\\
P_4(x)&=\frac{1}{8}(35x^4-30x^2+3)
\end{aligned}$$

$\delta_m$ in the definition of $\Theta_{\ell m}(\theta)$ is a phase factor which is not universally agreed upon. We will choose it to be $(-1)^m$ when $m>0$ and +1 when $m<0$. This is often called the Condon-Shortly choice of phase and is sometimes written as the requirement that

$$Y_\ell^{-m}=(-1)^m\left(Y_\ell^m\right)^*.$$

Note that the z component of the orbital angular momentum $\hat{L}_z=-i\hbar\frac{\partial}{\partial\phi}$ depends only on $\phi$ and when it acts on $Y_\ell^m(\theta,\phi)$ only effects $\Phi_m(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}$ so $Y_\ell^m(\theta,\phi)$ is also an eigenfunction of $\hat{L}_z$ with eigenvalue $m\hbar$

$$\hat{L}_z Y_\ell^m(\theta,\phi) = m\hbar Y_\ell^m(\theta,\phi)\,.$$

The first few spherical harmonics are given below along with their Cartesian representation obtained using

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

A more complete set is given in the appendix to this discussion. It's common to identify an orbital angular momentum with a letter corresponding to the orbital angular momentum quantum number $\ell$. This convention is of historical origin and refers to the nature of the spectroscopic lines in the hydrogen atom. The first four were called sharp, primary, diffuse and fundamental. The remaining letters continue in sequence with j being omitted.

| *l* | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| letter | s | p | d | f | g | h | i |

*s orbitals ,* $\ell = 0$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

*p orbitals,* $\ell = 1$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\,cos\theta = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r}$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\,sin\theta e^{\pm i\phi} = \mp\sqrt{\frac{3}{8\pi}}\,\frac{x+iy}{r}$$

*d orbitals, ℓ = 2*

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3cos^2\theta - 1) = \sqrt{\frac{5}{16\pi}}\frac{\left(2z^2 - x^2 - y^2\right)}{r^2}$$

$$Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\, cos\theta\, sin\theta e^{\pm i\phi} = \mp\sqrt{\frac{15}{8\pi}}\frac{\left(x + iy\right)z}{r^2}$$

$$Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\, sin^2\theta e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}}\frac{\left(x + iy\right)^2}{r^2}$$

The spherical harmonics are orthonormal in the sense

$$\int_0^{\pi} sin\theta\, d\theta \int_0^{2\pi} d\phi\ Y_\ell^m(\theta,\phi)Y_{\ell'}^{m'*}(\theta,\phi) = \delta_{\ell\ell'}\delta_{mm'}$$

## *Radial functions*

As noted above the radial wavefunctions $R(r)$ for a one-electron atom are the solutions to the differential equation

$$\left(-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)R(r) = ER(r)$$

and the detailed solution to this equation is given in appendix 2 of these notes. The radial functions depend on two quantum numbers $n\,\&\,\ell$. $n$ is called the principal quantum number and is a positive integer between 1 and $\infty$ while $\ell$ is the orbital angular momentum quantum number discussed above. For a given $n$, $\ell$ is constrained to be an integer between $0$ and $n-1$. The general form of the radial function is

$$R_{n\ell}\left(r\right) = -\left[\left(\frac{2Z}{na_0}\right)^3\frac{\left(n-\ell-1\right)!}{2n\left\{\left(n+\ell\right)!\right\}^3}\right]^{\frac{1}{2}} e^{-\frac{\rho}{2}}\rho^\ell L_{n+\ell}^{2\ell+1}\left(\rho\right),$$

in which

$$\rho = \frac{2Zr}{na_\mu}$$

and

$$a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

and $L_{n+\ell}^{2\ell+1}\left(\rho\right)$ is an associated Laguerre polynomial.

While the radial wavefunctions depend on $n \,\&\, l$ the energy eigenvalue $E$, given by $E_n = -\frac{Z^2e^2}{8\pi\varepsilon_0 a_\mu n^2}$ , depends only on $n$. Furthermore since the total wavefunction $\psi_{n\ell m} = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$ depends on $n, \ell \,\&\, m$ we may have several different wavefunctions with the same energy. An individual wavefunction $\psi_{n\ell m}$ defines a state while an energy $E_n$ defines a level and different states having the same energy are said to be degenerate. The number of states in a given energy level is called the degeneracy of the level. Because of the constraints on the quantum numbers $\ell \,\&\, m$, $0 \le \ell \le n-1$ and $-\ell \le m \le \ell$ the degeneracy of the level $E_n$ is $\sum_{\ell=0}^{n-1}(2\ell+1) = n^2$.

Note that $a_\mu$ depends on the reduced mass of the one-electron atom and thus varies from atom to atom. If we used the mass of the electron rather than the reduced mass of the nucleus-electron system $a_\mu$ would be the Bohr radius $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ and they are related by $a_\mu = a_0\left(1 + \frac{m_e}{m_N}\right)$.

The first few associated Laguerre polynomials are

| | | |
|---|---|---|
| $n=1$ | $\ell=0$ | $L_1^1(x)=-1$ |
| $n=2$ | $\ell=0$ | $L_2^1(x)=-2!(2-x)$ |
| | $\ell=1$ | $L_3^3(x)=-3!$ |
| $n=3$ | $\ell=0$ | $L_3^1(x)=-3!(3-3x+x^2/2)$ |
| | $\ell=1$ | $L_4^3(x)=-4!(4-x)$ |
| | $\ell=2$ | $L_5^5(x)=-5!$ |
| $n=4$ | $\ell=0$ | $L_4^1(x)=-4!(4-6x+2x^2-x^3/6)$ |
| | $\ell=1$ | $L_5^3(x)=-5!(10-5x+x^2/2)$ |
| | $\ell=2$ | $L_6^5(x)=-6!(6-x)$ |
| | $\ell=3$ | $L_7^7(x)=-7!$ |

and the first few radial functions are shown below. A more complete list is given in the appendix to this discussion.

$n$ = 1, $K$ shell:

$$\ell=0,\,1s \qquad R_{10}\left(r\right)=\left(Z/a_\mu\right)^{\frac{3}{2}}\bullet 2e^{-\frac{\rho}{2}}$$

$n$ = 2, $L$ shell:

$$\ell=0,2s \qquad R_{20}\left(r\right)=\frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{2\sqrt{2}}\left(2-\rho\right)e^{-\frac{\rho}{2}}$$

$$\ell=1,2p \qquad R_{21}\left(r\right)=\frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{2\sqrt{6}}\rho e^{-\frac{\rho}{2}}$$

$n$ = 3, $M$ shell:

$$\ell=0,3s \qquad R_{30}(r)=\frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{9\sqrt{3}}\left(6-6\rho+\rho^2\right)e^{-\frac{\rho}{2}}$$

$$\ell=1,3p \qquad R_{31}(r)=\frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{9\sqrt{6}}\left(4-\rho\right)\rho e^{-\frac{\rho}{2}}$$

$$\ell=2,3d \qquad R_{32}(r)=\frac{\left(Z/a_\mu\right)^{\frac{3}{2}}}{9\sqrt{30}}\rho^2 e^{-\frac{\rho}{2}}$$

These functions are all normalized to 1

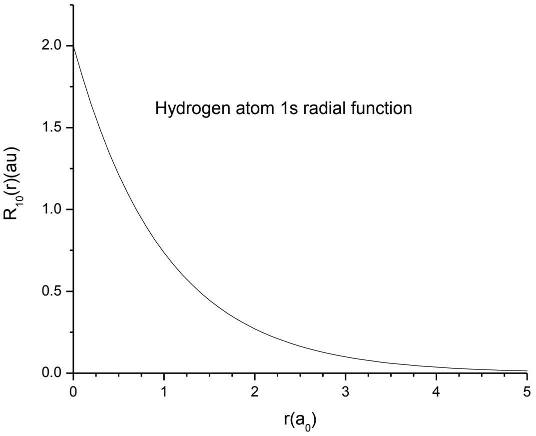
$$\int_0^\infty R_{n\ell}^2(r)r^2\,dr=1$$

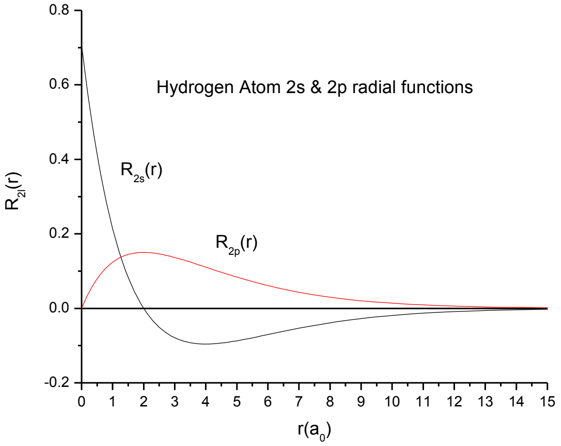
and are orthogonal within a given $l$

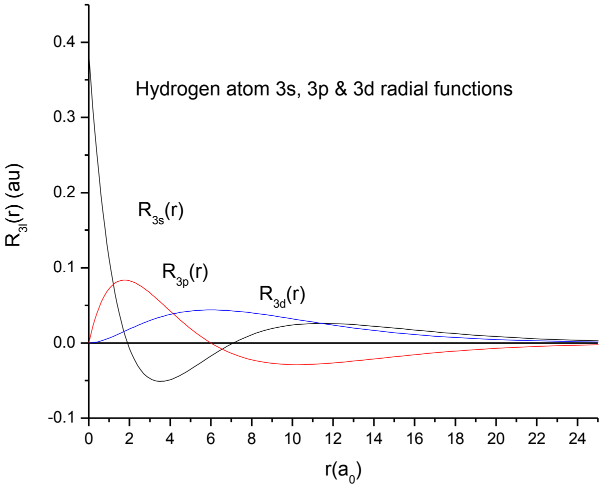
$$\int_0^\infty R_{n\ell}(r)R_{n'\ell}(r)r^2\,dr=\delta_{nn'}$$

This means that all radial *s* functions are orthogonal, as are all radial *p* functions, etc. but radial functions corresponding to different angular momenta are not. For example $R_{2s}(r)$ is not orthogonal to $R_{2p}(r)$. However, the complete $2s$ & $2p$ wavefunctions are orthogonal because of the angular not the radial functions. A more detailed discussion of the nature of the radial functions is given in the appendix.

These radial functions are plotted for $Z$=1 in the following figures. There are several features of the radial functions that deserve our attention and are illustrated in these plots. First, only the s functions are non-zero at the origin. Second, a given radial function $R_{n\ell}(r)$ has $n-\ell-1$ nodes between 0 and $\infty$. Third, functions sharing the same principal quantum number $n$ have comparable magnitudes and spatial extensions.


Hydrogen atom 1s radial function
$R_{10}(r)$(au)
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
$r(a_0)$


Hydrogen Atom 2s & 2p radial functions
$R_{2l}(r)$
$R_{2s}(r)$
$R_{2p}(r)$
0.8
0.6
0.4
0.2
0.0
-0.2
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
$r(a_0)$


Hydrogen atom 3s, 3p & 3d radial functions
$R_{3l}(r)$ (au)
$R_{3s}(r)$
$R_{3p}(r)$
$R_{3d}(r)$
0.4
0.3
0.2
0.1
0.0
-0.1
0
2
4
6
8
10
12
14
16
18
20
22
24
$r(a_0)$