Atomic Units
Helium-like atoms

The general Hamiltonian of the He-like ions is defined by the equation:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - k\frac{Ze^2}{r_1} - k\frac{Ze^2}{r_2} + k\frac{e^2}{r_{12}}$$

To avoid dealing with constant factors in the lengthy calculations and to make equations and integrals more clearly legible, it is common in theoretical atomic, molecular physics and quantum chemistry to use so-called atomic units. They are obtained by defining $\hbar = 1, m_e = 1, e = 1, k = 1/4\pi\varepsilon_o = 1$ (a.u) (The units in the electron's world.) and the above equation will be

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

Note that in equating $\hbar = 1, m_e = 1, e = 1, k = 1/4\pi\varepsilon_o = 1$ the dimensions of these quantities are ignored. Hence, equations written in atomic units are not dimensionally correct in the usual sense. The atomic unit of length, 1 Bohr, equals the radius of the lowest Bohr orbit in the hydrogen atom. In SI units,

$$a_o = \frac{\hbar^2}{kme^2} \approx 0.05 \ \text{nm.}$$

$$a_o = \frac{\hbar^2}{kme^2} = 1 \quad \text{(atomic units)}$$

The atomic unit of energy, 1 Hartree, is defined to be twice the ionization energy of the hydrogen atom ($= -E_{pot}$ for the electron in the lowest Bohr orbit with n = 1). In SI units,

$$E_{pot} = \frac{ke^4}{a_o\hbar^2 n^2} \approx 27.2 \ \text{eV}, \qquad n = 1$$

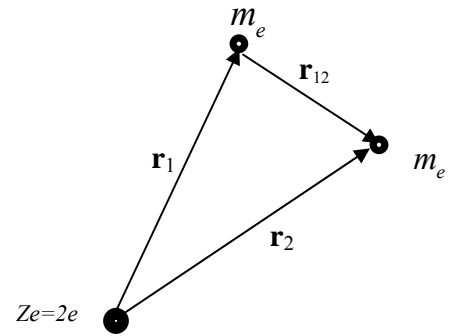$$E = \frac{ke^4}{a_o} = 1 \quad \text{(atomic units)}$$

$$1 \ \text{Hartree} = \frac{k^2 m e^2}{\hbar^2} = \frac{me^2}{(4\pi\varepsilon_o)^2\hbar^2} = \frac{(9.1091\text{x}10^{-31}\text{kg})(1.6021\text{x}10^{-19}\text{C})^4}{(1.1126\text{x}10^{-10}\text{C}^2.\text{J}^{-1}.\text{m}^{-1})^2(1.0545\text{x}10^{-34}\text{J.s})^2} = 4.3595\times10^{-18}\text{J}$$

$1 \ \text{Hartree} \ (1 \ \text{H}) = 4.3595\times10^{-18}\text{J} = 27.2 \ \text{eV} = 2 \ \text{Ry}$

$1 \ \text{Hartree} = 2625 \ \text{kJmol}^{-1}$

Use $E = h\nu = h\dfrac{c}{\lambda} = hc\overline{\nu}$, then

$$\overline{\nu} = \frac{1 \ \text{Hartree}}{hc} = \frac{4.36\times10^{-18}\text{J}}{(6.626\times10^{-34}\text{J.s})(3.0\times10^8\text{m/s})} = 2.195\times10^7\,\text{m}^{-1} = 2.195\times10^5\,\text{cm}^{-1}$$

Appendix 11

Table A11.3   Conversion factors

1 Å (angström) $= 0.1$ nm $= 10^{-10}$ m $= 10^{-8}$ cm

1 fm (femtometer or Fermi) $= 10^{-6}$ nm $= 10^{-15}$ m

λ (in Å) $\times \bar{\nu}$ (in cm^{-1}) $= 10^{8}$ (from $\lambda\bar{\nu} = 1$)

$a_0 = 5.29177 \times 10^{-11}$ m $= 0.529177$ Å

$a_0^2 = 2.80028 \times 10^{-21}$ m^2

$\pi a_0^2 = 8.79735 \times 10^{-21}$ m^2

1 Hz $= 1$ s^{-1}

1 electron mass $(m_e) = 0.511003$ MeV/c^2

1 proton mass $(M_p) = 938.280$ MeV/c^2

1 a.m.u. $= 1/12 M_{12_C} = 1.66057 \times 10^{-27}$ kg $= 931.502$ MeV/c^2

1 J $= 10^7$ erg $= 0.239$ cal $= 6.24146 \times 10^{18}$ eV

1 cal $= 4.184$ J $= 2.611 \times 10^{19}$ eV

1 eV $= 1.60219 \times 10^{-19}$ J $= 1.60219 \times 10^{-12}$ erg

1 MeV $= 1.60219 \times 10^{-13}$ J $= 1.60219 \times 10^{-6}$ erg

1 eV corresponds to:
   a frequency of 2.41797×10^{14} Hz (from $E = h\nu$)
   a wavelength of 1.23985×10^{-6} m $= 12398.5$ Å (from $E = hc/\lambda$)
   a wave number of 8.06548×10^5 m^{-1} $= 8065.48$ cm^{-1} (from $E = hc\bar{\nu}$)
   a temperature of 1.16045×10^4 K (from $E = kT$)

1 cm^{-1} corresponds to
   an energy of 1.23985×10^{-4} eV
   a frequency of 2.99792×10^{10} Hz

1 atomic unit of energy $= 27.2116$ eV corresponds to
   a frequency of 6.57968×10^{15} Hz
   a wavelength of 4.55633×10^{-8} m $= 455.633$ Å
   a wave number of 2.19475×10^7 m^{-1} $= 219475$ cm^{-1}
   a temperature of 3.15777×10^5 K

1 a.m.u. corresponds to an energy of 931.502 MeV $= 1.49244 \times 10^{-10}$ J

$kT = 8.61735 \times 10^{-5}$ eV at $T = 1$ K

$hc = 1.23985 \times 10^{-6}$ eV $\times$ m $= 12398.5$ eV $\times$ Å

$\hbar c = 1.97329 \times 10^{-7}$ eV $\times$ m $= 1973.29$ eV $\times$ Å

ΔE (in eV) $\times \Delta t$ (in s) $= 6.58218 \times 10^{-16}$ eV $\times$ s (from $\Delta E \Delta t = \hbar$)

ONE-ELECTRON ATOM IN SPHERICAL POLAR COORDINATES

Hydrogenic atoms are atoms with nucleus (H^+, Fe^{26+}, Pb^{82+}, $\cdots$) and one electron. The hydrogenic atom has an analytic solution. i.e., the solution is exact, no approximations are needed.

Coulomb Potential

From Coulomb's law, the potential energy between any two charges, q_1 and q_2, is

$$V(r) = k\frac{q_1 q_2}{r_{12}}, \qquad k = \frac{1}{4\pi\varepsilon_0}$$

- r_{12} is the distance between the two charges
- ε_0 is the permittivity of free space

For a hydrogenic atom, the potential energy can be written as

$$V(r) = -k\frac{Ze^2}{r}$$

- r is the distance of the electron from the nucleus.
- Z is the charge of the nucleus
- e is the fundamental unit of charge (i.e., the charge of e^-)

Center of Mass and Relative Coordinates

Hydrogenic atoms have two particles; therefore, the Hamiltonian can be written as

$$\mathcal{H} = \frac{\overline{p}_1^2}{2m_1} + \frac{\overline{p}_2^2}{2m_2} + V(\overline{r})$$

At this point we note that the potential energy does not depend on where the total system is in space. However, the potential energy does depend on the position of the particles relative to each other.

The simplest coordinate system one could choose is based on the Cartesian coordinates of each particle, so that, $\mathcal{H}$ is a function of $x_1, y_1, z_1, x_2, y_2, z_2$. This simple coordinate system can be transformed into a system described by center-of-mass coordinates and relative coordinates.
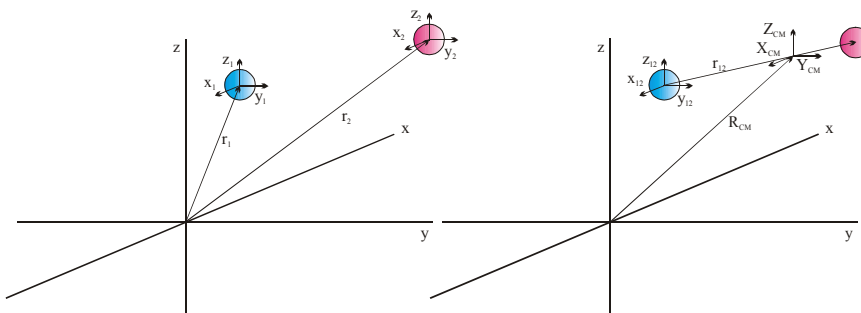
Thus the Hamiltonian can be rearranged in terms of the center-of-mass and relative coordinates.

$$\mathcal{H} = \frac{\overline{p}_{CM}^2}{2M} + \frac{\overline{p}_{rel}^2}{2\mu} + V(\overline{r}_{12})$$

where $M = m_1 + m_2$ and μ is the **reduced mass** of the system $= \dfrac{m_1 m_2}{m_1 + m_2}$ or $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$. Note

for the hydrogen atom

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p} = \frac{1}{5.48580 \times 10^{-4}\,\text{amu}} + \frac{1}{1.00727\,\text{amu}} \quad \Rightarrow \quad \mu = 5.48281 \times 10^{-4}\,\text{amu}$$

Schrödinger Equation

The Coulombic potential is radially symmetric, that is, the value of the electric field coming from the nucleus depends only on how far away from the nucleus we are. The value has no dependence on the orientation, i.e., the angular variables. Thus using a radially symmetric coordinate system such as the polar spherical coordinates system would be sensible.
The kinetic energy operator in polar spherical coordinates is

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

Note the relationship between the kinetic operator in polar spherical coordinates and the 3-D angular momentum operator.

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

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

$$= \frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right\}$$

Recall that the coulombic potential is $V(r) = -k\dfrac{Ze^2}{r}$

Thus, the Hamiltonian and the Schrödinger equation can be written as

$$\hat{\mathcal{H}} = \hat{T} + \hat{V} = \frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right\} - k\frac{Ze^2}{r}$$

$$\hat{\mathcal{H}}\psi = \frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial\psi}{\partial r} \right) - \frac{\hat{L}^2 \psi}{\hbar^2 r^2} \right\} - k\frac{Ze^2}{r}\psi = E\psi$$

To solve this partial differential equation, we will use the separation of variables technique.
Let $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$, then

$$\frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} R(r)\Theta(\theta)\Phi(\phi) \right) - \frac{\hat{L}^2}{\hbar^2 r^2} R(r)\Theta(\theta)\Phi(\phi) \right\} - \left\{ k\frac{Ze^2}{r} + E \right\} R(r)\Theta(\theta)\Phi(\phi) = 0$$

Allow the differential operators to operate.

$$\frac{-\hbar^2}{2\mu} \left\{ \frac{\Theta(\theta)\Phi(\phi)}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial R(r)}{\partial r} \right) - R(r)\frac{\hat{L}^2 \Theta(\theta)\Phi(\phi)}{\hbar^2 r^2} \right\} - \left\{ k\frac{Ze^2}{r} + E \right\} R(r)\Theta(\theta)\Phi(\phi) = 0$$

Recall that $\hat{L}^2 \Theta(\theta)\Phi(\phi) = \hbar^2 \ell(\ell+1)\Theta(\theta)\Phi(\phi)$, then

$$\frac{-\hbar^2}{2\mu}\left\{\frac{\Theta(\theta)\Phi(\phi)}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)-R(r)\Theta(\theta)\Phi(\phi)\frac{\ell(\ell+1)}{r^2}\right\}-\left\{k\frac{Ze^2}{r}+E\right\}R(r)\Theta(\theta)\Phi(\phi)=0$$

Now divide the equation by $\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$

$$\frac{-\hbar^2}{2\mu}\left\{\frac{1}{R(r)}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)-\frac{\ell(\ell+1)}{r^2}\right\}-k\frac{Ze^2}{r}-E=0$$

$$\frac{1}{R(r)}\frac{-\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}-k\frac{Ze^2}{r}-E=0$$

Radial Equation

Thus the radial equation for a hydrogenic atom is

$$\frac{-\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\left[\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}-k\frac{Ze^2}{r}-E\right]R(r)=0$$

The equation can be related to a differential equation called the associate Laguerre equation.
The solutions to the generalized Laguerre equation depend on two quantum numbers, n and ℓ.

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

$$=\left(\frac{2Z}{n}\right)^{3/2}\frac{1}{(2\ell+1)!}\sqrt{\frac{(n+\ell)!}{2n\,(n-\ell-1)!}}\,\rho^l e^{-\rho/2}F\left(-(n-\ell-1),2\ell+2,\rho\right)$$

The $L_{n+\ell}^{2\ell+1}(\rho)$ is the **associate Laguerre polynomials.** F is the (confluent) hypergeometric function:

$$F(\alpha,\beta,x)=1+\frac{\alpha}{\beta\cdot1!}x+\frac{\alpha(\alpha+1)}{\beta(\beta+1)2!}x^2+\cdots.$$

In general the hydrogenic wavefunction is a product of the radial wavefunction and the spherical harmonic. $\left|n\,\ell m\right\rangle=\Psi_{n\ell m}(r,\theta,\phi)=\dfrac{1}{r}P_{n\ell}(r)Y_\ell^{\,m}(\theta,\phi)=R_{nl}(r)Y_\ell^{\,m}(\theta,\phi)$

$$\left|n\,\ell m\right\rangle=\Psi_{n\ell m}(r,\theta,\phi)=\frac{1}{r}P_{n\ell}(r)Y_\ell^{\,m}(\theta,\phi)=R_{nl}(r)Y_\ell^{\,m}(\theta,\phi)$$

**Another useful function:

$$F(\alpha,\beta,\gamma,x)=\sum_\nu\frac{\alpha(\alpha+1)\cdots(\alpha+\nu-1)\beta(\beta+1)\cdots(\beta+\nu-1)}{\gamma\cdots(\gamma+\nu-1)\nu!}x^\nu$$

is the hypergeometric function.

Laguerre Differential equation

Differential equation

$$\left[x\frac{d^2}{dx^2} - (1-x)\frac{d}{dx} + n \right] L_n(x) = 0$$

Definition

$$L_n(x) = e^x \frac{d^n}{dx^n}\left(e^{-x} x^n \right), \qquad n = 0,1,2,3,\cdots$$

Orthogonality relation

$$\int_0^\infty e^{-x} L_n(x) L_m(x)\, dx = \left(\Gamma(n+1) \right)^2 \delta_{mn}$$

n	$L_n(x)$	n	$L_n(x)$
0	1	**2**	$x^2 - 4x + 2$
1	$-x + 1$	**3**	$-x^3 + 9x^2 - 18x + 6$

Associated Laguerre Polynomials

Differential equation

$$\left[x\frac{d^2}{dx^2} - (m+1-x)\frac{d}{dx} + (n-m) \right] L_n^m(x) = 0$$

Definition

$$L_n^m(x) = \frac{d^m}{dx^m}\left[L_n(x) \right] \qquad m,n = 0,1,2,3,\cdots$$

$$L_n^0(x) = L_n(x); \qquad L_n^m(x) = 0 \qquad \text{if } m > n$$

n	m	$L_n^m(x)$	n	m	$L_n^m(x)$
1	**1**	-1	**3**	**1**	$-3x^2 + 18x - 18$
2	**1**	$2x - 4$	**3**	**2**	$-6x + 18$
2	**2**	2	**3**	**3**	-6

A Table of Radial Wavefunctions, R_{nl}

n	l	orbit	R_{nl}
1	0	1s	$2(Z)^{3/2}e^{-Zr}$
2	0	2s	$\frac{1}{\sqrt{2}}(Z)^{3/2}(1-\frac{Zr}{2})e^{-Zr/2}$
	1	2p	$\frac{1}{2\sqrt{6}}(Z)^{5/2}re^{-Zr/2}$
3	0	3s	$\frac{2}{3\sqrt{3}}(Z)^{3/2}\left(1-\frac{2}{3}Zr+\frac{2}{27}(Zr)^2\right)e^{-Zr/3}$
	1	3p	$\frac{8}{27\sqrt{6}}(Z)^{3/2}\left(Zr-\frac{1}{6}(Zr)^2\right)e^{-Zr/3}$
	2	3d	$\frac{4}{81\sqrt{30}}(Z)^{7/2}r^2e^{-Zr/3}$
4	0	4s	$6(Z)^{\frac{3}{2}}\left(192-144Zr+24(Zr)^2+(Zr)^3\right)e^{-Zr/4}$
	1	4p	$\frac{1}{256\sqrt{15}}(Z)^{\frac{5}{2}}\left(80r-20Zr^2+Z^2r^3\right)e^{-Zr/4}$
	2	4d	$\frac{1}{768\sqrt{15}}(Z)^{\frac{7}{2}}\left(12r^2-Zr^3\right)e^{-Zr/4}$
	3	4f	$\frac{4}{768\sqrt{35}}(Z)^{\frac{9}{2}}r^4e^{-Zr/4}$

It is helpful for dealing with these functions to have some idea of their form which are shown in the figures below.
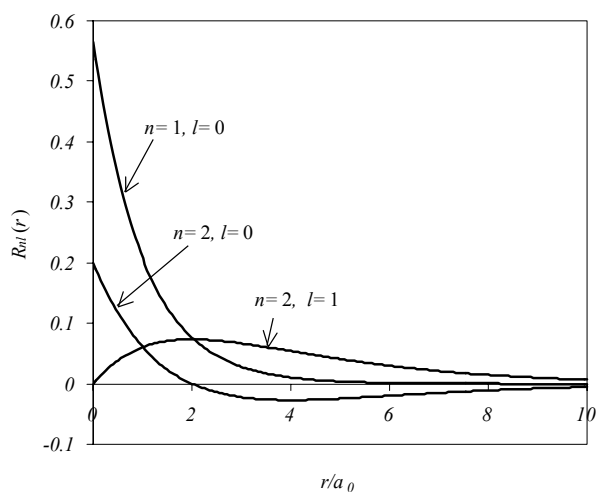

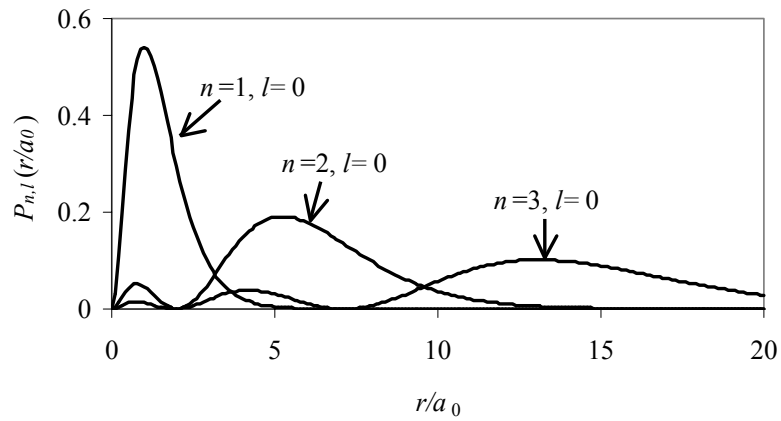**Figure 1: Radial part of the wavefunction** $R_{n,l}(r)$ **for** $n = 1, l = 0; n = 2, l = 0, 1.$

Figure 2: Radial extent of the probability density $P_{n,l}(r) = C_{n,l} r^2 \left| R_{n,l}(r) \right|^2$ for the hydrogen atom with $n = 1, 2, 3$ and $l = 0$.
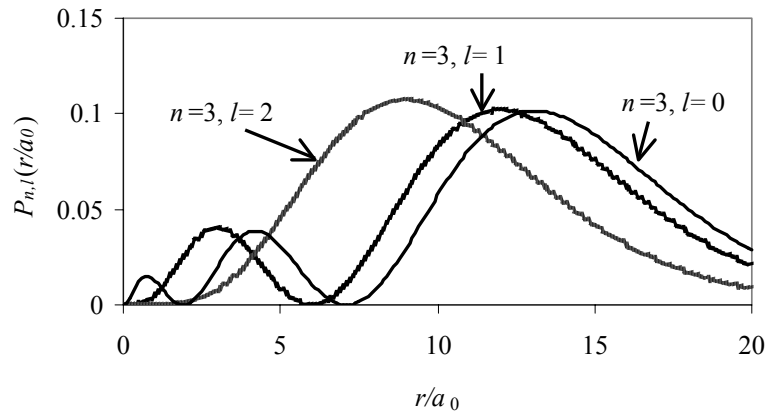

Figure 1: Radial extent of the probability density $P_{n,l}(r) = C_{n,l} r^2 \left| R_{n,l}(r) \right|^2$ for the hydrogen atom with $n = 3$, and $l = 0, 1, 2$.

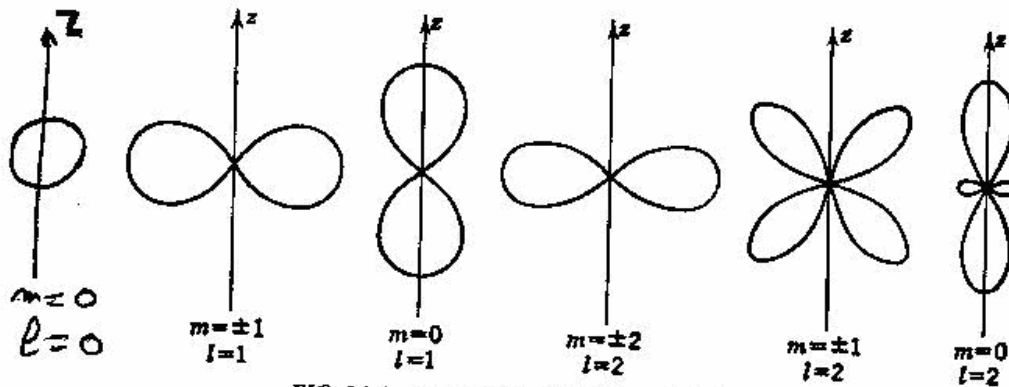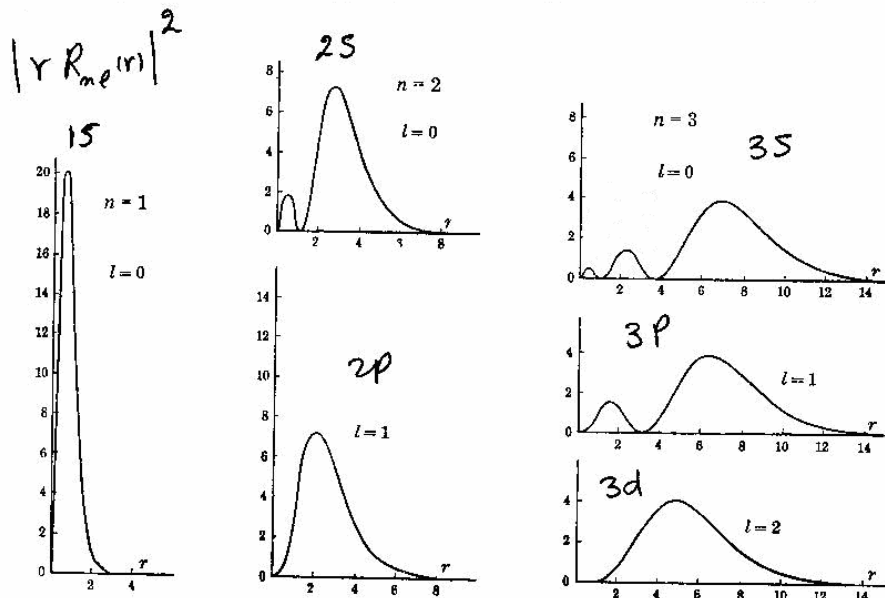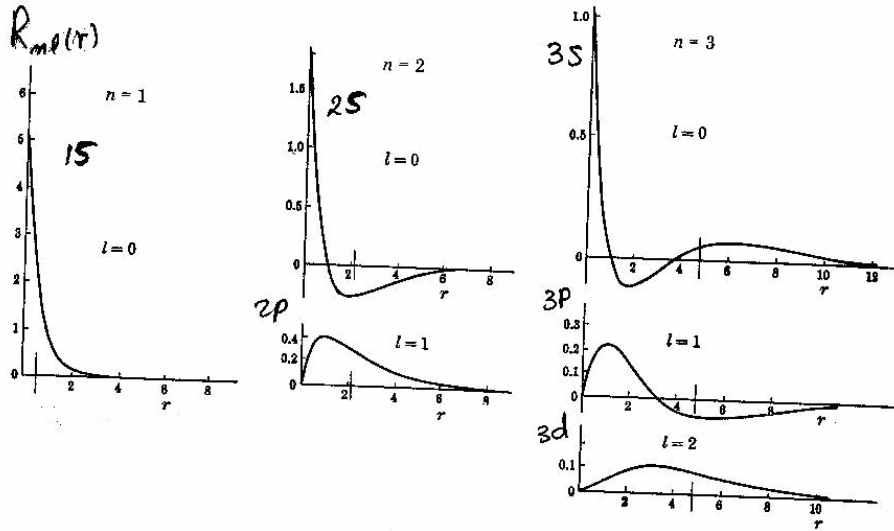*Plots of Radial Wave functions*

FIG. 16.4   Polar plots of $[P_l^{|m|}(\cos\theta)]^2$. (Slater, 1960)

It should be noted that

i) Ψ_{nlm} are orthonormal wave function, due to the fact:

$$\underbrace{\int_0^\infty R_{n',l'}^*(r)R_{n,l}(r)r^2 dr}_{\delta_{n,n'}\cdot\delta_{l,l'}}\underbrace{\int_0^{2\pi}\int_0^\pi Y_{l',m'}^*(\theta,\varphi)Y_{l,m}(\theta,\varphi)\sin\theta d\theta d\varphi}_{\delta_{l,l'}\cdot\delta_{m,m'}}=1$$

ii)   s-wavefunctions are non-zero at nucleus. p, d, f, … are zero at nucleus (for point nucleus).

iii) orbitals with larger *n* extend further from the nucleus,

iv) $P_{nl}(r)=r^2 R_{nl}^2$ is the probability that the electron be found in the spherical shell between r and r+dr.

v) $|Y_{lm}(\theta,\varphi)|^2 d\Omega \sim |P_l^m(\cos\theta)|^2 d\Omega$ is the probability that the electron be found at (θ,φ) of the element $d\Omega$. The probability does not depend on φ since we have spherically symmetric potential.

vi)   The probability density for finding an electron at the nucleus tends to zero in all cases. Remember that $R_{nl}(r)$ depends upon r^l.

vii) The radial nodes: where $L_n^\ell(x)=0$, there are $n-\ell-1$ nodes in the radial wavefunction.

viii) Mean values of power is $\left\langle r^k \right\rangle=\int_0^\infty r^{k+2}R_{n\ell}^2(r)\,dr$

$$<nl\,|\,r\,|\,nl>=\frac{1}{2Z}[3n^2-3l(l+1)],$$

$$<nl\,|\,r^2\,|\,nl>=\frac{n^2}{2Z^2}[5n^2+1-3l(l+1)],$$

$$<nl\,|\,\frac{1}{r}\,|\,nl>=\frac{Z}{n^2}$$

| k	Name
1	Dipole
2	Quadrupole
3	Octupole
-1	Coulomb

ATOMIC ORBITALS

Recall that the principal quantum number (*n*) describes the energy level (i.e., distance from nucleus) of the electron; the angular momentum quantum number (ℓ), the shape of the orbital, and; the magnetic quantum number (*m*), the x-, y-, and z-coordinate orientation of the orbital.

1. <u>Shapes</u> of the orbitals: (q.v., below figure)
    A. When l = 0, the only choice for *m* is 0. In other words, there is only one possible orientation for the orbital. What shape is the same in all three coordinates? A sphere! It is called the *s*-shaped orbital.

    B. When $\ell = 1$, there are three choices for *m* (–1, 0, +1). This means that there are three possible orientations for the orbital. Each orbital has looks like a small sphere is each of the upper and lower hemispheres. It is called the *p*-shaped orbital.

    C. When $\ell = 2$, there are five choices for *m* (–2, –1, 0, +1, +2). This means that there are five possible orientations for the orbital. It is called the *d*-shaped orbital.

    D. The last remaining ground-state shaped orbital is called the *f*-shaped orbital. There are seven possible orientations for it and a few ideas of what it looks like.

the one s-shaped orbital

three p-shaped orbitals

the five d-shaped orbital

(http://www.chemieseite.de/allgemein/ao.png)
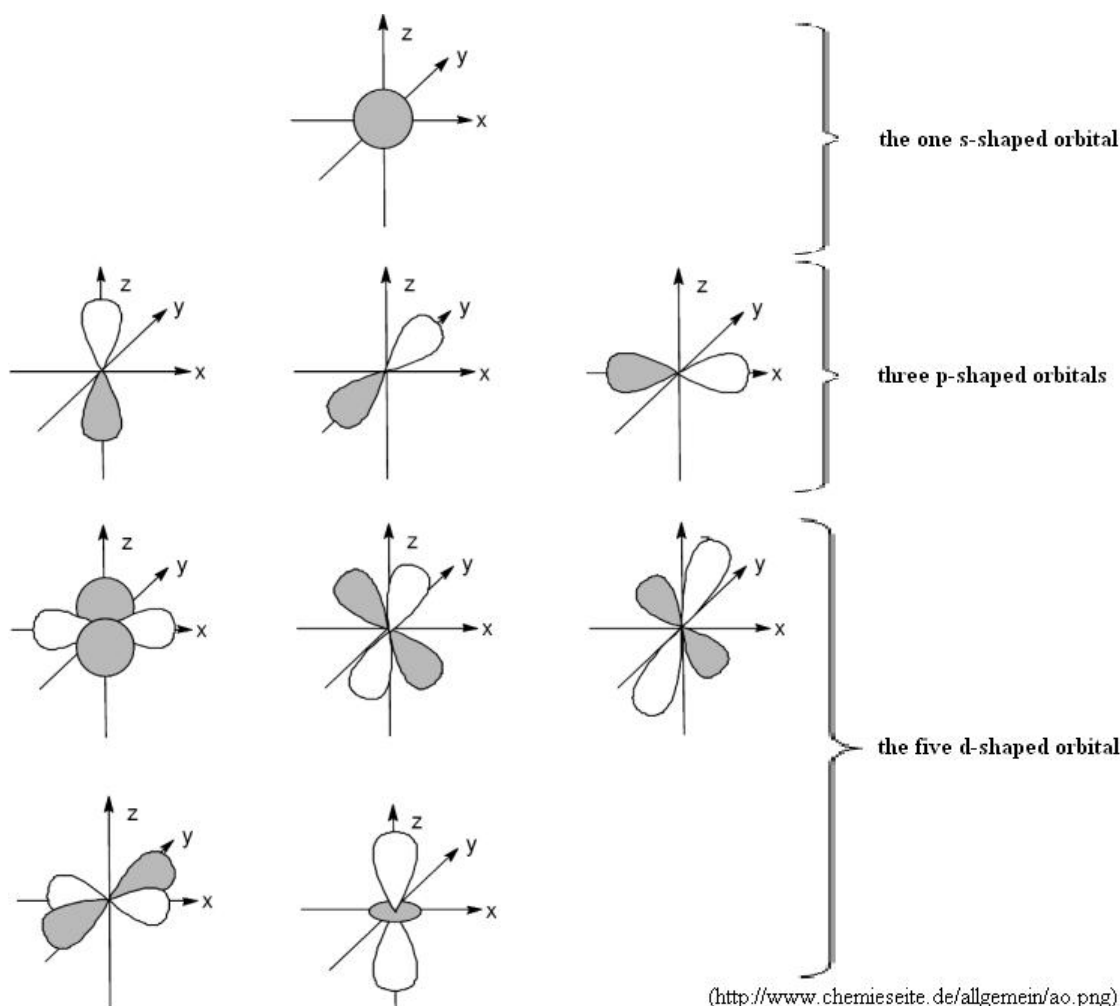
Introduction to Electronic Spectra

Spectrum is measured by observing how light interacts with matter, creating excitations and de-excitations.

For electronic spectra,
- the values the energy levels are of secondary importance
- the difference in energy levels is of primary importance

Energy of a hydrogenic atom

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \cdot \frac{1}{n^2} = -R_H \cdot \frac{1}{n^2}$$

This is exactly Bohr's result!!!

By substituting the values for all of the physical constants, we can write this energy in the more convenient form of

$$\boxed{E_n = -\frac{Z^2}{n^2} Ry = -\frac{Z^2}{2n^2} \text{a.u.} = -\frac{Z^2}{n^2}(13.6 \text{ eV})}$$

Spectral lines for a hydrogenic atom

$$\Delta E = \frac{Z^2}{2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \xrightarrow[\substack{n \gg 1 \\ \text{High Rydberg states}}]{} \frac{Z^2}{n^3}$$

Selection rules for hydrogenic atoms – the allowed changes in quantum numbers
        – i.e., **allowed transitions** between energy levels.

Change of the **principal quantum number**
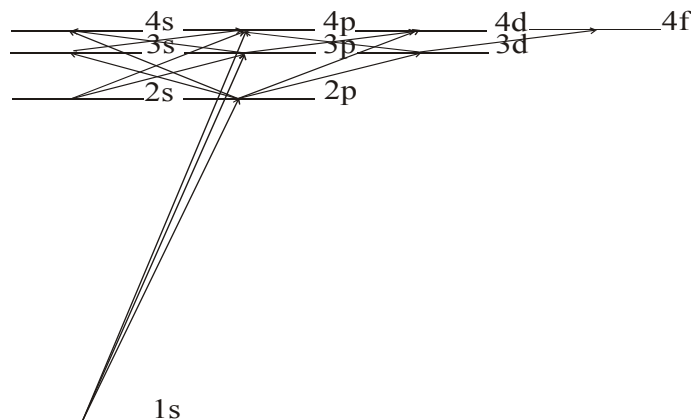$$\Delta n = \pm 1, \pm 2, \pm 3, \ldots$$

Change of the **azimuthal quantum number**
$$\Delta \ell = \pm 1$$

Change of the **magnetic quantum number**
$$\Delta m_\ell = 0, \pm 1$$

The $\Delta \ell = \pm 1$ selection rule implies that the $2s \leftarrow 1s$ transition is a **forbidden transition**

Energy level diagram of a hydrogenic atom

Note: For a hydrogenic atom, the energy levels depend only on the principal quantum number. For a multi-electron atom (i.e., two or more electrons), the energy levels depend on both the principal quantum number and the azimuthal quantum number.

Degeneracy of atomic orbitals

Degeneracy of p orbitals: The wavefunctions for p orbitals are in terms of the spherical harmonics $Y_\ell^{m_\ell}(\theta, \phi)$ are:

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta, \quad Y_1^1(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{i\phi}, \quad Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{-i\phi}$$

Note that: $Y_1^1(\theta, \phi)$ and $Y_1^{-1}(\theta, \phi)$ are complex functions and we are not able to visualize a complex orbital. However, since $Y_1^1(\theta, \phi)$ and $Y_1^{-1}(\theta, \phi)$ are degenerate, any linear combination of them is also a solution to the Schrödinger equation. We can make real wavefunction by taking the following linear combinations

$$p_x = \frac{1}{\sqrt{2}}\left(Y_1^1 + Y_1^{-1}\right) = \left(\frac{3}{16\pi}\right)^{\frac{1}{2}} \sin\theta\left(e^{i\phi} + e^{-i\phi}\right) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \sin\theta\cos\phi$$

$$p_y = \frac{-i}{\sqrt{2}}\left(Y_1^1 - Y_1^{-1}\right) = -i\left(\frac{3}{16\pi}\right)^{\frac{1}{2}} \sin\theta\left(e^{i\phi} - e^{-i\phi}\right) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \sin\theta\sin\phi$$

There is no substantial difference between the $Y_1^1(\theta, \phi)$ and $Y_1^{-1}(\theta, \phi)$ and the $p_x(\theta, \phi)$ and $p_y(\theta, \phi)$ orbitals. Choosing one set over another is matter of convenience.

State	Spherical Harmonics
s	$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$
p	$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta, \qquad Y_1^{\pm 1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{\pm i\phi}$
d	$Y_2^0(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} \left(3\cos^2\theta - 1\right), \quad Y_2^{\pm 1}(\theta, \phi) = \left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta\, e^{\pm i\phi}$ $Y_2^{\pm 2}(\theta, \phi) = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}} \sin^2\theta\, e^{\pm 2i\phi}$

After linear combination of d-state, we have:

$$d_{z^2}(\theta, \phi) = Y_2^0(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} \left(3\cos^2\theta - 1\right), \quad d_{xz} = \frac{1}{\sqrt{2}}\left(Y_2^1 + Y_2^{-1}\right) = \left(\frac{15}{4\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta\cos\phi$$

$$d_{yz} = \frac{-i}{\sqrt{2}}\left(Y_2^1 - Y_2^{-1}\right) = \left(\frac{15}{4\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta\sin\phi, \quad d_{x^2 - y^2} = \frac{1}{\sqrt{2}}\left(Y_2^2 + Y_2^{-2}\right) = \left(\frac{15}{16\pi}\right)^{\frac{1}{2}} \sin^2\theta\cos 2\phi$$

$$d_{xy} = \frac{-i}{\sqrt{2}}\left(Y_2^2 - Y_2^{-2}\right) = \left(\frac{15}{16\pi}\right)^{\frac{1}{2}} \sin^2\theta \sin 2\phi$$

TABLE 1.1
Spherical Harmonics[a]

l	m	$r^l Y_{lm}(x,y,z)$	$Y_{lm}(\theta,\varphi)$
0	0	$\sqrt{\dfrac{1}{4\pi}}$	$\sqrt{\dfrac{1}{4\pi}}$
1	0	$\sqrt{\dfrac{3}{4\pi}}\,z$	$\sqrt{\dfrac{3}{4\pi}}\cos\theta$
1	± 1	$\mp\sqrt{\dfrac{3}{8\pi}}(x\pm iy)$	$\mp\sqrt{\dfrac{3}{8\pi}}\sin\theta\,e^{\pm i\varphi}$
2	0	$\sqrt{\dfrac{5}{4\pi}}\dfrac{1}{4}(3z^2-r^2)$	$\sqrt{\dfrac{5}{4\pi}}\dfrac{1}{4}(3\cos^2\theta-1)$
2	± 1	$\mp\sqrt{\dfrac{5}{4\pi}}\sqrt{\dfrac{3}{2}}z(x\pm iy)$	$\mp\sqrt{\dfrac{5}{4\pi}}\sqrt{\dfrac{3}{2}}\cos\theta\sin\theta\,e^{\pm i\varphi}$
2	± 2	$\sqrt{\dfrac{5}{4\pi}}\sqrt{\dfrac{3}{8}}(x\pm iy)^2$	$\sqrt{\dfrac{5}{4\pi}}\sqrt{\dfrac{3}{8}}\sin^2\theta\,e^{\pm 2i\varphi}$
3	0	$\sqrt{\dfrac{7}{4\pi}}\dfrac{1}{4}z(5z^2-3r^2)$	$\sqrt{\dfrac{7}{4\pi}}\dfrac{1}{4}(2\cos^3\theta-3\cos\theta\sin^2\theta)$
3	± 1	$\mp\sqrt{\dfrac{7}{4\pi}}\sqrt{\dfrac{3}{16}}(x\pm iy)(5z^2-r^2)$	$\mp\sqrt{\dfrac{7}{4\pi}}\sqrt{\dfrac{3}{16}}(4\cos^2\theta\sin\theta-\sin^3\theta)e^{\pm i\varphi}$
3	± 2	$\sqrt{\dfrac{7}{4\pi}}\sqrt{\dfrac{15}{8}}z(x\pm iy)^2$	$\sqrt{\dfrac{7}{4\pi}}\sqrt{\dfrac{15}{8}}\cos\theta\sin^2\theta\,e^{\pm 2i\varphi}$
3	± 3	$\mp\sqrt{\dfrac{7}{4\pi}}\sqrt{\dfrac{5}{16}}(x\pm iy)^3$	$\mp\sqrt{\dfrac{7}{4\pi}}\sqrt{\dfrac{5}{16}}\sin^3\theta\,e^{\pm 3i\varphi}$
4	0	$\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{1}{64}}(35z^4-30z^2r^2+3r^4)$	$\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{1}{64}}(35\cos^4\theta-30\cos^2\theta+3)$
4	± 1	$\mp\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{5}{16}}(x\pm iy)z(7z^2-3zr^2)$	$\mp\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{5}{16}}\sin\theta(7\cos^3\theta-3\cos\theta)e^{\pm i\varphi}$
4	± 2	$\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{5}{32}}(x\pm iy)^2(7z^2-r^2)$	$\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{5}{32}}\sin^2\theta(7\cos^2\theta-1)e^{\pm 2i\varphi}$
4	± 3	$\mp\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{35}{16}}z(x\pm iy)^3$	$\mp\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{35}{16}}\sin^3\theta\cos\theta\,e^{\pm 3i\varphi}$
4	± 4	$\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{35}{128}}(x\pm iy)^4$	$\sqrt{\dfrac{9}{4\pi}}\sqrt{\dfrac{35}{128}}\sin^4\theta\,e^{\pm 4i\varphi}$

[a] In spectroscopic notation, functions that are proportional to Y_{lm} with $l = 0, 1, 2, 3, \ldots$ are called s, p, d, f, ... functions.

$$P_{nl}(r) = \sqrt{\dfrac{(n-l-1)!Z}{n^2[(n+l)!]^3 a_0}\left(\dfrac{2Zr}{na_0}\right)^{l+1}}\, e^{-Zr/na_0}\, L_{n+l}^{2l+1}\left(\dfrac{2Zr}{na_0}\right)$$

$$\int_0^\infty P_{nl}(r)P_{n'l}(r)\,dr = \delta_{nn'}$$

TABLE 1.2
Real Combinations of Spherical Harmonics

Notation	Cartesian coordinates	Polar coordinates	Spherical harmonics
s	1	1	$\sqrt{4\pi}\,Y_{00}$
p_x	x	$r\sin\theta\cos\varphi$	$\sqrt{\dfrac{4\pi}{3}}\sqrt{\dfrac{1}{2}}(-Y_{11}+Y_{1-1})r$
p_y	y	$r\sin\theta\sin\varphi$	$\sqrt{\dfrac{4\pi}{3}}\sqrt{\dfrac{1}{2}}i(Y_{11}+Y_{1-1})r$
p_z	z	$r\cos\theta$	$\sqrt{\dfrac{4\pi}{3}}Y_{10}r$
d_{z^2}	$\dfrac{1}{2}(3z^2-r^2)$	$\dfrac{1}{2}r^2(3\cos^2\theta-1)$	$\sqrt{\dfrac{4\pi}{5}}Y_{20}r^2$
$d_{x^2-y^2}$	$\dfrac{1}{2}\sqrt{3}(x^2-y^2)$	$\dfrac{1}{2}\sqrt{3}r^2\sin^2\theta\cos 2\varphi$	$\sqrt{\dfrac{4\pi}{5}}\sqrt{\dfrac{1}{2}}(Y_{22}+Y_{2-2})r^2$
d_{xy}	$\sqrt{3}xy$	$\sqrt{3}r^2\sin^2\theta\cos\varphi\sin\varphi$	$\sqrt{\dfrac{4\pi}{5}}\sqrt{\dfrac{1}{2}}i(-Y_{22}+Y_{2-2})r^2$
d_{yz}	$\sqrt{3}yz$	$\sqrt{3}r^2\sin\theta\cos\theta\sin\varphi$	$\sqrt{\dfrac{4\pi}{5}}\sqrt{\dfrac{1}{2}}i(Y_{21}+Y_{2-1})r^2$
d_{zx}	$\sqrt{3}zx$	$\sqrt{3}r^2\sin\theta\cos\theta\cos\varphi$	$\sqrt{\dfrac{4\pi}{5}}\sqrt{\dfrac{1}{2}}(-Y_{21}+Y_{2-1})r^2$

$$\langle nlm|n'l'm'\rangle = \int \psi^*_{nlm}(r,\theta,\varphi)\psi_{n'l'm'}(r,\theta,\varphi)\,d\tau = \delta_{nn'}\,\delta_{ll'}\,\delta_{mm'}.$$

TABLE 16.2
Radial Wave Functions in Hydrogen

$$P_{nl}(r) = r R_{nl}(r)$$

n	l	
1	0	$\left(\dfrac{Z}{a_0}\right)^{3/2} 2r\,e^{-Zr/a_0}$
2	0	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{\sqrt{2}}r\left(1-\dfrac{Zr}{2a_0}\right)e^{-Zr/2a_0}$
2	1	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{2\sqrt{6}}\dfrac{Zr^2}{a_0}e^{-Zr/2a_0}$
3	0	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{2}{3\sqrt{3}}r\left[1-\dfrac{2Zr}{3a_0}+\dfrac{2}{27}\left(\dfrac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}$
3	1	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{8}{27\sqrt{6}}\dfrac{Z r^2}{a_0}\left(1-\dfrac{Zr}{6a_0}\right)e^{-Zr/3a_0}$
3	2	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{4}{81\sqrt{30}}\dfrac{Z^2 r^3}{a_0^2}e^{-Zr/3a_0}$

TABLE 16.4
Expectation Values of r^k

$$\langle r^k\rangle = \int_0^\infty R\,r^k\,R\,r^2\,dr$$

k	
1	$\dfrac{a_0}{2Z}[3n^2-l(l+1)]$
2	$\dfrac{a_0^2}{Z^2}\dfrac{n^2}{2}[5n^2+1-3l(l+1)]$
3	$\dfrac{a_0^3}{Z^3}\dfrac{n^2}{8}[35n^2(n^2-1)-30n^2(l+2)(l-1)+3(l+2)(l+1)l(l-1)]$
4	$\dfrac{a_0^4}{Z^4}\dfrac{n^4}{8}[63n^4-35n^2(2l^2+2l-3)+5l(l+1)(3l^2+3l-10)+12]$
-1	$\dfrac{Z}{a_0}\dfrac{1}{n^2}$
-2	$\dfrac{Z^2}{a_0^2}\dfrac{1}{n^3(l+\frac{1}{2})}$

HY (14)

$-\dfrac{Z^2}{n^2}$

TABLE 16.3

Hydrogen Atom Wave Functions[a]

n	l	m	Notation $\left(n\,\ell_m\right)$	Wave function	Energy (Ry)	Degeneracy (n^2)
1	0	0	1s	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{\sqrt{\pi}}e^{-Zr/a_0}$	$-Z^2$	1
2	0	0	2s	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{\sqrt{32\pi}}\left(2-\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$	$-\dfrac{Z^2}{4}$	4
	1	0	$2p_0$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{\sqrt{32\pi}}\dfrac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$		
	1	± 1	$2p_{\pm 1}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{\sqrt{64\pi}}\dfrac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta\, e^{\pm i\varphi}$		
3	0	0	3s	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{81\sqrt{3\pi}}\left[27-18\dfrac{Zr}{a_0}+2\left(\dfrac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}$	$-\dfrac{Z^2}{9}$	9
	1	0	$3p_0$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{81}\sqrt{\dfrac{2}{\pi}}\left[6\dfrac{Zr}{a_0}-\left(\dfrac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}\cos\theta$		
	1	± 1	$3p_{\pm 1}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{81\sqrt{\pi}}\left[6\dfrac{Zr}{a_0}-\left(\dfrac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}\sin\theta\, e^{\pm i\varphi}$		
	2	0	$3d_0$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}(3\cos^2\theta-1)$		
	2	± 1	$3d_{\pm 1}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin\theta\cos\theta\, e^{\pm i\varphi}$		
	2	± 2	$3d_{\pm 2}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{162\sqrt{\pi}}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}\sin^2\theta\, e^{\pm 2i\varphi}$		
4	0	0	4s	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{1536\sqrt{\pi}}\left[192-144\dfrac{Zr}{a_0}+24\left(\dfrac{Zr}{a_0}\right)^2-\left(\dfrac{Zr}{a_0}\right)^3\right]e^{-Zr/4a_0}$	$-\dfrac{Z^2}{16}$	16
	1	0	$4p_0$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{2560}\sqrt{\dfrac{5}{\pi}}\left[80\dfrac{Zr}{a_0}-20\left(\dfrac{Zr}{a_0}\right)^2+\left(\dfrac{Zr}{a_0}\right)^3\right]e^{-Zr/4a_0}\cos\theta$		
	1	± 1	$4p_{\pm 1}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{2560}\sqrt{\dfrac{5}{2\pi}}\left[80\dfrac{Zr}{a_0}-20\left(\dfrac{Zr}{a_0}\right)^2+\left(\dfrac{Zr}{a_0}\right)^3\right]e^{-Zr/4a_0}\sin\theta\, e^{\pm i\varphi}$		
	2	0	$4d_0$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{3062\sqrt{\pi}}\left[12\left(\dfrac{Zr}{a_0}\right)^2-\left(\dfrac{Zr}{a_0}\right)^3\right]e^{-Zr/4a_0}(3\cos^2\theta-1)$		
	2	± 1	$4d_{\pm 1}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{1536}\sqrt{\dfrac{3}{2\pi}}\left[12\left(\dfrac{Zr}{a_0}\right)^2-\left(\dfrac{Zr}{a_0}\right)^3\right]e^{-Zr/4a_0}\sin\theta\cos\theta\, e^{\pm i\varphi}$		
	2	± 2	$4d_{\pm 2}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{3072}\sqrt{\dfrac{3}{2\pi}}\left[12\left(\dfrac{Zr}{a_0}\right)^2-\left(\dfrac{Zr}{a_0}\right)^3\right]e^{-Zr/4a_0}\sin^2\theta\, e^{\pm 2i\varphi}$		
	3	0	$4f_0$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{3072\sqrt{5\pi}}\left(\dfrac{Zr}{a_0}\right)^3 e^{-Zr/4a_0}(5\cos^3\theta-3\cos\theta)$		
	3	± 1	$4f_{\pm 1}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{6144}\sqrt{\dfrac{3}{5\pi}}\left(\dfrac{Zr}{a_0}\right)^3 e^{-Zr/4a_0}\sin\theta(5\cos^2\theta-1)e^{\pm i\varphi}$		
	3	± 2	$4f_{\pm 2}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{3072}\sqrt{\dfrac{3}{2\pi}}\left(\dfrac{Zr}{a_0}\right)^3 e^{-Zr/4a_0}\sin^2\theta\cos\theta\, e^{\pm 2i\varphi}$		
	3	± 3	$4f_{\pm 3}$	$\left(\dfrac{Z}{a_0}\right)^{3/2}\dfrac{1}{6144\sqrt{\pi}}\left(\dfrac{Zr}{a_0}\right)^3 e^{-Zr/4a_0}\sin^3\theta\, e^{\pm 3i\varphi}$		

[a] All the wave functions are written with a positive phase factor.

Appendix I

Spherical Coordinates
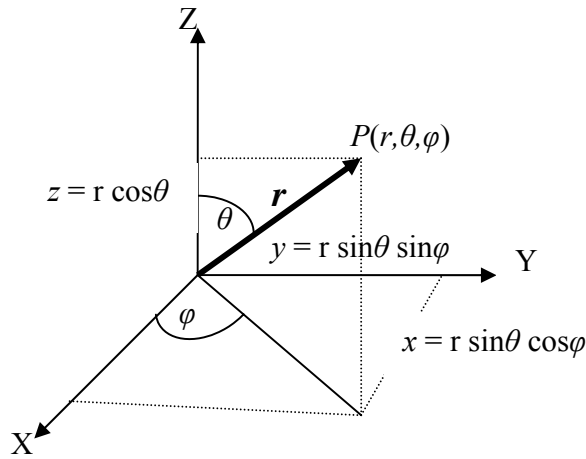
$$x = r \sin\theta \cos\varphi, \quad |\boldsymbol{r}| = \sqrt{x^2 + y^2 + z^2}$$

$$y = r \sin\theta \sin\varphi, \quad \theta = \tan^{-1} \frac{\sqrt{x^2 + y^2}}{z}, \quad \frac{\partial |\boldsymbol{r}|}{\partial x} = \frac{1}{2} \frac{2x}{|\boldsymbol{r}|} = \frac{x}{|\boldsymbol{r}|},$$

$$z = r \cos\theta, \quad \varphi = \tan^{-1} \frac{y}{x}$$

$$\theta \equiv \{0, \pi\}, \quad \varphi \equiv \{0, 2\pi\}, \quad r \equiv \{0, \infty\},$$

$$d\tau = r^2 \, dr \, d\Omega,$$

H.W. Prove the following:

$$\frac{\partial}{\partial x} = \underbrace{\frac{\partial r}{\partial x}}_{x/r} \frac{\partial}{\partial r} = \frac{x}{r} \frac{\partial}{\partial r}, \qquad \frac{\partial^2}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{x}{r} \frac{\partial}{\partial r} \right) = \left(\frac{1}{r} - \frac{x^2}{r^3} \right) \frac{\partial}{\partial r} + \frac{x^2}{r^2} \frac{\partial^2}{\partial r^2},$$

$\dfrac{\partial r}{\partial x} = \dfrac{x}{r} = \sin\theta \cos\varphi$	$\dfrac{\partial \theta}{\partial x} = \dfrac{\cos\theta \cos\varphi}{r}$	$\dfrac{\partial \varphi}{\partial x} = -\dfrac{\sin\varphi}{r \sin\theta}$	$\dfrac{\partial x}{\partial \varphi} = -y$
$\dfrac{\partial r}{\partial y} = \dfrac{y}{r} = \sin\theta \sin\varphi$	$\dfrac{\partial \theta}{\partial y} = \dfrac{\cos\theta \sin\varphi}{r}$	$\dfrac{\partial \varphi}{\partial y} = \dfrac{\cos\varphi}{r \sin\theta}$	$\dfrac{\partial y}{\partial \varphi} = x$
$\dfrac{\partial r}{\partial z} = \cos\theta$	$\dfrac{\partial \theta}{\partial z} = -\dfrac{\sin\theta}{r}$	$\dfrac{\partial \varphi}{\partial z} = 0$	$\dfrac{\partial z}{\partial \varphi} = 0$

H.W. Prove that the Laplace's equation in spherical coordinates is given by:

$$\nabla^2 V(r,\theta,\phi) = \frac{1}{r}\frac{\partial^2}{\partial r^2}(rV) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial V}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 V}{\partial\phi^2}$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial V}{\partial r}) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial V}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 V}{\partial\phi^2} = 0$$

H.W. Prove that: $\dfrac{1}{r}\dfrac{\partial^2}{\partial r^2}(rV) = \dfrac{1}{r^2}\dfrac{\partial}{\partial r}(r^2\dfrac{\partial V}{\partial r})$

Coulomb Potential Energy:

$$\boxed{V(r) = -k\frac{Ze^2}{r}, \qquad\qquad k = \frac{1}{4\pi\varepsilon_o}}$$ (1)

Time-independent Schrödinger Equation:

$$\boxed{-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)}$$ (2)

Transform Laplacian from rectangular to spherical polar coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Use the chain rule,

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial x}$$

$$\frac{\partial}{\partial y} = \frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial y}$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial z} + \frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial z}$$

to find:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$ (3)

Assume that the eigenfunction is <u>separable</u>:

$$\boxed{\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)}$$ (4)

Substituting (3)&(4) into (2) gives:

$$\frac{-\hbar^2}{2\mu}\left[\Theta\Phi\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + \frac{R\Phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta}{\partial\theta}) + \frac{R\Theta}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] + VR\Theta\Phi = ER\Theta\Phi$$ (5)

** Note that all of the derivatives are now *ordinary* derivatives so we can replace ∂ by *d*.

Multiply (5) by $\dfrac{-2\mu\, r^2 \sin^2\theta}{\hbar^2}\dfrac{1}{R\Theta\Phi}$ and rearrange terms to obtain:

$$\boxed{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}(r^2\frac{dR}{dr}) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) + \frac{2\mu}{\hbar^2}r^2\sin^2\theta(V(r)-E)} \qquad (6)$$

Notice that the LHS only involves functions of ϕ while the RHS only involves functions of *r* and θ. Thus, both sides must equal a constant which we'll call *C*.

----

1. **FINDING $\Phi(\phi)$**

Setting the LHS of (6) equal to this constant *C* gives:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = C \qquad \rightarrow \qquad \frac{d^2\Phi}{d\phi^2} = C\Phi \qquad (7)$$

A solution to (7) is

$$\Phi(\phi) = e^{\phi\sqrt{C}} \qquad (8)$$

The periodicity of ϕ requires that $\Phi(\phi) = \Phi(\phi+2\pi)$. Now a *sin* or *cos* function has this periodicity so let

$$C = -m_\ell^2 \qquad (9)$$

which gives:

$$\Phi(\phi) = e^{im_\ell\phi} \qquad (10)$$

This function now has the correct periodicity. Note that the condition that $\Phi(0)=\Phi(2\pi)$ gives

$$1 = e^{i2\pi m_\ell} \qquad (11)$$

Eq. (11) is only satisfied if

$$m_\ell = 0,\pm1,\pm1,\cdots \qquad (12)$$

Thus, m_ℓ can only have certain values, i.e. it is a *quantum number*.
----

2. FINDING $\Theta(\theta)$

Eq. (6) can now be written as

$$-m_\ell^2 = -\frac{\sin^2\theta}{R}\frac{d}{dr}(r^2\frac{dR}{dr}) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) + \frac{2\mu}{\hbar^2}(V(r)-E)r^2\sin^2\theta \qquad (13)$$

Dividing by $\sin^2\theta$ and rearranging terms gives:

$$\frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) = \frac{1}{R}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{2\mu}{\hbar^2}r^2(E-V(r)) \qquad (14)$$

Notice that the LHS only involves functions of θ while the RHS only involves functions of *r*. Thus, both sides must equal a constant which we'll call $\ell(\ell+1)$.

Setting the LHS of this equation equal to this constant gives an equation for $\Theta(\theta)$:

$$-\frac{1}{\Theta \sin \theta}\frac{d}{d\theta}(\sin \theta \frac{d\Theta}{d\theta}) + \frac{m_\ell^2}{\sin^2 \theta} = \ell(\ell+1) \tag{15}$$

By making a change of variables using $z = \cos\theta$, Eq. (15) is transformed into a differential equation called the *associated Legendre's equation*:

$$\frac{d}{dz}\left[(1-z^2)\frac{d\Theta}{dz}\right] + \left[\ell(\ell+1) - \frac{m_\ell^2}{1-z^2}\right]\Theta = 0 \tag{16}$$

A series solution is found for this equation involving polynomials of *z*. These polynomials are called *associated Legendre functions.*

The requirement that Θ remain finite (i.e. does not blow up) leads to integer values of ℓ and certain restrictions on m_ℓ as follows:

$$\ell = 0,1,2,\cdots; \tag{17}$$

and for a given allowed value of ℓ,

$$m_\ell = -\ell, -\ell+1, \cdots, +\ell \tag{18}$$

Thus, we have another *quantum number* ℓ which dictates possible values for the original quantum number m_ℓ.

We can write the associated Legendre functions with the quantum number subscripts as polynomials of *z*, or to be of more use, as polynomials of cosθ in the form $\Theta_{\ell m_\ell}(\cos\theta)$. The first few polynomials are given below:

$\Theta_{00} = 1$ $\Theta_{10} = \cos\theta$ $\Theta_{1\pm1} = (1-\cos^2\theta)^{1/2}$

$\Theta_{20} = 1-3\cos^2\theta$ $\Theta_{2\pm1} = (1-\cos^2\theta)^{1/2}\cos\theta$ $\Theta_{2\pm2} = 1-\cos^2\theta$

--------------- *The Spherical Harmonic Functions* -----------------------------

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:

$$\boxed{Y_\ell^{m_\ell}(\theta,\phi) = \Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\phi)} \tag{19}$$

The first few spherical harmonics are given below:

l	m	$Y_{\ell}^{m_{\ell}}(\theta,\phi)$
0	0	$1/\sqrt{4\pi}$
1	0	$\sqrt{\dfrac{3}{4\pi}}\cos\theta$
	± 1	$\mp\sqrt{\dfrac{3}{8\pi}}\sin\theta\,e^{\pm i\varphi}$
2	0	$\sqrt{\dfrac{5}{16\pi}}\left(3\cos^2\theta-1\right)$
	± 1	$\mp\sqrt{\dfrac{15}{8\pi}}\cos\theta\sin\theta e^{\pm i\varphi}$
	± 2	$\sqrt{\dfrac{15}{32\pi}}\sin^2\theta\,e^{\pm 2i\varphi}$

Spherical Harmonics:

Combining the Angular Eigenfunctions together, One gets the <u>Spherical Harmonics</u>:

$$Y_{\ell}^{m_{\ell}}(\theta,\phi)) = \boxed{(-1)^m}\left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}\right]^{1/2}P_{\ell}^{m}(\cos\theta)e^{im\varphi}; \qquad m\geq 0$$

$$Y_{\ell}^{-m_{\ell}}(\theta,\phi) = (-1)^m\,Y_{\ell}^{*m_{\ell}}(\theta,\phi); \qquad \ell=0,1,2,\cdots; \qquad m_{\ell}=-\ell,-\ell+1,\cdots,+\ell$$

which have the characteristic: $Y_{\ell}^{-m_{\ell}}(\theta,\phi) = (-1)^m\,Y_{\ell}^{*m_{\ell}}(\theta,\phi)$ and are normalized such that

$$\left\langle \ell m_{\ell}\big|\ell'm'_{\ell}\right\rangle = \int_{0}^{2\pi}d\varphi\int_{0}^{\pi}\sin\theta\,d\theta\,Y_{\ell}^{*m_{\ell}}(\theta,\varphi)Y_{\ell'}^{m'_{\ell}}(\theta,\varphi) = \delta_{\ell\ell'}\delta_{mm'}$$

$d\Omega$ =solid angle differential $d\Omega = \sin\theta d\theta d\phi$ $\int_{S^2}d\Omega = 4\pi$

The closure relation for Spherical Harmonics:

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}Y_{\ell}^{*m_{\ell}}(\theta',\phi')Y_{\ell}^{m_{\ell}}(\theta,\phi) = \delta(\phi-\phi')\delta(\cos\theta-\cos\theta')$$

The closure relation implies that the $Y_{\ell}^{m_{\ell}}$ are complete, i.e. we can represent any function on the sphere as

$$f(\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m_{\ell}=-\ell}^{\ell}a_{\ell m}Y_{\ell}^{m_{\ell}}(\theta,\phi)$$

Since the radial Eigenfunctions are given by $U(r) = Ar^{\ell}+Br^{-(\ell+1)}$, then $\Phi(r,\theta,\phi)$ can be decomposed as

$$\Phi(r,\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m_{\ell}=-\ell}^{\ell}\left(A_{\ell m_{\ell}}r^{\ell}+B_{\ell m_{\ell}}r^{-(\ell+1)}\right)Y_{\ell}^{m_{\ell}}(\theta,\phi)$$

Recurrence relations

$$\cos\theta\,Y_{\ell,m}(\theta,\varphi) = \left[\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}\right]^{1/2}Y_{\ell+1,m}(\theta,\varphi)+\left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right]^{1/2}Y_{\ell-1,m}(\theta,\varphi);$$

$$\sin\theta\,Y_{\ell,m}(\theta,\varphi) = \left[\frac{(\ell+1-m)(\ell+2-m)}{(2\ell+1)(2\ell+3)}\right]^{1/2}Y_{\ell+1,m-1}(\theta,\varphi)+\left\{\left[\frac{(\ell+m)(\ell+m-1)}{(2\ell+1)(2\ell-1)}\right]^{1/2}Y_{\ell-1,m-1}(\theta,\varphi)\right\}e^{i\varphi}$$

3 Finding *R(r)* and the quantized energies

Setting the RHS of Eq. (14) equal to the constant $\ell(\ell+1)$ gives:

$$\frac{1}{R}\frac{d}{dr}(r^2\frac{dR}{dr})+\frac{2\mu}{\hbar^2}r^2(E-V(r))=\ell(\ell+1) \tag{20}$$

We define two new variables, with equation (1):

$$\beta^2=\frac{-2\mu E}{\hbar^2}\quad\text{and}\quad\gamma=\frac{\mu Ze^2}{4\pi\varepsilon_o\hbar^2\beta} \tag{21}$$

Using these substitutions and multiplying Eq. (20) by R/r^2 gives:

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr})+\left[-\beta^2+\frac{2\beta\gamma}{r}-\frac{\ell(\ell+1)}{r^2}\right]R=0 \tag{22}$$

By making a change of variables using $r=2\beta\rho$ and dividing by $4\beta^2$, this Eq. (22) becomes:

$$\frac{1}{\rho^2}\frac{d}{d\rho}(\rho^2\frac{dR}{d\rho})+\left[-\frac{1}{4}+\frac{\gamma}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right]R=0 \tag{23}$$

We are looking for solutions to Eq. (23) in the form:

$$R(\rho)=F(\rho)e^{-\rho/2} \tag{24}$$

Substituting this function into Eq. (23) gives:

$$\frac{d^2F}{d\rho^2}+\left(\frac{2}{\rho}-1\right)\frac{dF}{d\rho}+\left[\frac{\gamma-1}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right]F=0 \tag{25}$$

Again, a series solution is found involving polynomials. The requirement that F(ρ) does not blow up as $\rho\rightarrow\infty$ demands that γ be an integer (which we'll call *n*) that obeys:

$$\gamma=n=\ell+1,\ell+2,\ell+3,\cdots \tag{26}$$

Note that this third *quantum number n* dictates the allowed values of the quantum number ℓ since for a given *n*, then ℓ can only have values of

$$\ell=0,1,2,\cdots,n-1 \tag{27}$$

And remember that the value of a particular ℓ dictates the possible values of m_ℓ via Eq. (18).

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$$\langle \sin^2(\theta) \rangle_{\ell,m} = \frac{2(\ell^2+\ell-1+m^2)}{(2\ell-1)(2\ell+3)}$$

$$\langle \cos^2(\theta) \rangle_{\ell,m} = \frac{2(\ell^2+\ell-\frac{1}{2}-m^2)}{(2\ell-1)(2\ell+3)}$$

where

$$\langle f(\theta,\phi) \rangle_{\ell m} = \int d\Omega\, f(\theta,\phi)\, |Y_{\ell m}(\theta,\phi)|^2$$

$$x = r \sin\theta \cos\phi = \sqrt{\frac{2\pi}{3}} \left(Y_{1,1} - Y_{1,-1} \right) r$$

$$y = r \sin\theta \sin\phi = i\sqrt{\frac{2\pi}{3}} \left(Y_{1,1} + Y_{1,-1} \right) r$$

$$z = r \cos\theta = \sqrt{\frac{4\pi}{3}}\, Y_{1,0}\, r$$

ex $r \sin^2\theta \cos 2\phi = 2\sin^2\theta \sin\phi \cos\phi$

$$= 2(\sin\theta\cos\phi)(\sin\theta\sin\phi)$$

$$= 2\left(\frac{x}{r}\right)\left(\frac{y}{r}\right) = \frac{2}{r^2}xy$$

ex2 $3\cos^2\theta - 1 = 3\cos^2\theta - \cos^2\theta - \sin^2\theta = 2\cos^2\theta - \sin^2\theta$

$$\left(\frac{x}{r}\right)^2 = \sin^2\theta \cos^2\phi, \quad \left(\frac{y}{r}\right)^2 = \sin^2\theta \sin^2\phi$$

$$\therefore \frac{1}{r^2}(x^2+y^2) = \sin^2\theta(\sin^2\phi + \cos^2\phi) = \sin^2\theta$$

$$\therefore 3\cos^2\theta - 1 = 2\left(\frac{z^2}{r^2}\right) - \frac{1}{r^2}(x^2+y^2) = \frac{1}{r^2}(2z^2 - x^2 - y^2)$$