Lecture 4 Highlights

The angular part of the Schrödinger equation:

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2} = -\ell(\ell+1)\sin^2\theta\, Y(\theta,\phi),$$

can now be written as an eigenvalue equation: $L^2 Y_\ell^m(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\phi)$. The eigenvalue of L^2 is $\hbar^2\ell(\ell+1)$, and the eigenfunction is the 'spherical harmonic' $Y_\ell^m(\theta,\phi)$.

One can find that the z-component of the angular momentum (vector) operator $\vec{L} = \vec{r}\times(-i\hbar\vec{\nabla})$ is given by: $L_z = -i\hbar\frac{\partial}{\partial\phi}$. When applied to the spherical harmonics, it gives: $L_z Y_\ell^m(\theta,\phi) = m\hbar Y_\ell^m(\theta,\phi)$. Hence the spherical harmonics are also eigenfunctions of the L_z operator, with eigenvalue $m\hbar$. The spherical harmonics are simultaneous eigenfunctions of L^2 and L_z.

We discussed the statistical interpretation of $\left|Y_\ell^m(\theta,\phi)\right|^2$ and examined the case of $\ell = 2$ (see Supplementary Material on the class web site).

The radial equation has an infinite number of bound states (E<0) for any given value of ℓ.

$$\frac{-\hbar^2}{2m}\frac{d^2(rR)}{dr^2} + \left[\frac{-e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right](rR) = E(rR)$$

Define $\kappa^2 \equiv \frac{-2mE}{\hbar^2}$ $(E<0)$, hence κ is real

$$\rho \equiv \kappa r$$

$$\rho_0 \equiv \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}$$

$$u(r) \equiv rR(r)$$

And the radial equation becomes:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

After 'peeling off' the asymptotic behavior of this equation at large and small ρ, we try this (ansatz) substitution:

$$u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho),$$

where $v(\rho)$ is an unknown function that should capture the wiggling between small and large ρ. The resulting equation for $v(\rho)$ is:

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$$

Try an infinite series solution around $\rho = 0$;

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$$

This leads to a recursion relation for the coefficients a_j:

$$a_{j+1} = a_j \frac{2j + 2(\ell + 1) - \rho_0}{(j+1)\left[j + 2(\ell + 1)\right]}$$

The recursion relation calculates the next value of a_j given the previous value. However this recursion relation leads to a non-normalizable solution for $R(r)$ $(\sim e^{+\rho})$ unless the series terminates at some finite upper limit. To terminate the series, one can make the numerator of the recursion relation equal to zero at some index value $j = j_{\max}$. This requires that;

$$2j_{\max} + 2(\ell + 1) - \rho_0 = 0 .$$

Now define $n \equiv j_{\max} + \ell + 1$. Note that since $\ell = 0,1,2,3,...$ (from the solution to the θ equation) and $j_{\max} = 0,1,2,3,...$ (since these are the index values in the series solution), it must be that n is an integer too, with the possible values $n = 1,2,3,4,...$

The above condition to terminate the infinite series now becomes: $\rho_0 = 2n$. Using the definition of ρ_0 and κ, we can solve for the only unknown, namely the eigen-energy E, which now becomes quantized. This forces a quantization condition on the total energy eigenvalue of the original Schrödinger equation:

$$E_n = -\frac{1}{n^2}\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

where m is the electron (reduced) mass (not to be confused with the magnetic quantum number!), $\hbar$ is Planck's constant divided by 2π, e is the electronic charge, ε_0 is the permittivity of free space, and n is an integer that is bigger than ℓ, i.e. $\ell \le n - 1$. This last condition originates from the need to terminate the infinite series solution to obtain a normalizable result for $R(r)$. Note than since $\ell = 0,1,2,3,...$, it must be that $n = 1,2,3,4,...$ Hence the lowest energy state available to an electron and proton in a bound state is $E_1 = -13.6\ eV$.

The Hydrogen atom Schrödinger equation solution has a characteristic size, called the Bohr radius:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}.$$

The Bohr radius is about 0.5 Angstroms. A hydrogen atom never gets "smaller" than about this size.

The solution for $v(\rho)$ is:

$$v(\rho) = \sum_{j=0}^{j_{\max}} a_j \rho^j = L_{n-\ell-1}^{2\ell+1}(2\rho),$$

where $\rho \equiv \kappa r$. This is the Associate Laguerre polynomial, Griffiths [4.88]. It is a polynomial of degree $n - \ell - 1$.

The full solution of the time-independent Schrödinger equation for the H-atom is found by multiplying the R(r) solution with the angular solution and properly normalizing the entire wavefunction:

$$\psi_{n\ell m}(r,\theta,\phi)=\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\left(\frac{2r}{na_0}\right)^{\ell}e^{-r/na_0}L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)Y_\ell^m(\theta,\phi)$$

There are three quantum numbers: n (principal), ℓ (ang. mom.) and m (magnetic). They have possible values given by:

$n = 1,2,3,4,...$

$\ell = 0,1,2,...n-1$

$m = -\ell,-\ell+1,...0,...\ell-1,\ell$

The hydrogen atom wavefunctions are orthonormal, Griffiths [4.90]. The ground state ($n=1,\ell=0,m=0$) wavefunction is a ‘fuzzy ball’, given by;

$$\psi_{100}(r,\theta,\phi)=\sqrt{\frac{1}{\pi\, a_0^3}}\; e^{-r/a_0}$$