Hydrogen Atom

The Hamiltonian in spherical polar coordinates is

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\ell_{op}^2}{2\mu r^2} - \frac{Ze^2}{r}$$

where is the square of angular momentum operator ℓ_{op}^2. Note that the potential depends only on r and so H commutes with ℓ_{op}^2 and ℓ_z. Thus eigenfunctions of H can be written in the form $R_{n,\ell}(r)Y_{\ell,m}(\theta,\varphi)$, where $R_{n,\ell}(r)$ satisfies

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

To proceed, examine the solution for r large, and also need to examine behavior as r goes to zero, because of the singular nature of Coulomb potential. It is sometimes convenient to introduce a new function $u_{n,\ell}(r) = rR_{n,\ell}(r)$ in terms of which the above equation is

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} - E_n\right]u_{n\ell}(r) = 0$$

(**Prove this for homework**).

Re-write as

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{2r^2} + \frac{2\mu Ze^2}{r\hbar^2} + \frac{2\mu E_n}{\hbar^2}\right]u_{n\ell}(r) = 0$$

as usual, get the asymptotic solution. The differential equation is then

$$\left[\frac{d^2}{dr^2} + \frac{2\mu E_n}{\hbar^2}\right]u_{n\ell}(r) = 0$$

and recall that E_n is negative. So the asymptotic solution is of the form

$$u_{n\ell}(r) \sim \exp(-\kappa r)$$
$$\kappa = \sqrt{-\frac{2\mu E_n}{\hbar^2}} \quad .$$

Near the origin, and for $\ell > 0$ the differential equation is

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{2r^2}\right]u_{n\ell}(r) = 0 .$$

The general solution is $u_{n\ell}(r) = Ar^{\ell+1} + Br^{-\ell}$, but B must equal zero for an acceptable solution. Thus, the general solution is of the form

$$u_{n\ell}(r) = r^{\ell+1}e^{-\kappa r}v(r)$$

Introduce a new variable as follows $\rho = \kappa r$, and then let

$$u_{n\ell}(r) = \rho^{\ell+1}e^{-\rho}v_{n\ell}(\rho)$$

and the equation for v is

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

where V is the Coulomb potential. Develop a series for v and examine the asymptotic form, and see that the series diverges as $e^{2\rho}$ unless it terminates at some power N. Doing that gives the result that $\frac{Ze^2\kappa}{|E|} = 2(N + \ell + 1)$ and re-arranging give

$$E_n = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2}; \quad n = (N + \ell + 1).$$

Thus, as in the two-dimensional isotropic harmonic oscillator, there is a degeneracy in the eigenvalues, i.e., for each n ℓ varies from 0 to n-1, and so there are n+1 values of ℓ. In addtion, for each ℓ there are 2ℓ+1 values of m. Recall -ℓ≤ m ≤ ℓ. So, the total degeneracy is

$$g_n = \sum_{l=0}^{n-1} 2\ell + 1 = 1 + 3 + 5 + \ldots + 2(n-1) + 1 = n^2$$