6/5/08 Lecture 19 outline

• Last time : Consider spherically symmetric $H = \frac{1}{2m}\vec{p}^2 + V(r)$. Since $[H, L_i] = 0$, we can find simultaneous eigenstates $|E, \ell, m\rangle$ of H, L^2, and L_z. Indeed, note that

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2} + V(r)$$

where in position space the first terms correspond to

$$\vec{p}^2 \to -\hbar^2\,\nabla^2 = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}\right) \equiv p_r^2 + \frac{L^2}{r^2}.$$

It is common, also in classical mechanics, to note that this looks like a 1d problem now, with $V_{eff}(r) = V(r) + (L^2/2\mu r^2)$. Here μ is the mass, not to be mistaken for the m integer appearing in $|\ell, m\rangle$. The energy eigenvalue equation then becomes

$$\left(\frac{p_r^2}{2\mu} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right)|E, \ell, m\rangle = E|E, \ell, m\rangle.$$

In position space, write this equation and discuss solution by separation of variables. We then have $\psi_{E,\ell,m}(r, \theta, \phi) = \langle r, \theta, \phi|E, \ell, m\rangle = R_{n,\ell}(r)Y_{\ell,m}(\theta, \phi)$, where

$$\left(-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right)R_{n,\ell}(r) = E_{n,\ell}R_{n,\ell}(r),$$

where n labels the solutions of this equation. The energy is quantized, via n, because we're considering bound states of the potential. Note that the energy eigenvalues $E_{n,\ell}$ don't depend on the L_z eigenvalue m; this is as expected from the spherical symmetry, which implies that $[H, L_\pm] = 0$. The derivative terms become a little simpler if we define $R_{n,\ell}(r) = U_{n,\ell}(r)/r$:

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right)U_{n,\ell}(r) = E_{n,\ell}U_{n,\ell}(r).$$

• Consider the limit $r \to 0$. If $\ell \neq 0$, and if $V(r)$ is less singular than r^{-2} as $r \to 0$, then the terms $V(r)$ and the term E become negligible as $r \to 0$, and we have $U_\ell''(r) \approx \ell(\ell+1)r^{-2}U_\ell(r)$, i.e. for $r \to 0$, we have $R_\ell(r) = U_\ell(r)/r \to A_\ell r^\ell + B_\ell r^{-(\ell+1)}$, as is familiar from solving the Laplace eqn. in spherical coordinates. We need to set $B_\ell = 0$ to have a regular solution at $r = 0$. Now consider $r \to \infty$ and suppose that $V \to 0$ in this limit. Then the $E < 0$ bound state wavefunctions behave for $r \to \infty$ as $U(r) \sim e^{-\kappa r}$ in this limit, with $\kappa = \sqrt{2\mu|E|/\hbar^2}$.

• Consider $V(r) = -Ze^2/4\pi\epsilon_0 r$. Define $\rho \equiv \sqrt{8\mu|E|/\hbar^2} r$ and $\lambda \equiv \frac{Ze^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{\mu}{2|E|}} = Z\alpha\sqrt{\frac{\mu c^2}{2|E|}}$. To account for above asymptotic behaviors, define $R(r) = e^{-\rho/2}\rho^\ell H(\rho)$. The equation for $H(\rho)$ is then

$$H''(\rho) + (\frac{2\ell+2}{\rho} - 1)H'(\rho) + \frac{\lambda-\ell-1}{\rho}H = 0.$$

Take $H(\rho) = \sum_k a_k \rho^k$ and plug into above eqn to get

$$\sum_k \rho^{k-1}\left((k+1)(k+2\ell+2)a_k + (\lambda-\ell-1-k)a_k\right) = 0.$$

Set each term to zero, so get recursion relation:

$$\frac{a_{k+1}}{a_k} = \frac{k+\ell+1-\lambda}{(k+2\ell+2)(k+1)},$$

For large k this would imply $a_{k+1}/a_k \to 1/k$ for $k \to \infty$, which would imply the wrong behavior for large r (corresponding to $R(r) \sim e^{+\rho/2}$) unless the series terminates.

$H(\rho)$ must be a polynomial of finite degree, i.e. the recursion relation must truncate at some k_{max}, so that $a_{k_{max}+1} = 0$. Define $n \equiv k_{max} + \ell + 1$. Then $\lambda = n$. This gives E in terms of n.

• Summary: $E_n = -\frac{1}{2}\mu(Ze^2/4\pi\epsilon_0\hbar)^2 \cdot n^{-2} = -\frac{1}{2}\mu c^2(Z\alpha)^2/n^2$, where $n \geq \ell+1$. Then $\rho = 2\mu Ze^2 r/4\pi\epsilon_0\hbar^2 n \equiv 2Zr/na_0$ where $a_0 = \hbar^2 4\pi\epsilon_0/\mu e^2 = \hbar/\mu c\alpha$ is the Bohr radius, numerically $a_0 \approx 0.5\mathring{A}$. So $R_{n,\ell}(r) = (Zr/na_0)^\ell e^{-Zr/na_0} H_{n,\ell}(Zr/na_0)$, where $H_{n,\ell}(\rho)$ is a degree $k_{max} = n-\ell-1$ polynomial (related to what's called the associated Laguerre polynomial, $H_{n,\ell}(\rho) \sim L^{2\ell+1}_{n-\ell-1}(\rho)$).

• Count the degeneracy of solutions with $E = E_n$: since k_{max} is a non-negative integer, the value of ℓ can go from zero to $n-1$. For each ℓ value, there is a $2\ell+1$ fold degeneracy of $L_z = m\hbar$ quantum numbers. (The ℓ degeneracy is related to Lenz vector $\vec{A} = (\vec{L}\times\vec{p} - \vec{p}\times\vec{L})/2\mu\alpha + \vec{r}/r$). So the total degeneracy here is

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2.$$

• The radial probability distribution is $|\psi_{n,\ell,m}|^2 \sim r^2 R_{n,\ell}(r)^2$. Draw some plots.

• Put it all together, for $Z = 1$:

$$\psi_{1,0,0} = (\pi a_0^3)^{-1/2} e^{-r/a_0} \qquad \text{groundstate.}$$

$$\psi_{2,0,0} = (32\pi a_0^3)^{-1/2}(2 - r/a_0)e^{-r/2a_0},$$

$$\psi_{2,1,0} = (32\pi a_0^3)^{-1/2}(r/a_0)e^{-r/2a_0}\cos\theta$$

$$\psi_{2,1,\pm 1} = \mp(64\pi a_0^3)^{-1/2}(r/a_0)e^{-r/2a_0}\sin\theta e^{\pm i\phi}.$$

• Consider $\langle r^k \rangle = \int_0^\infty dr r^{2+k}(R_{n\ell}(r))^2$. Get e.g. $\langle r \rangle = (3n^2 - \ell(\ell+1))a_0/2Z$ and $\langle r^{-1} \rangle = Z/a_0 n^2$. The simplicity of the last expression is related to the Virial theorem, which says that if $V \sim r^k$ then $\langle K.E \rangle = \frac{k}{2}\langle V \rangle$, so $E = \frac{k+2}{2}\langle V \rangle$. Let's pause to prove the Virial theorem. Use

$$\frac{d}{dt}\langle \vec{r}\cdot\vec{p}\rangle = \frac{1}{i\hbar}\langle[\vec{r}\cdot\vec{p}, H]\rangle = 2\langle T\rangle - \vec{r}\cdot\nabla V,$$

where the last step follows upon writing everything out and using the commutators of position and momentum. The time derivative of any operator expectation value will vanish in any energy eigenstate, so the Virial theorem holds in every energy eigenstate.

Note also that, e.g. for $\ell = n-1$, the probability density is maximum at solution of $\frac{d}{dr}(e^{-2r/na_0}r^{2n}) = 0$, i.e. at $r = n^2 a_0$. This happens to agree with what Bohr found in the early era, by using classical mechanics and his (close, but not quite correct) quantization of L.

• Free particle with angular momentum ℓ:

$$\left(\frac{d}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right)R + k^2 R = 0,$$

where $E = \hbar^2 k^2/2\mu$. The solutions are spherical Bessel functions, $R(r) = j_\ell(kr)$, which behave as $j_\ell(kr) \sim (kr)^\ell$ for $r \to 0$. (There is another solution, $R(r) = n_\ell(kr)$, called the spherical Neumann function, but it corresponds to the unacceptable behavior $n_\ell(kr) \sim (kr)^{-\ell-1}$ for $r \to 0$, so we discard it.). So the general solution is

$$\psi(r,\theta,\phi) = \int dk \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} C_{k,\ell,m} j_\ell(kr) Y_{\ell,m}(\theta,\phi).$$

• Free particle in an infinite spherical well. The difference from the above is that the wavefunction must vanish for $r \geq R$, where R is the radius of the well. So require $j_\ell(k_{n,\ell}R) = 0$, which is an equation for the $k_{n,\ell}$. The solutions of this equation requires working out the zeros of the spherical Bessel functions. For each ℓ, there are a discrete infinite of zeros, labeled by $n = 1, 2, 3\ldots$. For $kR \gg \ell$, the solutions are approximately given by $kR \approx (n + \frac{1}{2}\ell)\pi$.