

7.3 Radial for 3D central potential

Our Schroedinger equation now looks like

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) = \frac{L^2 Y}{\hbar^2 Y}$$

but we know $L^2 Y = l(l+1)\hbar^2 Y$ so

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) = l(l+1)$$

$$\frac{1}{R_{Elm}} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R_{Elm}}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) - l(l+1) = 0$$

This is an equation only for R_{Elm} - but is not dependent on m , so we'll shorten it to R_{El} . and partial derivatives are then standard derivatives. then the radial part of the Schroedinger reduces

$$\frac{d}{dr} \left(r^2 \frac{dR_{Elm}}{dr} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) R_{lm} = l(l+1) R_{lm}$$

let $U_{El} = rR_{El}$. then $dU/dr = rdR/dr + R$ so

$$dR/dr = (dU/dr - R)/r = (dU/dr - U/r)/r = (rdU/dr - U)/r^2$$

$$\frac{d}{dr} \left(r^2 dR/dr \right) = \frac{d}{dr} \left(r \frac{dU}{dr} - U \right) = r \frac{d^2 U}{dr^2} + \frac{dU}{dr} - \frac{dU}{dr} = r \frac{d^2 U}{dr^2}$$

substitute this back in

$$r \frac{d^2 U}{dr^2} - \frac{2mr}{\hbar^2} (V(r) - E) r R_{lm} - l(l+1) \frac{U_{lm}}{r} = 0$$

$$\frac{d^2U}{dr^2} - \frac{2m}{\hbar^2}(V(r) - E)U_{lm} - l(l+1)\frac{U_{lm}}{r^2} = 0$$

so all we do now is multiply through by $-\hbar^2/(2m)$ and rearrange and we have something called the radial equation which is identical in form to the 1D schrodinger equation except that potential $V(r)$ is replaced by the effective potential $V(r) + \hbar^2 l(l+1)/(2mr^2) = V(r) + L^2/(2mr^2)$.

$$\frac{-\hbar^2}{2m} \frac{d^2U}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] U_{El} = EU_{El}$$

We can see directly from this equation that $L^2/(2mr^2)$ has exactly the same role in the equation as $V(r)$. This is not just a coincidence. Consider an electron in a circular orbit. There is a centripetal force associated with the rotation of $F = mv^2/r$. But the angular momentum $L = mvr$ so $v^2 = L^2/(m^2r^2)$ and so $F = m/r \times L^2/(m^2r^2) = L^2/(mr^3)$. A (conservative) force is related to potential via $dU/dr = -F$ so integrating means that angular momentum forms an effective potential $V_{eff} = L^2/(2mr^2)$

8 The hydrogen atom

so now we can actually use this for real on the hydrogen atom. Here we have 2 particles rather than one, and we know that the proton is not infinitely larger in mass than the electron, so we should really replace mass of a single particle with the reduced mass of the total system $\mu = M_z m_e / (M_z + m_e)$ rather than m_e but otherwise, everything is the same

we know our radial schrodinger equation for a central potential is

$$\frac{-\hbar^2}{2\mu} \frac{d^2U_{El}}{dr^2} + \left(\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right) U_{El} = EU_{El}$$

where $U_{El} = rR_{El}$ and $\psi_{Elm}(r, \theta, \phi) = R_{El}(r)Y_{lm}(\theta, \phi)$

so all we have to do is put in our proper central potential $V(r) = -Ze^2/(4\pi r\epsilon_0)$ (where we leave the Z in so we can easily solve for any hydrogenic ion) and solve for R_{El} .

$$-\frac{\hbar^2}{2\mu} \frac{d^2 U_{El}}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} U_{El} - \frac{Ze^2}{4\pi\epsilon_0 r} U_{El} = E U_{El}$$

multiply through by $-\hbar^2/2\mu$, and rearrange

$$\frac{d^2 U_{El}}{dr^2} - \frac{l(l+1)}{r^2} U_{El} + \frac{2\mu Ze^2}{4\pi\epsilon_0 r \hbar^2} U_{El} = -\frac{2\mu E}{\hbar^2} U_{El}$$

for bound states, $E < 0$ so let $k^2 = -2\mu E/\hbar^2$ so that k is real.

$$\frac{d^2 U_{El}}{dr^2} = \left(k^2 + \frac{l(l+1)}{r^2} - \frac{2\mu Ze^2}{4\pi\epsilon_0 r \hbar^2} \right) U_{El}$$

divide by k^2

$$\frac{1}{k^2} \frac{d^2 U_{El}}{dr^2} = \left(1 - \frac{\mu Ze^2}{2\pi\epsilon_0 r \hbar^2 k^2} + \frac{l(l+1)}{r^2 k^2} \right) U_{El}$$

so let $\rho = kr$ so $d\rho/dr = k$ and $d^2 U/dr^2 = (d\rho/dr)^2 d^2 U/d\rho^2 = k^2 d^2 U/d\rho^2$.
then

$$\frac{d^2 U_{El}}{d\rho^2} = \left(1 - \frac{\mu}{\hbar^2} \cdot \frac{Ze^2}{2\pi\epsilon_0 \rho k} + \frac{l(l+1)}{\rho^2} \right) U_{El} = 0$$

this will look better if we set $\rho_0 = \mu Ze^2/(2\pi\hbar^2\epsilon_0 k)$ so

$$\frac{d^2 U_{El}}{d\rho^2} = \left(1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right) U_{El}$$

This is nasty but well known mathematically (again!). this time the solution is related to the Laguerre polynomials $L_q(x)$ and associated Laguerre polynomials $L_{q-p}^p(x)$ where

$$L_q(x) = e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q) \quad L_{q-p}^p = (-1)^p \left(\frac{d}{dx} \right)^p L_q(x)$$

the highest power of each L_{q-p}^p is x^p when $q = 0$, or x^{p-1} for $q = 1$. For L_0^p the polynomial is a constant and cannot be differentiated further. so the associated Laguerre polynomials can only be defined for $q - p > 0$.

using these, the solution to our scaled Schroedinger equation is

$$U_{El} \propto \rho^{l+1} e^{-\rho} L_{n-l-1}^{2l+1}(2\rho)$$

with the condition that $\rho_0 = 2n$ with $n = 1, 2, 3, \dots$ but this condition means that k is quantised and hence E is quantised too

$$E = -\frac{\hbar^2 k^2}{2\mu} \quad \text{where } k = \frac{\mu Z e^2}{2\pi\epsilon_0 \hbar^2 \rho_0} = \frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2 n}$$

$$E = -\frac{\mu}{2\hbar^2} \left(Z \frac{e^2}{4\pi^2\epsilon_0^2} \right)^2 \frac{1}{n^2}$$

$$= -13.6 \frac{Z^2}{n^2} \frac{\mu}{\mu_H} \text{eV}$$

This only depends on n , not on l and we can see from the Laguerre polynomials that $n - l - 1 \geq 0$ so $l \leq n - 1$. These are only features of our $1/r$ potential - other central potentials don't do this though ALL have energies not dependent on m .

Thus for a given n there are n values of l which have the same energy, so the level is n degenerate. and remember that for each l there are also

$2l + 1$ degenerate values of m , so in fact each level is n^2 degenerate (or $2n^2$ degenerate when we get around to counting spin)

and it also means that ρ also depends on n as $\rho = kr$.

$$\rho = kr = \frac{\mu e^2}{2\pi\epsilon_0\hbar^2\rho_0}r = \frac{\mu e^2}{4\pi\epsilon_0\hbar^2 n}r$$

define $a = (4\pi\epsilon_0\hbar^2)/(\mu Z e^2) = 5.29 \times 10^{-11} \text{ m}^{-1}$ for hydrogen so $\rho = r/(an)$. so a better way to write our radial function is

$$U_{El} \propto \frac{r^{l+1}}{an} e^{-r/(an)} L_{n-l-1}^{2l+1}(2r/(an))$$

since $U_{El} = rR_{El}$ then we can normalise

$$\int R_{El}^* R_{El} r^2 dr = \int U^*(r) U(r) dr = 1$$

so this gets us to

$$R_{nl} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3}} \left(\frac{2r}{na}\right)^l e^{-r/(an)} L_{n-l-1}^{2l+1}([2r/(an)])$$

$$R_{10} = 2a^{-3/2} e^{-r/a}$$

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

$$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} e^{-r/2a}$$

The full wavefunction is $\psi_{nlm} = R_{nl} Y_{lm}$ and the radial probability density is $D_{nl} dr = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} R_{nl}^2 Y_{lm}^* Y_{lm} r^2 \sin\theta d\theta d\phi dr$ so $D(r) = R_{nl}^2 r^2$. This gives us a way to visualise these in the 1 radial dimension.