Hydrogen Atom

Before we go into the Hydrogen Problem, let's discuss the orthonormality some more

For 3D T.I.S.E. with isotropic potential that is $V(\vec{r}) = V(r)$, we found that spherical coordinate is the best, and

$$H(r,\theta,\varphi)\,\psi(r,\theta,\varphi) = E\,\psi(r,\theta,\varphi)$$

$\Rightarrow$ with $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

This led to

$$H^{l}_{eff}(r)\,u(r) = E\,u(r)$$

$$, \text{with } u(r) = r R(r)$$

and $H^{l}_{eff} = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V^{l}_{eff}(r)$

$$, V^{l}_{eff}(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

Because H^{l}_{eff} must be hermitian

$\Rightarrow \langle u_E | u_{E'} \rangle = \delta_{EE'}$

But this works only if they share the same "l".

If we break down the angular parts as well, $Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$

$$\Theta(\theta) \Downarrow P_\ell^m(\cos\theta) \qquad \Phi(\varphi) \Downarrow e^{im\varphi}$$

$$\psi(r,\theta,\varphi) = R_{E,\ell}(r)\cdot\Theta_\ell^m(\theta)\cdot\Phi^m(\theta)$$

Orthogonality comes from

$$\langle R_E | R_{E'}\rangle_{\text{same } \ell} = \delta_{EE'}$$

for E we typically use index "n"
so this is equivalent to

$$\langle R_n | R_{n'}\rangle_\ell = \delta_{nn'}$$

Similarly $\langle \Theta_\ell | \Theta_{\ell'}\rangle_{\text{same } m} = \delta_{\ell\ell'}$

also $\langle \Phi^m | \Phi^{m'}\rangle = \delta_{mm'}$

With all these combined,

$$\langle \psi_{E_n \ell m} | \psi_{E_{n'}\ell' m'}\rangle = \delta_{E_n E_{n'}}\delta_{\ell\ell'}\delta_{mm'}$$

From previous class, we have found that for a system whose potential energy is independent of orientation, the time independent 3D Schrödinger Eq. reduces to the 1D radial equation

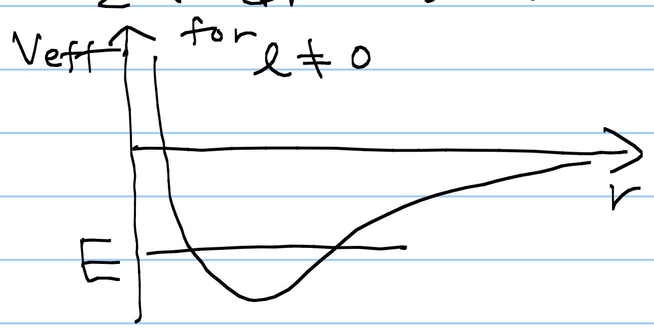
$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u=Eu$$

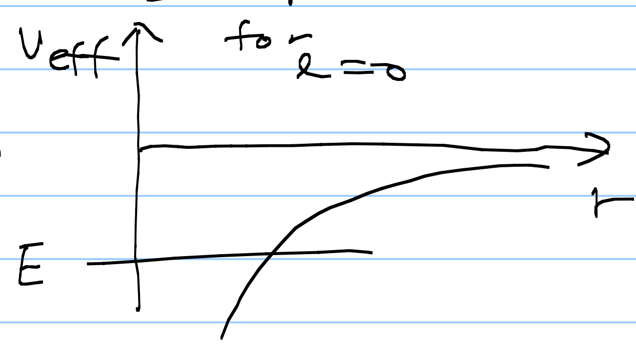
, where $u(r)=rR(r)$ and remember the full stationary state is $\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$.

For the electron in the hydrogen atom, we can assume that the proton is at rest with its position as the origin. Then the Coulomb potential energy for the electron is $V(r)=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

Then

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\Bigg[\overbrace{-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}}^{V_{eff}}\Bigg]u=Eu$$





As we can see from the effective potential plot, the bound states should have $E<0$.

Now dividing the above equation by E,

$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} = \left[1+\frac{e^2}{4\pi\epsilon_0 E}\frac{1}{r} - \frac{\hbar^2}{2mE}\frac{l(l+1)}{r^2}\right]u$$

with $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$ u

$$\Rightarrow \frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1-\frac{e^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2\kappa^2}\frac{1}{r}+\frac{1}{\kappa^2}\frac{l(l+1)}{r^2}\right]$$

with $\kappa r=\rho$ and $\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \equiv \rho_0$

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

If we consider $\rho\to 0$ & $\rho\to\infty$ limit, we find

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

, where $v(\rho)$ is a polynomial of order $n-(l+1)\geq 0$, and this leads to

$$\rho_0 = 2n \Rightarrow \kappa = \frac{me^2}{2\pi\epsilon_0\hbar^2\rho_0} = \frac{me^2}{4\pi\epsilon_0\hbar^2 n}$$

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{\hbar^2}{2m}\cdot\left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)^2\frac{1}{n^2}$$

$$\Rightarrow E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$

$l=0$ $\overbrace{1,\ 2,\ 3,\ 4\ \cdots\ \cdots}^{n}$

$l=1$ $2,\ 3,\ 4,\ \cdots\ \cdots$

$l=2$ $3,\ 4,\ 5\ \cdots$

* "n" called the principal quantum number.

For each n, possible l values are $l = 0, 1, 2, \cdots n-1$.

Since for each l, there are $2l+1$ "m" values are possible,

the total # of states for each "n" is

* $$d(n) = \sum_{l=0}^{n-1}(2l+1) = n^2$$

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

$$\Rightarrow R_{nl}(r) = \frac{u(r)}{r} = r^l e^{-\kappa r} P_{n-(l+1)}(r)$$

$$= r^l e^{-\frac{r}{an}} P_{n-(l+1)}(r)$$

$$\frac{1}{\kappa} = \frac{4\pi\epsilon_0\hbar^2}{me^2} n = an$$

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} \text{ : Bohr radius}$$

$$= 0.529\ \mathring{A}$$

Here $P_{n-(l+1)}(r)$ is a polynomial of order $n-(l+1)$

As an example, for $n=4$

$$R_{43} = r^3 e^{-\frac{r}{4a}} \cdot \text{const}$$

$$R_{42} = r^2 e^{-\frac{r}{4a}} \cdot \left(\cdots \frac{r}{a} \right)$$

$$R_{41} = r^1 e^{-\frac{r}{4a}} \left(\cdots \left(\frac{r}{a}\right)^2 \right)$$

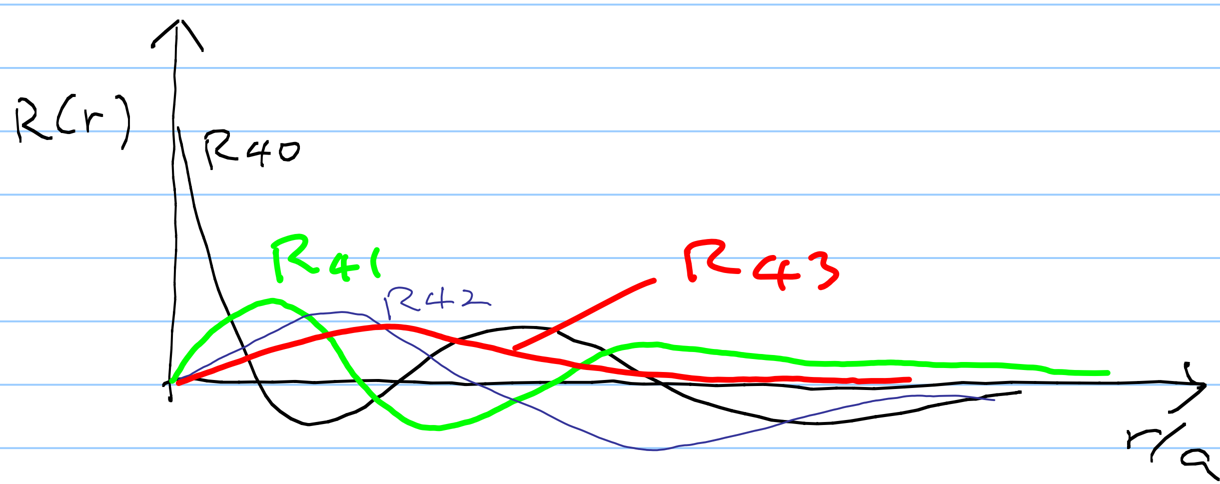
$$R_{40} = r^0 e^{-\frac{r}{4a}} \left(\cdots \left(\frac{r}{a}\right)^3 \right)$$

3 nodes

2 nodes

1 node

0 node



Looking back at the radial equation,

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right)u = Eu$$

Each "l" has its own set of eigenfcns U_{nl} and eigenenergies E_n.

Because of the orthonormality,

$$\langle U_{nl} | U_{n'l} \rangle = \delta_{nn'}$$

Thus $\int_{r=0}^{\infty} R^*_{nl}(r)\, R_{n'l}(r)\, r^2 dr = \delta_{nn'}$

In Dirac notations

$$\langle R_{nl} | R_{n'l} \rangle \equiv \int R^*_{nl}(r)\, R_{n'l}(r)\, r^2 dr$$

$$= \delta_{nn'}$$

Combining with the angular parts,

$$\langle \psi_{nlm} | \psi_{n'l'm'} \rangle$$

$$= \langle R_{nl} | R_{n'l} \rangle \langle Y_l^m | Y_{l'}^{m'} \rangle$$

meaningless if $l \neq l'$

$$= \delta_{nn'}\, \delta_{ll'}\, \delta_{mm'}$$

Note here that the full stationary states of the hydrogen atom are

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi)$$

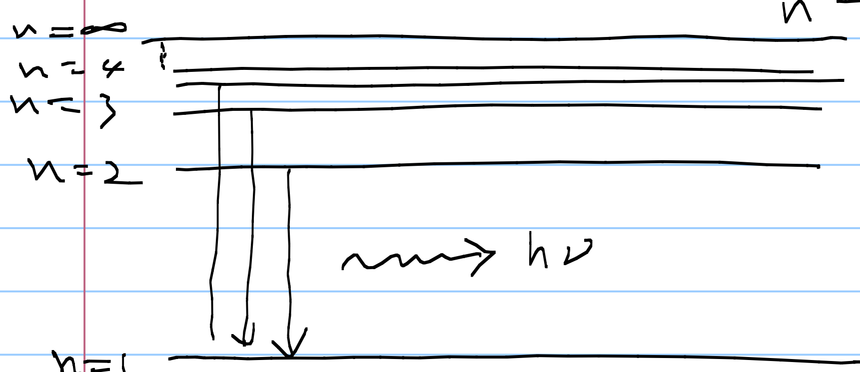
and

$$\langle Y_\ell^m | Y_{\ell'}^{m'} \rangle = \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} Y_\ell^{*m}\, Y_{\ell'}^{m'} \sin\theta\, d\theta\, d\varphi$$

Spectrum of Hydrogen

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

$$= -13.6\,\text{eV} \cdot \frac{1}{n^2}$$



$$h\nu = E_i - E_f = -13.6\,\text{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

With $\nu = \frac{c}{\lambda}$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

, where R is called the Rydberg constant, and is given as $R = 1.097 \times 10^{7}\ m^{-1}$.