Central Potential

Lecture # 25

- $V(\vec{r}) = V(r) \longrightarrow$ use (r, θ, φ) coordinates

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(r)$$

$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] + \hat{V}(r)$$

$$= \frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{L}^2}{\hbar^2 r^2}\right] + V(r)$$

- For a spherically symmetric potential $V(r)$

$$[\vec{L}, L^2] = [V(r), \vec{L}] = [V(r), L^2] = 0$$

$$\Longrightarrow [\hat{H}, \vec{L}] = [\hat{H}, \hat{L}^2] = 0$$

Solutions can be simultaneous eigenfunctions of $\hat{H}, \hat{L}^2, \hat{L}_z$

$$\psi_{Elm}(\vec{r}) = \underbrace{R_{Elm}(r)}_{\text{Radial function}}\ \underbrace{Y_{lm}(\theta, \varphi)}_{\text{spherical harmonics}}$$

$\rightarrow$ substitute into Schrödinger eqn

Radial Equation
$$\left[\frac{-\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right]R_{El}(r) = E R_{El}(r)$$

• Note that m_l (i.e. $\hat{L}_z$) does not appear in the equation. We can then drop it from the eigenfunctions: $\psi_{Elm}(\vec{r}) = R_{El}(\vec{r}) Y_{lm}(\theta,\varphi)$ ②

To normalize the wavefunction,

$$|\psi_{Elm}(r,\theta,\varphi)|^2 = |R_{El}(r)|^2 |Y_{lm}(\theta,\varphi)|^2$$

$$\int_0^\infty dr\, r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi\, |\psi_{Elm}(r,\theta,\varphi)|^2 = 1$$

Y_{lm} already normalized.

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

• Can rewrite the radial equation in terms of $u_{El}(r) = r R_{El}(r)$

$$\longrightarrow \quad \frac{-\hbar^2}{2M} \frac{d^2 u_{El}(r)}{dr^2} + V_{eff}(r)\, u_{El}(r) = E\, u_{El}(r)$$

where $V_{eff}(r) = V(r) + \dfrac{l(l+1)\hbar^2}{2\mu r^2}$

• We require $R_{El}(r)$ to be finite at $r=0$, thus $u_{El}(0) = 0$

Note that for a potential not more singular than $1/r$,   ③

$u(r) \sim r^{l+1}$ and $R \sim r^l$ if $r \to 0$

<u>Examples</u>:

- Free particle

Cartesian coordinates : $e^{\pm i\vec{k}\cdot\vec{r}}$

Radial equation : $\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + k^2\right] R_{El}(r) = 0$

$k^2 = \frac{2mE}{\hbar^2}$ V_{eff} = centrifugal force $= \frac{l(l+1)\hbar^2}{2mr^2}$

in terms of $u(r)$:

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2\right] u_{El}(r) = 0$$

- For $l = 0$, $u_{E0}(r) \propto \sin(kr)$

$$R_{E0}(r) \propto \frac{\sin(kr)}{r}$$

- For $l = 0$, let $\rho = kr$ $R_l(\rho) \equiv R_{El}(r)$

$$\left[\frac{d^2}{d\rho^2}+\frac{2}{\rho}\frac{d}{d\rho}+\left(1-\frac{\ell(\ell+1)}{\rho^2}\right)\right]R_\ell(\rho)=0 \qquad (4)$$

$\Downarrow$ Spherical Bessel differential equation

$\Downarrow$ Solutions are spherical Bessel functions

$$j_\ell(\rho)=\left(\frac{\pi}{2\rho}\right)^{1/2}J_{\ell+1/2}(\rho)$$

$$n_\ell(\rho)=(-1)^{\ell+1}\left(\frac{\pi}{2\rho}\right)^{1/2}J_{-\ell-\frac{1}{2}}(\rho)$$

ordinary Bessel functions

- $j_0(\rho)=\dfrac{\sin\rho}{\rho} \qquad n_0(\rho)=-\dfrac{\cos\rho}{\rho}$

$$j_1(\rho)=\frac{\sin\rho}{\rho^2}-\frac{\cos\rho}{\rho} \qquad n_1(\rho)=-\frac{\cos\rho}{\rho^2}-\frac{\sin\rho}{\rho}$$

Keep j since it is regular (finite) at origin

$\rightarrow \quad R_{E\ell}(r)=C\,j_\ell(kr)$

C: constant

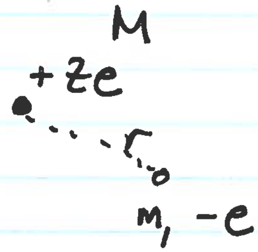
$$\psi_{E\ell m}(r)=C\,j_\ell(kr)\,Y_{\ell m}(\theta,\varphi)$$

- We can expand cartesian plane waves into spherical Bessel functions

$$e^{i\vec{k}\cdot\vec{r}}=\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}C_{\ell m}\,j_\ell(kr)\,Y_{\ell m}(\theta,\varphi)$$

✓ Eigenvalues &

The Hydrogen Atom: Wavefunctions Lecture # 26



$$V(r) = -\frac{Ze^2}{(4\pi\epsilon_0)r}$$

- Separate into COM and relative coordinates.

$$\hat{H} = \frac{\hat{p}^2}{2\mu} - \frac{Ze^2}{(4\pi\epsilon_0)r} \qquad \mu = \frac{mM}{m+M} \qquad p\text{: relative momentum}$$

Schrodinger Equation:

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

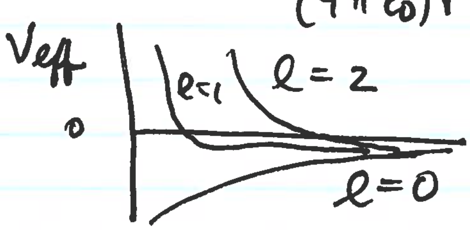
Target Solution:

$$\psi_{Elm} = R_{El}(r)\,Y_{lm}(\theta,\varphi)$$

$$u_{El}(r) = r R_{El}(r)$$

$$\frac{d^2u_{El}(r)}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - V_{eff}(r)\right]u_{El}(r) = 0$$

$$V_{eff}(r) = \frac{-Ze^2}{(4\pi\epsilon_0)r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$



$V_{eff} \to 0$ for large r

Thus, for $E > 0$ $u_{E\ell}(r)$ will have oscillatory behavior

for $E < 0$ we have bound states

- Again require $u_{E\ell}(0) = 0$ (R finite at 0)

let $\rho = \left(-\frac{8\mu E}{\hbar^2}\right)^{1/2} r$ $\quad \lambda = \frac{Ze^2}{(4\pi\varepsilon_0)\hbar}\left(\frac{-\mu}{2E}\right)^{1/2}$

$$= Z\alpha\left(\frac{-\mu c^2}{2E}\right)^{1/2}$$

where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \simeq \frac{1}{137}$ fine structure constant!

$$\left[\frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right] u_{E\ell}(\rho) = 0$$ Radial Equation

- Asymptotic Behavior

When $\rho \to \infty$, ρ^{-1} and ρ^{-2} terms are negligible

$$\left[\frac{d^2}{d\rho^2} - \frac{1}{4}\right] u_{E\ell}(\rho) = 0, \quad u_{E\ell}(\rho) \sim e^{-\rho/2}$$

(ignore $e^{+\rho/2}$ bc $\to \infty$ as $\rho \to \infty$)

Thus, let $u_{E\ell}(\rho) = e^{-\rho/2} f_{E\ell}(\rho)$, substitute back.

③

$$\left[\frac{d^2}{d\rho^2} - \frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} + \frac{\lambda}{\rho}\right] f(\rho) = 0$$

$$f(\rho) = \rho^{\ell+1} g(\rho)$$

behavior as $\rho \to 0$

$$g(\rho) = \sum_{k=0}^{\infty} c_k \rho^k \qquad c_0 \neq 0$$

$$\rightarrow \rho \frac{d^2}{d\rho^2} + (2\ell + 2 - \rho)\frac{d}{d\rho} + (\lambda - \ell - 1) g(\rho) = 0$$

Now substitute in series expansion,

$$\sum_{k=0}^{\infty} \Big[k(k-1) c_k \rho^{k-1} + (2\ell+2-\rho) k c_k \rho^{k-1} + (\lambda - \ell - 1) c_k \rho^k\Big] = 0$$

Collect terms:

$$\sum_{k=0}^{\infty} \Big\{ \big[k(k+1) + (2\ell+2)(k+1)\big] c_{k+1} + (\lambda - \ell - 1 - k) c_k \Big\} \rho^k = 0$$

setting each coeff. to zero:

$$c_{k+1} = \frac{k + \ell + 1 - \lambda}{(k+1)(k+2\ell+2)} c_k$$

Recursion relation.

If the series does not terminate, for large k

$$\frac{c_{k+1}}{c_k} \sim \frac{1}{k}\,,$$

same as expansion coefficients for $\rho^p e^\rho$

The asymptotic behavior as $\rho \to \infty$ would be

$$u_{El}(\rho) \sim f \cdot g \cdot e^{-\rho/2} \sim \rho^{l+1+p} e^{\rho/2} \to \infty$$

$f \to \rho^{l+1}$, $g \to \rho^p e^\rho$

$\longrightarrow$ must terminate series

$g(\rho)$ must be a polynomial in ρ

Let highest power be ρ^{n_r} call it radial quantum #

$$n_r = 0, 1, 2, \ldots \qquad C_{n_r+1} = 0$$

$$\longrightarrow \lambda = n_r + l + 1$$

let $n = n_r + l + 1$ be <u>principal</u> quantum #

$$= 1, 2, 3, \ldots$$

eigenvalues are thus $\lambda = n$

Going back to dimensioned units.

$$E_n = \frac{-\mu}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{1}{n^2} = -\frac{1}{2}\mu c^2\left(\frac{Z\alpha}{n}\right)^2$$

a_μ is the (modified) Bohr radius

(i.e. μ vs. m_e)

$\longrightarrow$ agrees with Bohr's calculation!

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

degenerate w.r.t. l, m

$1/r$ potential, central pot.

Wavefunctions of Atomic Hydrogen Lecture # 27

- Recall the radial equation:

$$\rho \frac{d^2}{d\rho^2} + (2\ell+2-\rho)\frac{d}{d\rho} + (\lambda-\ell-1)\, g(\rho) = 0$$

$\longrightarrow$ c.f. Kummer-Laplace equations

$$z\frac{d^2w}{dz^2} + (c-z)\frac{dw}{dz} - aw = 0$$

Can match up if we let $z=\rho,\ w=g,\ a=\ell+1-\lambda$
$c=2\ell+2$

Within a multiplicative constant, regular solution at the origin is

the Confluent Hypergeometric Function ${}_1F_1(a,c,z)$

$${}_1F_1(a,c,z) = 1 + \frac{az}{c\,1!} + \frac{a(a+1)z^2}{c(c+1)\,2!} + \cdots$$

$$= \sum_{k=0}^{\infty} \frac{(a)_k z^k}{(c)_k\, k!} \quad \text{where } (\alpha)_k = \alpha(\alpha+1)\cdots(\alpha+k-1)$$

$$(\alpha)_0 = 1$$

For large, positive values of the argument,

$${}_1F_1(a,c,z) \longrightarrow \frac{\Gamma(c)}{\Gamma(a)} e^{z} z^{a-c}$$

Euler gamma function

Here
$$ {}_1F_1(\ell+1-\lambda, 2\ell+2, \rho) \sim \rho^{-\ell-1-\lambda} e^{\rho} $$

$$ \longrightarrow \quad u_{E\ell}(\rho) \sim \rho^{-\lambda} e^{\rho/2} \longrightarrow \infty \rightarrow $$ must truncate series

$\rightarrow$ ${}_1F_1$ reduces to polynomial of degree n_r

$\rightarrow$ related to the Associated Laguerre Polynomials

$$ L^{2\ell+1}_{n+\ell}(\rho) = \frac{-[(n+\ell)!]^2}{(n-\ell-1)!(2\ell+1)!} \cdot {}_1F_1(\ell+1-n, 2\ell+2, \rho) $$

Laguerre polynomial $$ L_q(\rho) = e^{\rho} \frac{d^q}{d\rho^q}(\rho^q e^{-\rho}) $$

Associated Laguerre Polynomial $$ L^p_q(\rho) = \frac{d^p}{d\rho^p} L_q(\rho) $$

$\rightarrow$ Full radial wavefunction

$$ R_{n\ell}(r) = N e^{-\rho/2} \rho^{\ell} L^{2\ell+1}_{n+1}(\rho) $$

N: normalization.

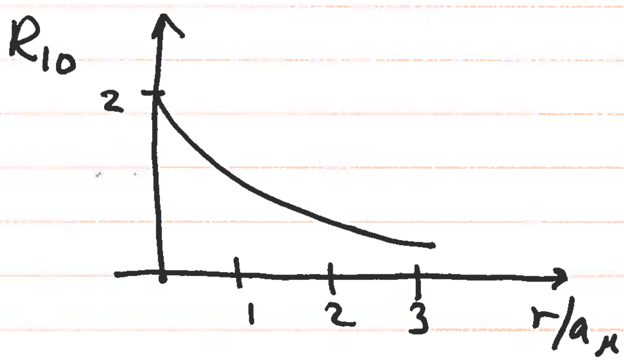
$$ = -\left\{ \left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^{\ell} L^{2\ell+1}_{n+\ell}(\rho) $$

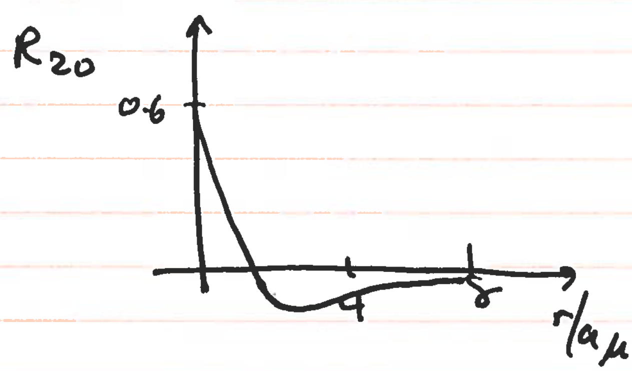
First few functions,

$$R_{10}(r) = 2\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu}$$

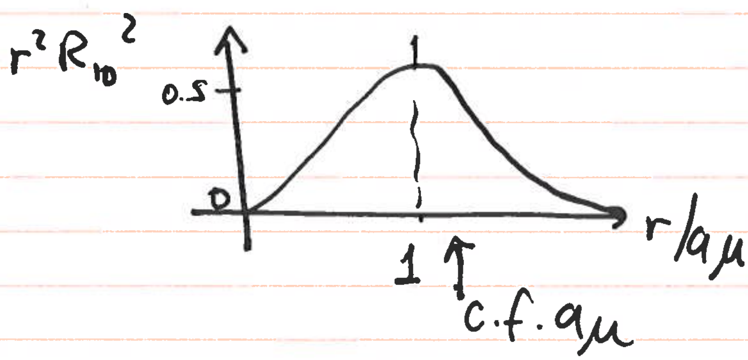
$$R_{20}(r) = 2\left(\frac{Z}{2a_\mu}\right)^{3/2}\left(1 - \frac{Zr}{2a_\mu}\right) e^{-Zr/2a_\mu}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_\mu}\right)^{3/2}\left(\frac{Zr}{a_\mu}\right) e^{-Zr/2a_\mu}$$





For probability density, plot r^2R^2



Shell	Quantum #'s n	ℓ	m		$\psi(r,\theta,\varphi)$
K	1	0	0	1s	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu}$
L	2	0	0	2S	$\frac{2}{\sqrt{2\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2}\left(1-\frac{Zr}{2a_\mu}\right) \cdot e^{-Zr/2a_\mu}$
	2	1	0	$2P_0$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2}\left(\frac{Zr}{a_\mu}\right) \cdot e^{-Zr/2a_\mu}\cos\theta$
	2	1	± 1	$2P_{\pm 1}$	$\mp\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2}\left(\frac{Zr}{a_\mu}\right) \cdot e^{-Zr/2a_\mu}\sin\theta\, e^{\pm i\varphi}$

Important Observations

(i) Only for s states ($\ell = 0$) are the radial eigenfunctions not zero at $r=0$

Thus $$|\psi_{n00}(0)|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{Z^3}{\pi a_\mu^3 n^3}$$

since $Y_{00} = \frac{1}{\sqrt{4\pi}}$

(ii) $R_{n\ell}(r) \propto r^\ell$ as $r \to 0$

(iii) $r^2|R(r)|^2$ has $n-\ell$ maxima. For largest $\ell = n-1$, only one maxima $R_{n,n-1}(r) \sim r^{n-1} e^{-Zr/na_\mu}$

Thus, the probability density will exhibit a maximum @

$$\frac{d}{dr}\left(r^2|R|^2\right)=0 \qquad r^2R^2 = \cancel{A}\, r^{2n} e^{-2Zr/na_\mu}$$

$$= \left(2n r^{2n-1} - \frac{2Z}{na_\mu} r^{2n}\right) e^{-2Zr/na_\mu} = 0$$

$$\longrightarrow r = \frac{n^2 a_\mu}{Z} \, !$$

Recall Bohr calculation: $mvr = n\hbar \qquad V = \frac{-Ze^2}{(4\pi\varepsilon_0)r}$

$T = mv^2/2$

$\downarrow$

$$r = \frac{n^2}{Z} a_\mu \, !$$

In QM, this is the <u>most probable</u> distance!

$\boxed{\text{FIN}}$