7. Hydrogen Atoms, 2

lecture 26, October 30, 2017

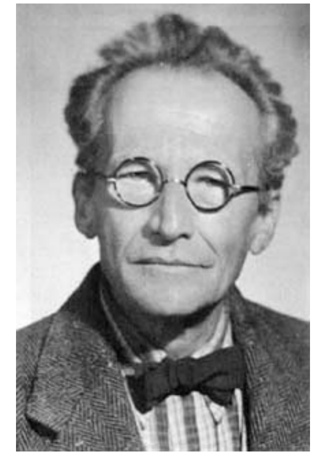
housekeeping

I got nothin'

today

Hydrogen atom

Schroedinger



move much?

1914 Vienna Habilitation, WWI, 1920 Jena, 1920 Stuttgart, 1921 Breslau, 1921 Zurich, (TB treatment 1923), 1927 Berlin, 1934 Oxford, 1933 Nobel, 1934 Princeton? nope, Edinburgh? nope, 1936 Graz…nope, 1933 Oxford, Ghent, Dublin, 1955 Vienna, 1961 died.

1925

learned of deBroglie's work

1926:

January: Quantization as an Eigenvalue Problem: Hydrogen

February: harmonic oscillator, rigid rotator, diatomic molecules

May: equivalence with Heisenberg and Stark Effect

WHERE WE WERE!

Schrodinger equation for 3 dimensional configuration

- central electrostatic potential ⟶ hydrogen = 1 $+e, M_p$ & $-e, m_e$
- spherical symmetry ⟶ spherical coordinates: $\psi(r,\theta,\varphi) = R(r)T(\theta)P(\varphi)$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\phi)$$

$$-\frac{e^2}{4\pi\epsilon_0 r}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

reduced mass

Solution technique: "separation of variables"

this side = that side

arrange to NOT be function of that variable

arrange to be function of 1 variable

THEN

= constant

We did it twice.

this side (r, θ) = that side (ϕ) $= -m^2$ (constant, not mass)

convention

solved for the 'φ' part in terms of m

$= m^2$

set up new equation & do it again.

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)}_{\text{only } r \text{ dependence}} = \underbrace{\frac{m^2}{\sin^2\theta} - \frac{1}{T(\theta)\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{dT(\theta)}{d\theta}\right)}_{\text{only } \theta \text{ dependence}}$$

this side (r) = that side (θ & stuck in m here)

THEN

= new constant $= \dfrac{\lambda}{\hbar^2}$ (more convention)

The ϕ equation & solution: $\frac{1}{\Phi(\varphi)} \frac{d^2\Phi(\varphi)}{d\varphi^2} = -m^2$ $\quad \Phi(\varphi) = e^{im\varphi}$.

The θ equation: $-\frac{1}{\sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{dT(\theta)}{d\theta}\right) + \frac{m^2}{\sin^2\theta} T(\theta) = \frac{\lambda}{\hbar^2} T(\theta)$

The r equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR(r)}{dr}\right) + \left[\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{\lambda}{\hbar^2 r^2}\right] R(r) = 0$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) = \frac{m^2}{\sin^2\theta} \frac{1}{T(\theta)\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dT(\theta)}{d\theta}\right) = \frac{\lambda}{\hbar^2}$$

① $$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dT(\theta)}{d\theta}\right) + \frac{m^2}{\sin^2\theta}T(\theta) = \frac{\lambda}{\hbar^2}T(\theta)$$

② $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \left[\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{\lambda}{\hbar^2 r^2}\right]R(r) = 0$$

①: change variables $\xi \equiv \cos\theta$ $\quad 0 < \theta < \pi \Rightarrow -1 < \xi < 1$

$T(\theta) \rightarrow f(\xi)$

new equation

$$\frac{d}{d\xi}(1-\xi^2)\frac{d}{d\xi}f(\xi) + \left(\frac{\lambda}{\hbar^2} - \frac{m^2}{1-\xi^2}\right)f(\xi) = 0$$

a well-known differential equation.

N.B. Singularities at $\xi = \pm 1$ $\longrightarrow$ solve for $m = 0$

Legendre's Equation

$$\frac{d}{d\xi}(1-\xi^2)\frac{d}{d\xi}f(\xi) + \frac{\lambda}{\hbar^2}f(\xi) = 0$$

Power series: $f(\xi) = \sum_n c_n \xi^n$

- substitute
- find recursion relation for coefficients: $c_{n+2} = \frac{n(n+1) - \lambda/\hbar^2}{(n+1)(n+2)} c_n$

- assume that at some m, the series must terminate. for $n >$ that, $\xi^n \to 0$

CALL THAT PARTICULAR $n \to \ell$

$$n = \ell \Rightarrow \quad \ell(\ell+1) - \lambda/\hbar^2 = 0$$ from recursion

$$\lambda = \hbar^2 \ell(\ell+1)$$

So, the polynomial solutions depend on ℓ: $f_\ell(\xi)$

Legendre Polynomials

Conventionally:

1) $$f_\ell(\xi) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\xi^\ell} (\xi^2-1)^\ell$$

2) $P_\ell(\xi)$ or $P_\ell(\cos\theta)$

First few:

$$f_0(\xi) = 1$$

$$f_1(\xi) = \xi$$

$$f_2(\xi) = \frac{1}{2}(3\xi^2-1)$$

Need normalized functions & orthogonality for ℓ, ℓ'

$$\int_{-1}^{1} f_\ell(\xi) f_{\ell'}(\xi)\, d\xi = 0 \qquad \ell \neq \ell'$$

n-fold integration by parts: $\displaystyle\int_{-1}^{1} f_\ell(\xi)^2\, d\xi = \frac{2}{2\ell+1}$

WHEW... that was for $m=0$

generally: $$f_\ell^m(\xi) = (1-\xi^2)^{m/2} \frac{d^m}{d\xi^m} f_\ell(\xi)$$

$$= \frac{1}{2^\ell \ell!} (1-\xi^2)^{m/2} \frac{d^{\ell+m}}{d\xi^{\ell+m}} (\xi^2-1)^\ell$$

we have $m \le \ell$ and then $f_\ell^m(\xi)$ are solutions to the original equation plus:

$$\int_{-1}^{1} f_\ell^m(\xi)^2 \, d\xi = \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!}$$

Going all the way back: $\psi(r,\theta,\varphi) = R(r)\,T(\theta)\,\Phi(\varphi)$

$$= R(r)\,T(\theta)\,e^{im\varphi}$$

$$= R(r)\,Y_{\ell m}(\theta,\varphi)$$

These define the "spherical Harmonics" $Y_{\ell m}(\theta,\varphi)$

$$Y_{\ell m}(\theta,\varphi) = \left[\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}\right]^{\frac{1}{2}} (-1)^m e^{im\varphi} f_\ell^m(\cos\theta)$$

Features: $\ell \geq m$

$+m$ & $-m$ have same f's $\Rightarrow$ need $e^{im\varphi}$ to distinguish

Explicitly: $m = -\ell, -\ell+1, -\ell+2, \dots \ell-1, \ell$

aaaand ... the ℓ's vary: $\ell = 0, 1, 2 \dots$

So:

$\ell = 0$ $\quad$ $m = 0$

$\ell = 1$ $\quad$ $m = -1, 0, 1$

$\ell = 2$ $\quad$ $m = -2, -1, 0, 1, 2$

$\vdots$ $\quad$ $\vdots$

a few: $Y_{\ell m}$

l = 0[1] [edit]

$$Y_0^0(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{1}{\pi}}$$

l = 1[1] [edit]

$$Y_1^{-1}(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta=\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x-iy)}{r}$$

$$Y_1^0(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta=\frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\frac{z}{r}$$

$$Y_1^1(\theta,\varphi)=-\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta=-\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x+iy)}{r}$$

l = 2[1] [edit]

$$Y_2^{-2}(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)^2}{r^2}$$

$$Y_2^{-1}(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot\cos\theta=\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)z}{r^2}$$

$$Y_2^0(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta-1)=\frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{(2z^2-x^2-y^2)}{r^2}$$

$$Y_2^1(\theta,\varphi)=-\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta=-\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}$$

$$Y_2^2(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)^2}{r^2}$$

l = 3[1] [edit]

$$Y_3^{-3}(\theta,\varphi)=\frac{1}{8}\sqrt{\frac{35}{\pi}}\cdot e^{-3i\varphi}\cdot\sin^3\theta=\frac{1}{8}\sqrt{\frac{35}{\pi}}\cdot\frac{(x-iy)^3}{r^3}$$

$$Y_3^{-2}(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta\cdot\cos\theta=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot\frac{(x-iy)^2z}{r^3}$$

$$Y_3^{-1}(\theta,\varphi)=\frac{1}{8}\sqrt{\frac{21}{\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot(5\cos^2\theta-1)=\frac{1}{8}\sqrt{\frac{21}{\pi}}\cdot\frac{(x-iy)(4z^2-x^2-y^2)}{r^3}$$

$$Y_3^0(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{7}{\pi}}\cdot(5\cos^3\theta-3\cos\theta)=\frac{1}{4}\sqrt{\frac{7}{\pi}}\cdot\frac{z(2z^2-3x^2-3y^2)}{r^3}$$

$$Y_3^1(\theta,\varphi)=-\frac{1}{8}\sqrt{\frac{21}{\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot(5\cos^2\theta-1)=\frac{-1}{8}\sqrt{\frac{21}{\pi}}\cdot\frac{(x+iy)(4z^2-x^2-y^2)}{r^3}$$

$$Y_3^2(\theta,\varphi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta\cdot\cos\theta=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot\frac{(x+iy)^2z}{r^3}$$

$$Y_3^3(\theta,\varphi)=-\frac{1}{8}\sqrt{\frac{35}{\pi}}\cdot e^{3i\varphi}\cdot\sin^3\theta=\frac{-1}{8}\sqrt{\frac{35}{\pi}}\cdot\frac{(x+iy)^3}{r^3}$$

l = 4[1] [edit]

$$Y_4^{-4}(\theta,\varphi)=\frac{3}{16}\sqrt{\frac{35}{2\pi}}\cdot e^{-4i\varphi}\cdot\sin^4\theta=\frac{3}{16}\sqrt{\frac{35}{2\pi}}\cdot\frac{(x-iy)^4}{r^4}$$

$$Y_4^{-3}(\theta,\varphi)=\frac{3}{8}\sqrt{\frac{35}{\pi}}\cdot e^{-3i\varphi}\cdot\sin^3\theta\cdot\cos\theta=\frac{3}{8}\sqrt{\frac{35}{\pi}}\cdot\frac{(x-iy)^3z}{r^4}$$

$$Y_4^{-2}(\theta,\varphi)=\frac{3}{8}\sqrt{\frac{5}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta\cdot(7\cos^2\theta-1)=\frac{3}{8}\sqrt{\frac{5}{2\pi}}\cdot\frac{(x-iy)^2\cdot(7z^2-r^2)}{r^4}$$

$$Y_4^{-1}(\theta,\varphi)=\frac{3}{8}\sqrt{\frac{5}{\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot(7\cos^3\theta-3\cos\theta)=\frac{3}{8}\sqrt{\frac{5}{\pi}}\cdot\frac{(x-iy)\cdot z\cdot(7z^2-3r^2)}{r^4}$$

$$Y_4^0(\theta,\varphi)=\frac{3}{16}\sqrt{\frac{1}{\pi}}\cdot(35\cos^4\theta-30\cos^2\theta+3)=\frac{3}{16}\sqrt{\frac{1}{\pi}}\cdot\frac{(35z^4-30z^2r^2+3r^4)}{r^4}$$

$$Y_4^1(\theta,\varphi)=\frac{-3}{8}\sqrt{\frac{5}{\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot(7\cos^3\theta-3\cos\theta)=\frac{-3}{8}\sqrt{\frac{5}{\pi}}\cdot\frac{(x+iy)\cdot z\cdot(7z^2-3r^2)}{r^4}$$

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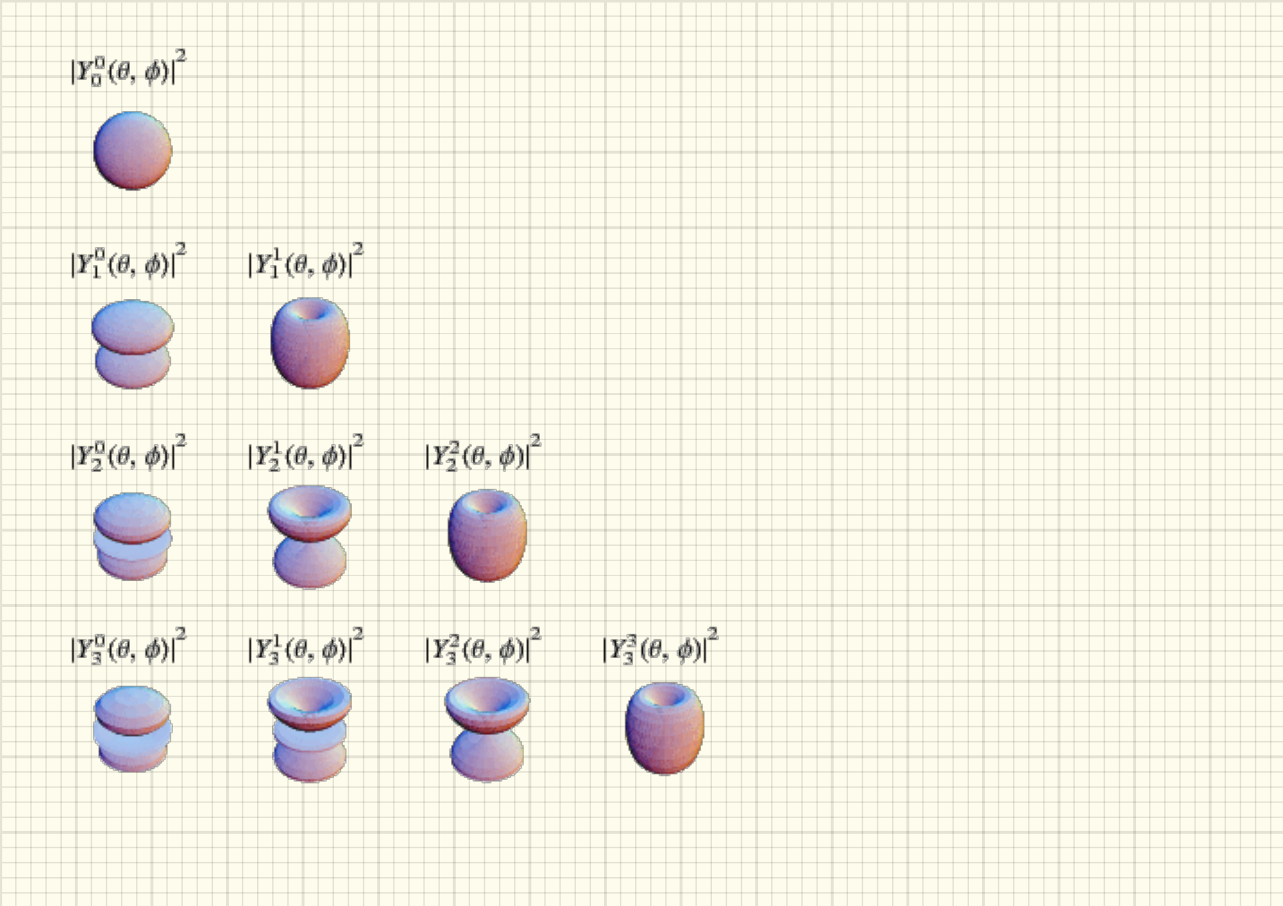
MATHEMATICA

Orthogonal Polynomials

LegendreP[n, x]	Legendre polynomials $P_n(x)$
LegendreP[n, m, x]	associated Legendre polynomials $P_n^m(x)$
SphericalHarmonicY[l, m, θ, ϕ]	spherical harmonics $Y_l^m(\theta, \phi)$
GegenbauerC[n, m, x]	Gegenbauer polynomials Null
ChebyshevT[n, x], ChebyshevU[n, x]	Chebyshev polynomials $T_n(x)$ and $U_n(x)$ of the first and second kinds
HermiteH[n, x]	Hermite polynomials $H_n(x)$
LaguerreL[n, x]	Laguerre polynomials $L_n(x)$
LaguerreL[n, a, x]	generalized Laguerre polynomials $L_n^a(x)$
ZernikeR[n, m, x]	Zernike radial polynomials $R_n^{(m)}(x)$
JacobiP[n, a, b, x]	Jacobi polynomials $P_n^{(a,b)}(x)$

Orthogonal polynomials.


$|Y_0^0(\theta, \phi)|^2$
$|Y_1^0(\theta, \phi)|^2$
$|Y_1^1(\theta, \phi)|^2$
$|Y_2^0(\theta, \phi)|^2$
$|Y_2^1(\theta, \phi)|^2$
$|Y_2^2(\theta, \phi)|^2$
$|Y_3^0(\theta, \phi)|^2$
$|Y_3^1(\theta, \phi)|^2$
$|Y_3^2(\theta, \phi)|^2$
$|Y_3^3(\theta, \phi)|^2$

The radial equation 2

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \left[\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{\lambda}{\hbar^2 r^2}\right]R(r) = 0$$

insert the λ: $\lambda = \hbar^2 \ell(\ell+1)$

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\right)R(r) + \frac{2\mu}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E - \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]R(r) = 0$$

E can be + (free states like Rutherford Scattering)

✓ − (bound states ... $E \to -|E|$)

Variable substitution: $\rho \equiv \left(\frac{8\mu|E|}{\hbar^2}\right)^{1/2} r$

$$\delta \equiv \frac{e^2}{\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2}\frac{1}{4\pi\epsilon_0}$$

so:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R + \left(\frac{\delta}{\rho} - \frac{1}{4}\right)R = 0$$

guess what? another famous differential equation w/ orthogonal function solutions: The Laguarre Equation

- clever manipulations, asymptotic solutions, new variable substitutions $\longrightarrow$ another

$$\frac{d^2H}{d\rho^2} + \frac{(2l+2-\rho)}{\rho}\frac{dH}{d\rho} + \frac{\delta-l-1}{\rho}H = 0$$

same song, yet another verse: series solution!

$H(\rho) = \sum_k a_k \rho^k$ substitute

$$\sum_{k=0}^{\infty} \rho^{k-1} \left\{ (k+1)[k+2l+2] a_{k+1} + (\delta - 1 - l - k) a_k \right\} = 0$$

$\{ \} = 0 \rightarrow$ recursion relation $a_{k+1} = \dfrac{k+l+1-\delta}{(k+1)(k+2l+2)} a_k$

terminate the series $\longrightarrow$ condition

$\delta = n_r + l + 1$

$\hookrightarrow$ the k at which series terminates.

δ is the principle quantum number

usually called: $n = n_r + l + 1$

$n_r \geq 0$ so n is integer $\geq l+1$

$\therefore \quad l \leq n-1$

$$\delta = n \text{, now } = \frac{e^2}{4\pi\epsilon_0 \hbar}\left(\frac{\mu}{2E}\right)^{1/2}$$

quantized

$$E_n = \frac{e^4}{(4\pi\epsilon_0)^2}\frac{\mu}{\hbar^2 2n^2}$$

THE BOHR ENERGY

HOW COOL IS THAT!

Still need the wavefunctions

The series defines the $H(\rho)$'s

$$R(\rho) = e^{-\rho/2}\rho^{\ell} H(\rho)$$

related to "Associated Laguerre Polynomials"

$$H(\rho) = -L_{n+\ell}^{2\ell+1}(\rho)$$

a few:

Laguerre

Associated Laguerre

$$L_q^p(x) = \frac{d^p}{dx^p} L_q(x)$$

$L_0(x) = 1$

$L_1(x) = 1 - x$

$L_1^1(x) = -1$

$L_2(x) = 2 - 4x + x^2$

$L_2^1(x) = -4 + 2x$

$L_2^2(x) = 2$

The radial functions:

$$R_{n\ell}(\rho) = N\left(-e^{-\rho/2} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho)\right) \qquad N = \sqrt{\frac{2n[(n+\ell)!]^3}{(n-\ell-1)!}}$$

so ...

$$R_{n\ell}(r) = -\left[\left(\frac{2}{na_0}\right)\frac{(n-\ell+1)!}{2n[(n+\ell)!]^3}\right]^{\frac{1}{2}} \left(\frac{2r}{na_0}\right)^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = \text{Bohr radius}$$

WHOLE ENCHILADA:

$$\psi_{nml}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi)$$

a few; (Z):

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} 2\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} 3^{-1/2}\,\frac{Zr}{a_0}\, e^{-Zr/2a_0}$$

$\vdots$

MATHEMATICA

QUANTUM NUMBERS of the QUANTUM CENTRAL FORCE SOLUTION

$\boxed{n:}$ Principle Quantum Number

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

$\boxed{l:}$ Orbital Angular Momentum Quantum Number

$l = 0, 1, 2 \ldots (n-1)$ $\quad\quad 0 \leq l \leq n$

connected to R

$\boxed{m_l:}$ Magnetic Quantum Number

$m_l = -l, -l+1, -l+2, \ldots, -1, 0, 1, \ldots l-1, l$

$-l \leq m_l < l$

Why ℓ & "angular momentum"?

glad you asked...

Remember $\vec{L} = \vec{r} \times \vec{p}$

$$L_x = y p_z - z p_y \qquad L_y = z p_x - x p_z \qquad L_z = x p_y - y p_x$$

$\downarrow$ QM recipe

$$\hat{L}_x = -i\hbar\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right) \ \ldots\ \hat{L}_y \ \ \&\ \ \hat{L}_z$$

Form $L^2 = L_x^2 + L_y^2 + L_z^2 \xrightarrow{\text{spherical coordinates}}$

$$L^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

same as the $T(\theta)$ piece

$$L^2\, Y_{\ell m}(\theta,\phi) = \lambda Y_{\ell m}(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\varphi)$$

I'll probably sometimes write $Y_\ell^m(\theta,\phi)$

your book: $L^2 = \hbar^2\ell(\ell+1) \qquad L = \hbar\sqrt{\ell(\ell+1)}$

Remember what Bohr did:

$L = n\hbar$ here: $L = \hbar\sqrt{\ell(\ell+1)}$

$= 0, \; n=0$ $= 0 \quad \ell = 0 \Rightarrow n = 0$

$= \hbar, \; n=1$ $= \hbar\sqrt{n^2+n} \quad \ell = n$

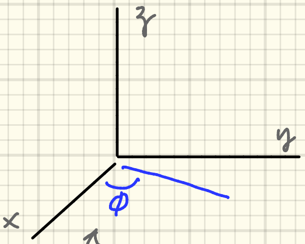
$= \hbar\sqrt{2} \quad n = 1 = \ell$

$= 2\hbar, \; n=2$ $= \hbar\sqrt{6} \quad n = \ell = 2$

Bohr's circular orbits don't work

strange $L = \hbar\underbrace{\sqrt{\ell(\ell+1)}}_{\text{because wave-like solutions}}$

L is a vector ... ℓ determines its magnitude, not its direction



determines rotation about z of the $\vec{L}$ vector

$$L_z = m_\ell \hbar$$

integer.

So: $|\vec{L}|$ is quantized $\Rightarrow$ only certain orientations in space are possible "space quantization"

L_z is quantized

WHAT ABOUT L_x & L_y ?

Glad you asked

we could quantize L_x, say ... and L_y → we'd know $\vec{L}$

& a precise component of the electron's position

↓ uncertainty → NO

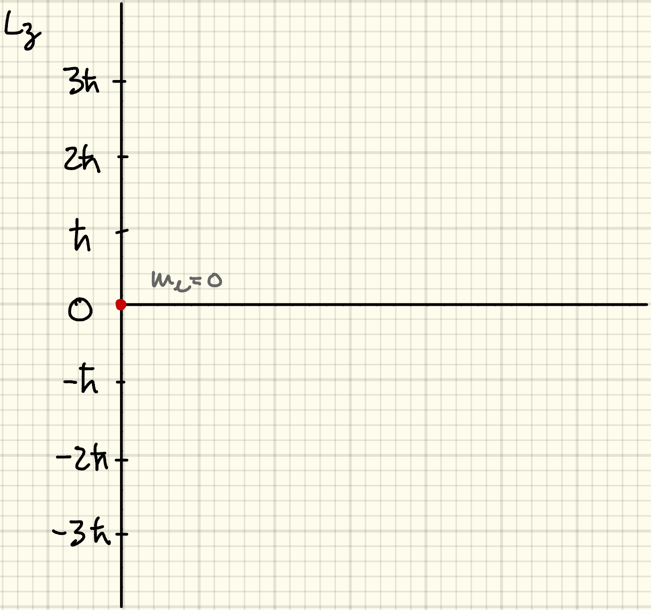
Only $|\vec{L}|$ and 1 component can be quantized...

and hence simultaneously known

convention : L_z

$$l = 0$$

$$L = \hbar\sqrt{l(l+1)}$$
$$= \hbar\sqrt{0}$$



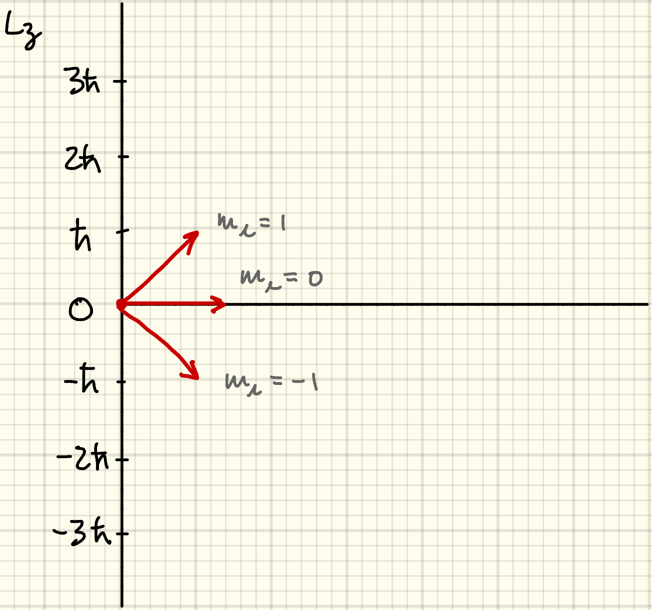
$$L_z = m_l \hbar$$
$$= 0$$

$$m_l = -l, -l+1, -l+2, \ldots, -1, 0, 1, \ldots l-1, l$$

$l = 1$

$$L = \hbar\sqrt{l(l+1)}$$
$$= \hbar\sqrt{2}$$

$$L_z = m_l \hbar$$
$$= 0,\ 1,\ -1$$

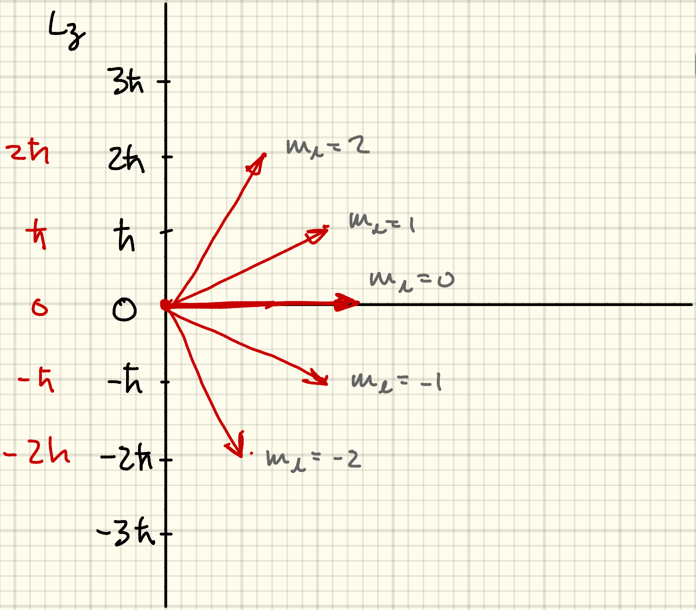


$$m_l = -l,\ -l+1,\ -l+2,\ \ldots,\ -1,\ 0,\ 1,\ \ldots\ l-1,\ l$$

$\ell = 2$

$$L = \hbar\sqrt{\ell(\ell+1)}$$

$$L = \hbar\sqrt{6}$$



$$L_z = m_\ell \hbar$$

$$= 0, 1, -1, 2, -2$$

$m_\ell = -\ell, -\ell+1, -\ell+2, \ldots, -1, 0, 1, \ldots \ell-1, \ell$

OLD TIMEY NOTATION

$\ell =$	0	1	2	3	4	5
	"s"	"p"	"d"	"f"	"g"	"h"

say like

$$\left.\begin{array}{l} n = 3 \\ \ell = 4 \end{array}\right\} \quad \text{"3p state"}$$

WAVE FUNCTIONS ? not the physics

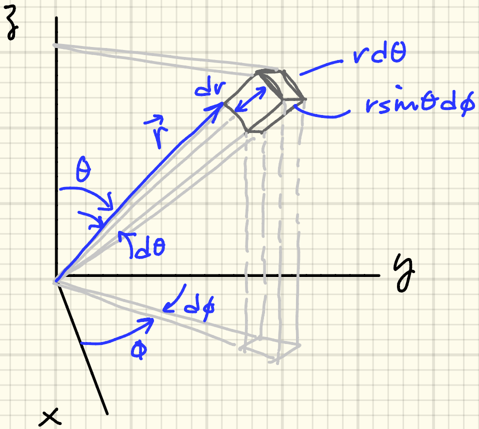
Probability... that's the physics

$$P(\vec{r})\,dv = \psi^*(r,\theta,\varphi)\,\psi(r,\theta,\varphi)\,dv = |\psi|^2 dv$$

probability that electron will be in infinitesimal volume, dv

Many states

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



$$dv = r^2\,dr\,\sin\theta\,d\theta\,d\phi$$

Normalization:

$$1 = \iiint_{\text{all space}} |R(r)|^2 |Y(\theta,\phi)|^2 r^2 dr \sin\theta \, d\theta \, d\phi$$

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

can sort of visualize 2 different probability distributions:

$$r^2 |R(r)|^2 dr$$

$$|Y_\ell^m(\theta,\varphi)|^2 \sin\theta \, d\theta \, d\varphi$$

radial distributions

$$P(r)\,dr = \int_0^{\pi}\int_0^{2\pi} |\psi|^2\, r^2 dr \sin\theta\, d\theta\, d\varphi$$

$$= \underbrace{\int_0^{\pi}\int_0^{2\pi} \sin\theta\, |Y_\ell^m|^2 d\theta\, d\varphi}_{=1} \cdot r^2 |R|^2 dr$$

look at lowest: $\psi_{n\ell m} = \psi_{100}$

$$\psi_{100}(r,\theta,\varphi) = R_{10}(r)\, Y_0^0(\theta,\varphi)$$

$$Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$$

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-Zr/a_0}$$

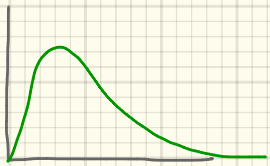
Probability of a ground-state electron to be

between r and $r+dr$ is:

$$P_{10}(r)\,dr = |R_{10}(r)|^2 r^2\,dr$$

$$= \left[\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}\right]^2 r^2\,dr$$

$$= 4\frac{Z^3}{a^3} r^2 e^{-2Zr/a_0}\,dr$$



The Y_0^0 → just a number

So the probability density is spherically symmetric... but varying in r

Most probable? in hydrogen, $z=1$

$$P_{10} = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

$$\frac{dP_{10}(r)}{dr} = \frac{4}{a_0^3}\left[2r\, e^{-2r/a_0} - r^2\left(\frac{2r}{a_0}\right) e^{-2r/a_0}\right]$$

$= 0$ for extremum

$$= \frac{4}{a_0^3} e^{-2r/a_0}\left[2r - \frac{2r^2}{a_0}\right]$$

$$\underset{\displaystyle 0}{\shortparallel} \quad \Rightarrow \quad r = a_0$$

HOW COOL IS THAT?