TRIUMF
Canada's national laboratory for particle and nuclear physics and accelerator-based science

2017 Student Seminar

Elementary Quantum Theory (2/4)

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September 22, 2017

Outline

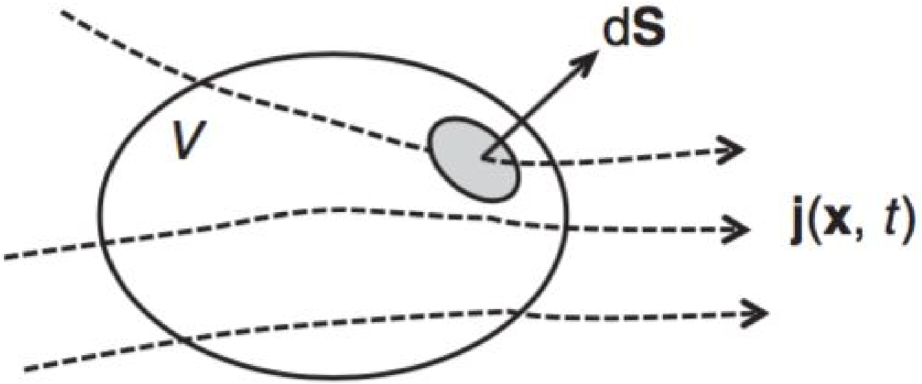
1) Continuity Equation and Born’s Rule
2) Angular Momentum
3) TISE for Central Potential
4) Angular ODE and Spherical Harmonics
5) Radial ODE
6) Hydrogen Atom

Continuity Equation

"density"

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \circ \vec{\jmath} = 0$$

"current"



[source: Thomson]

Continuity Equation (cont'd)

trick! $\rightarrow$ $$\Psi^\dagger \times (\text{wave eq'n}) - (\text{wave eq'n})^\dagger \times \Psi$$

for the TDSE $\rightarrow$ $$\begin{cases} \rho(\vec{\boldsymbol{x}},t) = \Psi^*(\vec{\boldsymbol{x}},t)\Psi(\vec{\boldsymbol{x}},t) \\ \vec{\boldsymbol{j}} = \frac{1}{2im}(\Psi^*\vec{\boldsymbol{\nabla}}\Psi - \Psi\vec{\boldsymbol{\nabla}}\Psi^*) \end{cases}$$

Born's Rule

$$\rho(\vec{\boldsymbol{x}}, t) = \Psi^*(\vec{\boldsymbol{x}}, t)\Psi(\vec{\boldsymbol{x}}, t)$$

probability density

$$\Psi(\vec{\boldsymbol{x}}, t) = \psi(\vec{\boldsymbol{x}})e^{-iE_n t} \Longrightarrow \Psi^*(\vec{\boldsymbol{x}}, t)\Psi(\vec{\boldsymbol{x}}, t) = \psi^*(\vec{\boldsymbol{x}})\psi(\vec{\boldsymbol{x}})$$

$$(1\mathrm{D}) \quad \int_a^b dx\, \psi^*(x)\psi(x) =$$

the probability of detecting the particle between ***a*** and ***b***

Angular Momentum

(first quantization) → $\vec{\boldsymbol{L}} = \vec{\boldsymbol{r}} \times \vec{\boldsymbol{p}} \ \mapsto \ \widehat{\boldsymbol{L}} = \widehat{\boldsymbol{r}} \times \widehat{\boldsymbol{p}}$

$$\widehat{\boldsymbol{p}} = -i\vec{\boldsymbol{\nabla}} \quad \Longrightarrow \quad \widehat{\boldsymbol{L}} = -i\widehat{\boldsymbol{r}} \times \vec{\boldsymbol{\nabla}}$$

$$\widehat{\boldsymbol{L}} = -i \begin{vmatrix} \widehat{\boldsymbol{\imath}} & \widehat{\boldsymbol{\jmath}} & \widehat{\boldsymbol{k}} \\ \widehat{x} & \widehat{y} & \widehat{z} \\ \partial_x & \partial_y & \partial_z \end{vmatrix}$$

Angular Momentum (cont'd)

$$\text{using,} \quad [\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{x}, \hat{p}_y] = i \quad \text{and,} \quad \widehat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}$$

$$\Longrightarrow \quad [\widehat{L}_a, \widehat{L}_b] = i \sum_{c=1}^{3} \epsilon_{abc} \widehat{L}_c, \quad \text{eg)} \quad [\widehat{L}_x, \widehat{L}_y] = i \widehat{L}_z$$

"Levi-Civita symbol"

$$\text{where,} \quad \epsilon_{abc} \doteq \begin{cases} 1, & abc \in \{(123)\} = \{123, 231, 312\} \\ -1, & abc \in \{(213)\} = \{213, 132, 321\} \\ 0, & \text{o.w.} \end{cases}$$

The components of ang. mom. are NOT compatible => they are NOT simultaneously diag.

Angular Momentum (cont'd)

$$\widehat{L}^2 \doteq \widehat{\boldsymbol{L}} \circ \widehat{\boldsymbol{L}} = (\widehat{L}_x, \widehat{L}_y, \widehat{L}_z) \circ (\widehat{L}_x, \widehat{L}_y, \widehat{L}_z)$$
$$= \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2$$

turns out! $[\widehat{L}^2, \widehat{L}_i] = 0 \ \text{ for, } \ i = 1, 2, 3 \leftrightarrow x, y, z$

The components of ang. mom. ARE compatible (sim. diag.) with full ang. mom. ^2

Angular Momentum (cont'd)

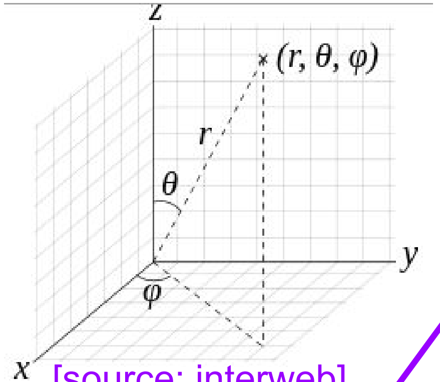
$$\implies \quad \exists\,|\psi\rangle \;\; \text{s.t.} \;\; \widehat{L}_z|\psi\rangle \propto |\psi\rangle \;\; \text{and,} \;\; \widehat{L}^2|\psi\rangle \propto |\psi\rangle$$

$$\text{label it,} \;\; |\psi\rangle = |l, m\rangle$$

ladder operators => (wiki. it)

$$\begin{cases} \widehat{L}_z|l,m\rangle = m|l,m\rangle, & -l \leq m \leq l \\ \widehat{L}^2|l,m\rangle = l(l+1)|l,m\rangle, & l \in \mathbb{N}_0 \end{cases}$$

Spherically Symmetric Central Potential



[source: interweb]

$$\widehat{L}^2 = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$V(\vec{\boldsymbol{x}}) \longrightarrow V(r), \quad \widehat{H} \longrightarrow \frac{\widehat{p}^2}{2m} + V(r)$$

(can show)

$$[\widehat{H}, \widehat{\boldsymbol{L}}] = 0 \implies m \text{ is a constant of motion}$$

by the Heisenberg EoM

$$[\widehat{H}, \widehat{L}^2] = 0 \implies l \text{ is a constant of motion}$$

Spherically Symmetric Central Potential (cont'd)

(TISE) $$\widehat{H}\psi_n = E_n\psi_n$$

We'll need more quantum numbers...

$$-\frac{1}{2m}\nabla^2\psi_n(\vec{\boldsymbol{x}}) + V(r)\psi_n(\vec{\boldsymbol{x}}) = E_n\psi_n(\vec{\boldsymbol{x}})$$

ansatz for SoV $$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

...therefore we'll leave them blank for now. #Lazy

Laplacian in Spherical Coordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Left as an exercise for the masochistic...

(likewise with the SoV math)

Angular Equation (from SoV)

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y(\theta,\phi)\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi)\propto Y(\theta,\phi)$$

recognize all these derivatives from an earlier slide!?

$$\implies \quad -\widehat{L}^2 Y \propto Y$$

$$\text{separation constant} = -l(l+1)$$

$$\text{since,} \quad \widehat{L}^2|l,m\rangle = l(l+1)|l,m\rangle$$

$$\text{recall,} \quad [\widehat{H},\widehat{L}^2]=0 \quad \implies \quad \widehat{H} \text{ and } \widehat{L}^2 \text{ are sim. diag!}$$

We can identify the Y-part of the solution to the TISE as our angular momentum eigenstates! :0

“Spherical Harmonics”

$$Y_{lm}(\theta,\phi) = \varepsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}e^{im\phi}P_{lm}(\cos\theta)$$

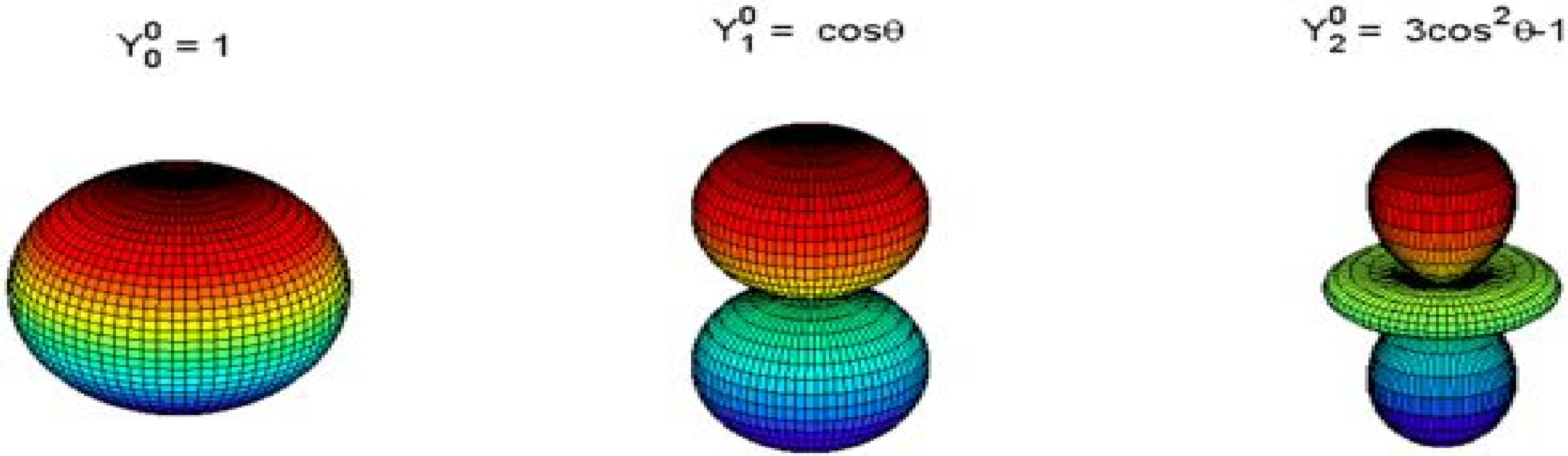
Condon-Shortley Phase

$$\varepsilon = \begin{cases} (-1)^m, & m > 0 \\ 1, & m \leq 0 \end{cases}$$

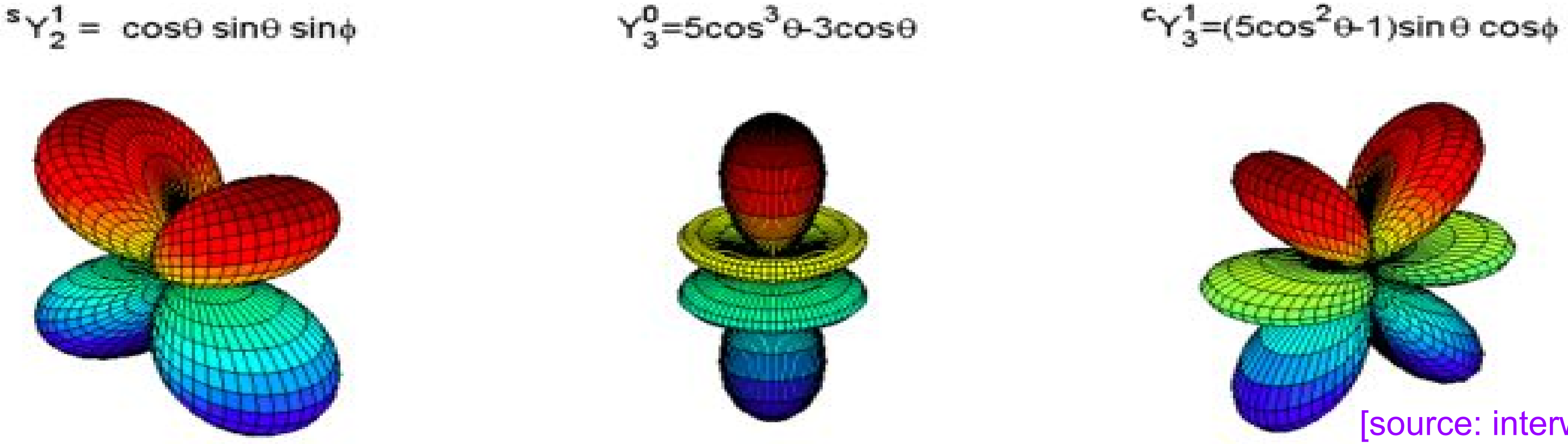
“Associated Legendre Polynomials”

$$P_{lm}(x) = \frac{1}{2^l l!}(1-x^2)^{\frac{m}{2}}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l$$ Rodrigues Formula

$$\hat{L}_z Y_{lm} = -i\frac{\partial}{\partial\phi}Y_{lm} = mY_{lm}$$ (can show)



$$Y_l^m, \quad l = 0, 1, 2, 3, \ldots \leftrightarrow s, p, d, f, \ldots$$



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Radial Equation (from SoV)

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

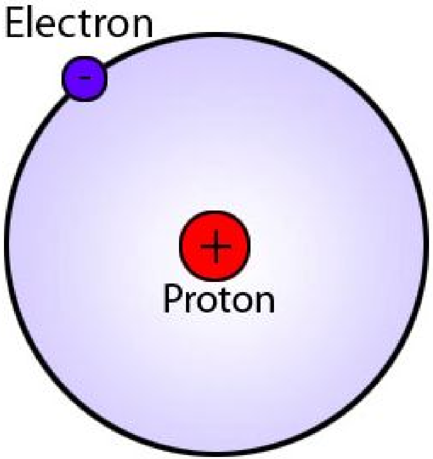
(undoing natural units now...)

$$\text{where,} \quad u \doteq rR(r)$$

$$R(r) \longrightarrow R_{nl}(r)$$

“Effective Potential”

Hydrogen Atom



$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

Coulomb Potential

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

"Radial Wave Function"

"Associated Laguerre Polynomials"

Rodrigues Formula

$$L_\alpha^\beta(x) = \frac{x^{-\beta}e^x}{\alpha!}\frac{d^\alpha}{dx^\alpha}\left(e^{-x}x^{\alpha+\beta}\right)$$

Bohr Model (Reproduced!)

(via analysis of radial eq'n / wave-FN)

$$|nlm\rangle \longleftrightarrow \psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

"Bohr Radius"

$$a \doteq \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.53\,\text{Å}, \qquad \frac{d}{dr}(\underline{r^2 R^*_{10} R_{10}}) = 0 \implies r = a$$

radial probability

discretized energy levels of H-orbitals

$$E_n = \frac{E_1}{n^2} \quad \text{for,} \quad n = 1, 2, 3, ..., \quad \text{and,} \quad l = 0, 1, ..., n-1$$

$$E_1 = -\left[\frac{m_e}{2\hbar}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] \approx -13.6\,\text{eV}$$

[source: interweb]

Thanks! Questions?