

Title: 13/14 PSI - Quantum Mechanics - Lecture 2

Date: Aug 28, 2013 10:30 AM

URL: <http://pirsa.org/13080033>

Abstract:

Schrödinger eq in 3D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi$$

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Schrödinger eq in 3D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi$$

$$\text{where } \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

General soln:

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}) e^{-\frac{i}{\hbar} E t}$$

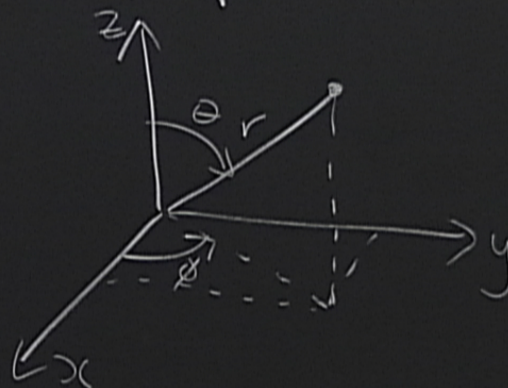
ψ_n is a soln to,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

$$\psi_n(\vec{r}) e^{-\frac{i}{\hbar} E t}$$

$$\psi = E \psi$$

If V is func of distance from origin
 $\rightarrow$ Spherical coord's are nice!



SE:

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

SE:

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Separation of variables; $\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$

Rewrite

$$\left[\frac{1}{r^2 \sin \theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V \psi = E \psi$$

$$\psi(r) Y(\theta, \phi)$$

Rewrite:

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0$$

$$\left[\frac{1}{r^2 \sin \theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V\psi = E\psi$$

$$\psi(\theta, \phi)$$

Rewrite:

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} = l(l+1)$$

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = -l(l+1)$$

Angular equation

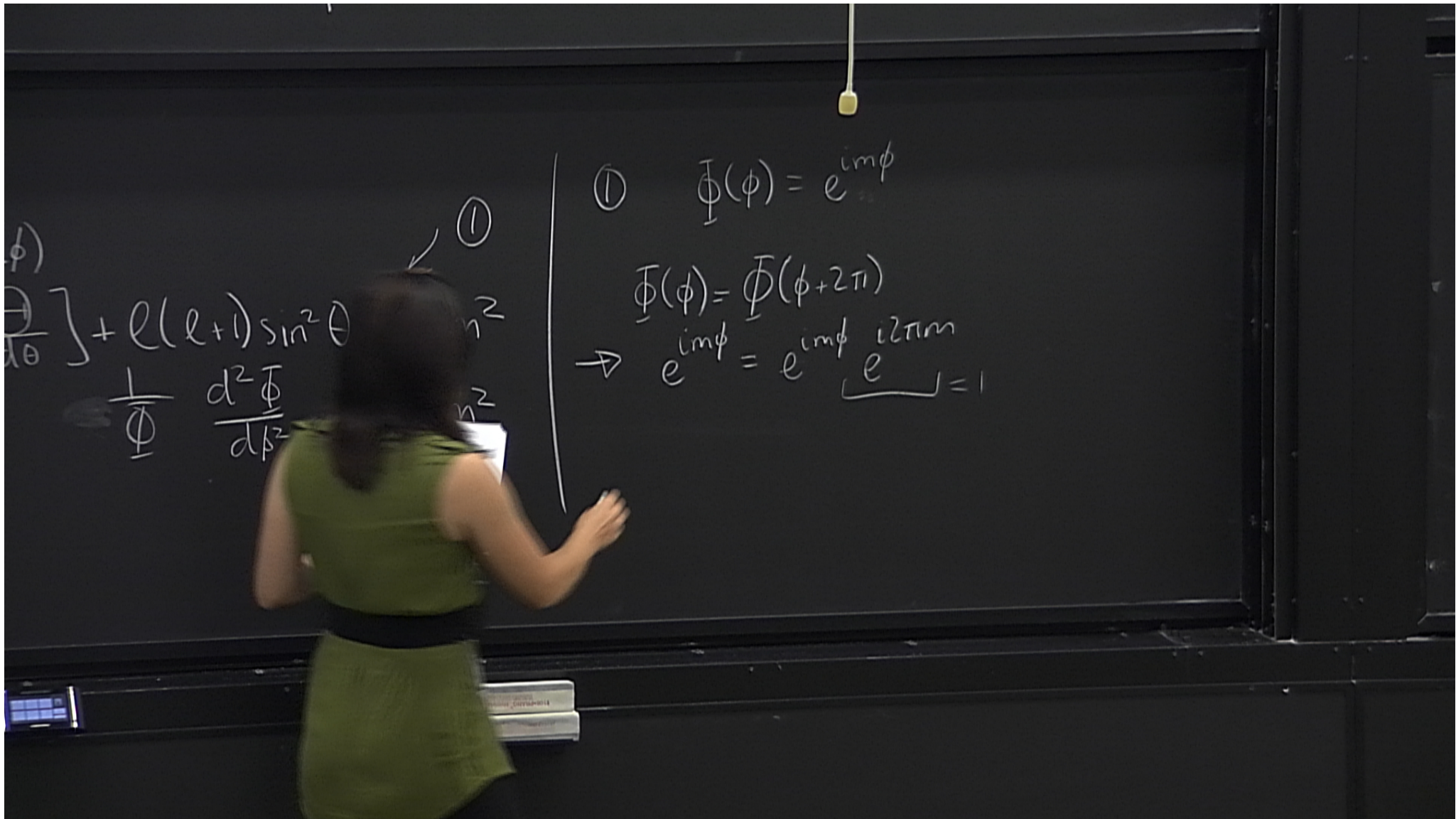
Radial equation

Angular eqn

S.o.v: $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$

Rewrite: $\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + \ell(\ell+1) \sin^2 \theta = m^2$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$$



$$\left. \frac{d}{d\theta} \right\} + \ell(\ell+1) \sin^2 \theta$$
$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}$$

$$\textcircled{1} \quad \Phi(\phi) = e^{im\phi}$$
$$\Phi(\phi) = \Phi(\phi + 2\pi)$$
$$\rightarrow e^{im\phi} = e^{im\phi} \underbrace{e^{i2\pi m}}_{=1}$$

$$\frac{\partial}{\partial \theta} \left. \right\} + \ell(\ell+1) \sin^2 \theta = m^2$$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$$

①

②

① $\Phi(\phi) = e^{im\phi}$

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

$$\Rightarrow e^{im\phi} = e^{im\phi} \underbrace{e^{i2\pi m}}_{=1}$$

$$m = 0, \pm 1, \pm 2, \dots$$

Solution to (2).

$$\Theta(\theta) = A P_l^m(\cos \theta)$$

where:

$$P_l^m(x) = (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x) \quad \text{"associated Legendre function"}$$

where:

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2-1)^l$$

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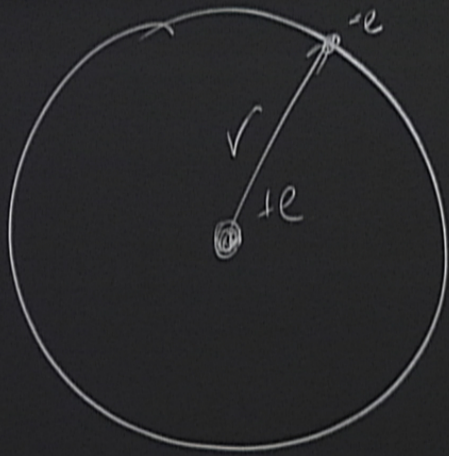
"associated Legendre function"

where:

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2-1)^l$$

"Legendre polynomial"

The radial eqn for Hydrogen atom;



Coulomb's law:

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

Radial eqn;

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - 2mr^2$$

Hydrogen atom;

Coulomb's law:

$$V(r) = -\frac{e^2}{r}$$

Radial eqn;

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

Hydrogen atom:

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Soln for R:

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} L_{n-\ell-1}^{2\ell+1}(2\rho)$$

$$\text{where } \rho = \frac{r}{a_n}$$

en atom;

Coulomb's law:

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

Radial eqn:

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

Soln for R:

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} L_{n-l-1}^{2l+1}(2\rho)$$

$$\text{where } \rho = \frac{r}{a_n}$$

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

Radial eqn:

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

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

"Associated
Laguerre
polynomial"

Radial eqn;

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"Associated
Laguerre
polynomial"

$$l = 0, 1, 2, \dots, n-1$$

Radial eqn;

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

Soln for R:

$$R_{nl}(r) = \frac{1}{r} \rho^{(l+1)} e^{-\rho} L_{n-l-1}^{2l+1}(2\rho)$$

where $\rho = \frac{r}{a_n}$

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

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"Associated
Laguerre
polynomial"

$$\Psi_{nlm} = N_{nl} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) Y_l^m(\theta, \phi)$$

corresponding energies

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \right] \frac{1}{n^2} \quad n=1,2,3,\dots$$

$$|\Psi_{200}|^2$$



$$\frac{1}{r} \left(\frac{2r}{na} \right) Y_l^m(\theta, \phi)$$

$$n = 1, 2, 3, \dots$$

$$|\psi_{200}|^2$$



$$|\psi_{210}|^2$$



$$|\psi_{320}|^2$$



Angular momentum

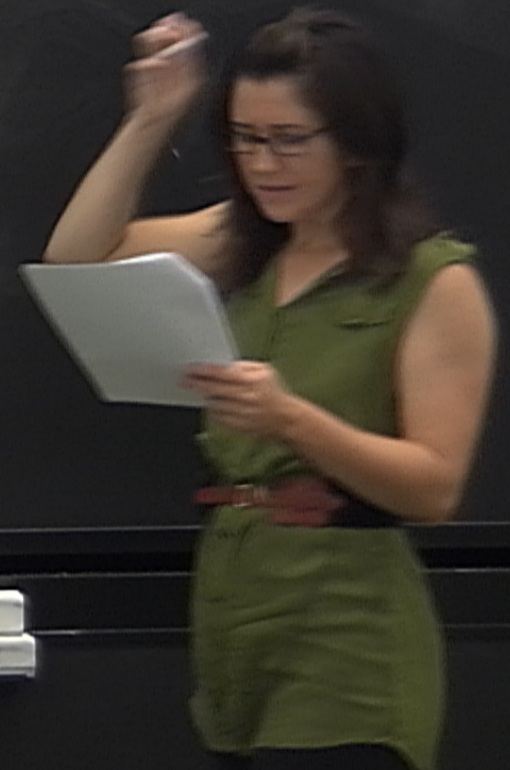
$$\vec{L} = \vec{r} \times \vec{p}$$

$$\rightarrow L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

Substitute $p_j \rightarrow i\hbar \frac{\partial}{\partial j}$



Angular momentum

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$$\rightarrow L_x = y p_z - z p_y$$

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$$L_z = x p_y - y p_x$$

Substitute $p_j \rightarrow i\hbar \frac{\partial}{\partial j}$

$$[L_x, L_y] = i\hbar L_z$$

$$[L_z, L_x] = i\hbar L_y$$

$$[L_y, L_z] = i\hbar L_x$$

Angular momentum

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

$$\rightarrow L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

Substitute $p_j \rightarrow i\hbar \frac{\partial}{\partial x_j}$

$$[L_x, L_y] = i\hbar L_z$$

$$[L_z, L_x] = i\hbar L_y$$

$$[L_y, L_z] = i\hbar L_x$$

"fundamental
commutation relations"

Angular momentum

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

$$\rightarrow L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

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Substitute $p_j \rightarrow i\hbar \frac{\partial}{\partial x_j}$

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$$[L_y, L_z] = i\hbar L_x$$

"fundamental
commutation relations"

This operator commutes

L

← ②

$$m = 0, \pm 1, \pm 2$$

Substitute $p_j \rightarrow i\hbar \frac{\partial}{\partial j}$

$$[L_x, L_y] = i\hbar L_z$$

$$[L_z, L_x] = i\hbar L_y$$

$$[L_y, L_z] = i\hbar L_x$$

"fundamental
commutation relations"

This operator commutes w L_j 's.

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\text{i.e. } [L^2, \vec{L}] = 0.$$

Find simultaneous e-states of L^2 and L_z

$$L^2 f = \lambda f$$

$$L_z f = m f$$

Radial equation

Define:

$$L_{\pm} = L_x \pm iL_y.$$

Can show that:

$$L^2(L_{\pm}f) = \lambda(L_{\pm}f)$$

$$L_z(L_{\pm}f) = (\mu \pm \hbar)(L_{\pm}f)$$

Define:

$$L_{\pm} = L_x \pm iL_y$$

Can show that:

$$L^2(L_{\pm}f) = \lambda(L_{\pm}f)$$

$$L_z(L_{\pm}f) = (\mu \pm \hbar)(L_{\pm}f)$$

Define:

$$L_+ f_+ = 0$$

$$L_- f_- = 0$$

Define:

$$L_{\pm} = L_x \pm iL_y$$

Can show that:

$$L^2(L_{\pm}f) = \lambda(L_{\pm}f)$$

$$L_z(L_{\pm}f) = (\mu \pm \hbar)(L_{\pm}f)$$

Define:

$$L_+ f_t = 0$$

$$L_- f_b = 0$$

Define eigenvalues λ_t and λ_b

$$L^2 f_t = \lambda f_t ; L_z f_t = \hbar \ell f_t$$

$$L^2 f_b = \lambda f_b ; L_z f_b = -\hbar \ell f_b$$

Define:

$$L_+ f_t = 0$$

$$L_- f_b = 0$$

Define eigenvalues l_t and $\bar{l}_t$.

$$\textcircled{3} \quad L^2 f_t = \lambda f_t ; \quad L_z f_t = \hbar l f_t$$

$$\textcircled{4} \quad L^2 f_b = \lambda f_b ; \quad L_z f_b = \hbar \bar{l} f_b$$

evaluate $L_+ L_-$:

$$L^2 = L_+ L_- + L_z^2 + \hbar L_z$$

Insert into $\textcircled{3}$

Define eigenvalues $l\hbar$ and $\bar{l}\hbar$

$$\textcircled{3} \quad L^2 f_l = \lambda f_l ; \quad L_z f_l = \hbar l f_l$$

$$\textcircled{4} \quad L^2 f_{\bar{l}} = \lambda f_{\bar{l}} ; \quad L_z f_{\bar{l}} = -\hbar \bar{l} f_{\bar{l}}$$

to find:

$$\lambda = \hbar^2 l(l+1) = \hbar^2 \bar{l}(\bar{l}+1)$$

either:

$$\begin{aligned} l &= \bar{l}+1 \\ \bar{l} &= -l \end{aligned}$$

l -values of L_z are $m\hbar$
where m goes from $-l$ to l
in N integer steps.

$$l = -l + N \rightarrow l = N/2$$