Chapter 3. Simple quantum systems

I. Translational motion

Free particle (plane wave):

$$\Psi(x) = e^{\pm ikx}, \qquad k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

$$E = \frac{(\hbar k)^2}{2m}, \qquad p = \pm k\hbar \qquad \text{(not quantized)}$$

Particle in a 1D box:

Infinite square well (e^- in π systems)

$$\begin{aligned} V(x) &= 0, \quad 0 \le x \le L \\ &= \infty, \quad x < 0, and \ x > L \end{aligned}$$

Schrödinger eqn (inside the well):

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi = E\Psi$$

Solution:

$$\begin{aligned} \Psi(x) &= A\,e^{+ikx} + B\,e^{-ikx} \\ &= C\cos kx + D\sin kx \end{aligned}$$

where we used $e^{\pm i\theta} = \cos\theta \pm i\sin\theta$

Verification

$$rhs = E\Psi = \left(\frac{k^2\hbar^2}{2m}\right)\Psi$$

$$lhs = -\left(\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2}(C\cos kx + D\sin kx)$$

$$= -\left(\frac{\hbar^2}{2m}\right)(-Ck^2\cos kx - Dk^2\sin kx)$$

$$= \left(\frac{\hbar^2 k^2}{2m}\right)(C\cos kx + D\sin kx)$$

rhs = *lhs*, it is a solution.

<u>Acceptable solutions and quantization:</u>

For regions outside the well, rearrange the Schrödinger eqn.

$$\Psi'' = \frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}(V - E)\Psi$$

Note that $V - E > 0$, so
when $\Psi > 0$, at $x > L$
$\Psi'' > 0$, so $\Psi \to \infty$ when $x \to \infty$
when $\Psi < 0$, at $x > L$
$\Psi'' < 0$, so $\Psi \to -\infty$ when $x \to \infty$

Both solutions are unacceptable.

Boundary condition:

$$\Psi = 0 \qquad \text{at } x \le 0 \text{ and } x \ge L$$

Probability of finding the particle is zero outside the well.

Acceptable solution:

$$\Psi(x) = C\cos kx + D\sin kx$$

At $x = 0$, $\quad 0 = \Psi(0) = C$
At $x = L$, $\quad 0 = \Psi(L) = D\sin kL$

so $\quad kL = n\pi, \quad n = 1, 2, \ldots \quad (n \neq 0)$

$$E_n = \frac{(k\hbar)^2}{2m} = \frac{(n\pi\hbar)^2}{2mL^2} = \frac{(nh)^2}{8mL^2},$$

Energy is quantized because of the motion is restricted.

Uncertainty principle

$$\Delta x = L$$

$$\Delta p = \frac{\hbar}{2\Delta x} = \frac{\hbar}{2L}$$

$$\frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{8mL^2} \propto E_0$$

Normalization:

$$\Psi_n = D\sin\left(\frac{n\pi x}{L}\right) \qquad D \text{ is undetermined.}$$

$$\begin{aligned}1 &= \int \Psi_n^* \Psi_n dx \\ &= \int_0^L D^2 \sin^2(kx)dx \\ &= D^2\left(\frac{x}{2} - \frac{1}{4k}\sin(2kx)\right)_0^L = D^2\frac{L}{2}\end{aligned}$$

where we have used $\sin^2 x = (1-\cos 2x)/2$. So, $D = \sqrt{2/L}$ and normalized wavefunction:

$$\Psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Example: Probability of finding a particle between x=0 and x=l inside a box of 1.0 nm length (assuming in its ground state).

The probability to find the particle in (0,l) is

$$\begin{aligned}P &= \int_0^l \Psi_n^* \Psi_n dx \\ &= \left(\frac{2}{L}\right)\int_0^l \sin^2\left(\frac{n\pi x}{L}\right)dx\end{aligned}$$

$$= \left(\frac{2}{L}\right)\left[\frac{x}{2} - \frac{L}{4n\pi}\sin\left(\frac{2n\pi x}{L}\right)\right]_0^l$$

$$= \left(\frac{2}{L}\right)\left(\frac{l}{2} - \frac{L}{4n\pi}\sin\left(\frac{2n\pi l}{L}\right)\right)$$

$$= 0.0064 \qquad when\, l = 0.1\,\text{nm}$$

$$= 0.048 \qquad when\, l = 0.2\,\text{nm}$$

$$= 0.50 \qquad when\, l = 0.5\,\text{nm}$$

$$= 1.00 \qquad when\, l = 1.0\,\text{nm}$$

Properties of the solution

Zero-point energy, lowest energy level, $n = 1$:

$$E = \frac{h^2}{8mL^2} \qquad (> 0) \qquad \text{(quantum effect)}$$

Orthogonality:

$$\langle \Psi_1 | \Psi_2 \rangle = \left(\frac{2}{L}\right)\int_0^L \sin\frac{\pi x}{L}\sin\frac{2\pi x}{L}\,dx$$

$$= 2\left(\frac{2}{L}\right)\int_0^L \sin\frac{\pi x}{L}\sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\,dx$$

$$= \left(\frac{4}{L}\right)\int_0^L \sin^2\frac{\pi x}{L}\,d\left(\sin\frac{\pi x}{L}\right)\frac{L}{\pi}$$

$$= \left(\frac{4}{3\pi}\right)\sin^3\frac{\pi x}{L}\Bigg|_0^L = 0$$

<u>Nodal structure:</u> The *n*th state has (*n*-1) nodes.

$$\Psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) = 0 \qquad \text{at} \quad \frac{n\pi x}{L} = m\pi\,,\ m = 0,1,2,\,..$$

Positions of the node:

$x = mL/n$ and $0 < x < L$

<u>Energy separation</u>

$$\Delta E_{n\to n+1} = \frac{[(n+1)^2 - n^2]h^2}{8mL^2} = \frac{(2n+1)h^2}{8mL^2}$$

$\Delta E \to 0$ as m or L increases.

Example: An electron is in a 1D box with L = 1 nm. Calc. zero-point energy and photon frequency for 1→2 transition.

$$E_1 = \frac{h^2}{8m_e L^2}$$

$$= \frac{(6.626\times10^{-34}\,Js)^2}{8(9.1\times10^{-31}\,kg)(1.0\times10^{-9}\,m)^2} = 6.03\times10^{-20}\,J$$

$$\Delta E_{1\to2} = \frac{(2\times1+1)h^2}{8mL^2} = 3E_1 = 1.81\times10^{-19}\,J$$

$$\nu = \frac{\Delta E}{h} = \frac{1.81\times10^{-19}\,J}{6.626\times10^{-34}\,Js} = 2.73\times10^{14}\,s^{-1}$$

Expectation values:

$$\langle x \rangle = \int_0^L \Psi_n x \Psi_n dx = \frac{L}{2}$$

$$\langle p \rangle = \int_0^L \Psi_n \left(-i\hbar \frac{d}{dx} \right) \Psi_n dx = 0$$

$$\langle x^2 \rangle = \int_0^L \Psi_n x^2 \Psi_n dx$$

$$= \int_0^L x^2 \sin^2 \frac{n\pi x}{L} dx = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

Let us define a useful quantity, the variance:

$$\sigma_\Omega^2 = \langle \Omega^2 \rangle - \langle \Omega \rangle^2$$

so

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4} = \left(\frac{L^2}{4n^2\pi^2} \right) \left(\frac{\pi^2 n^2}{3} - 2 \right)$$

Standard deviation of *x*:

$$\sigma_x = \left(\frac{L}{2n\pi} \right) \sqrt{\frac{\pi^2 n^2}{3} - 2}$$

It can be shown that standard derivation of *p* is

$$\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \frac{n\pi\hbar}{L}$$

Interestingly,

$$\sigma_x \sigma_p = \left(\frac{L}{2n\pi} \right) \sqrt{\frac{\pi^2 n^2}{3} - 2} \frac{n\pi\hbar}{L} = \frac{\hbar}{2} \sqrt{\frac{\pi^2 n^2}{3} - 2} > \frac{\hbar}{2}$$

because the term in square root is never less than 1.

Particle in a two-dimensional box:

$$\begin{aligned} V(x, y) &= 0, \qquad 0 \le x \le L_1, 0 \le y \le L_2 \\ &= \infty, \qquad \textit{otherwise} \end{aligned}$$

Schrödinger eqn.:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \Psi = E\Psi$$

Assume the wavefunction is separable

$$\Psi(x, y) = \Psi^x(x) \Psi^y(y)$$

Differentiate the wavefunction

$$\frac{\partial^2 \Psi}{\partial x^2} = \Psi^y \frac{d^2 \Psi^x}{dx^2}, \qquad \frac{\partial^2 \Psi}{\partial y^2} = \Psi^x \frac{d^2 \Psi^y}{dy^2},$$

so the Schrödinger eqn becomes

$$-\frac{\hbar^2}{2m}\left(\Psi^y \frac{d^2 \Psi^x}{dx^2} + \Psi^x \frac{d^2 \Psi^y}{dy^2} \right) = E\Psi^x \Psi^y$$

Divide by $\Psi^x \Psi^y$:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\Psi^x}\frac{d^2 \Psi^x}{dx^2} + \frac{1}{\Psi^y}\frac{d^2 \Psi^y}{dy^2} \right) = E$$

So, we can write two separated equations:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\Psi^x}\frac{d^2 \Psi^x}{dx^2} \right) = E^x$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\Psi^y}\frac{d^2 \Psi^y}{dy^2} \right) = E^y$$

where $E = E^x + E^y$, and the solutions are

$$\Psi_{n_1}^{x}(x) = \left(\frac{2}{L_1}\right)^{1/2} \sin\left(\frac{n_1 \pi x}{L_1}\right)$$

$$\Psi_{n_2}^{y}(y) = \left(\frac{2}{L_2}\right)^{1/2} \sin\left(\frac{n_2 \pi y}{L_2}\right)$$

Energy:

$$E_{n_1,n_2} = \left[\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2\right]\frac{h^2}{8m}, \qquad n_1, n_2 = 1, 2, ...$$

If $L_1 = L_2 = L$,

$$E_{n_1,n_2} = \frac{(n_1^2 + n_2^2)h^2}{8mL^2}$$

<u>Degeneracy</u>: different wavefunctions with the same energy.

$$E_{1,2} = E_{2,1} = \frac{5h^2}{8mL^2}$$

Their wavefunctions are different:

$$\Psi_{1,2} = \left(\frac{2}{L}\right)\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)$$

$$\Psi_{2,1} = \left(\frac{2}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)$$

<u>Tunneling over 1D barrier:</u>

Incident wave → reflection + transmission

Wavefunction is not zero inside the barrier.

<u>Tunneling</u>: particle can penetrate a thin wall. (quantum effect)

$$P \propto \frac{E}{V}\left(1-\frac{E}{V}\right)e^{-2L\sqrt{2m(V-E)}/\hbar}$$

Favors smaller mass and thin barrier.

Cold fusion

H + H → He + energy (Tunnelling ?)

II. Vibrational motion

Schrödinger equation of **<u>Harmonic oscillator</u>**:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right]\Psi = E\Psi$$

Wavefunction

$$|\upsilon\rangle = \Psi_\upsilon(x) = N_\upsilon H_\upsilon(y)e^{-y^2/2}$$

where

$$y=\frac{x}{\alpha}, \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

$H_\upsilon(y)$ is the <u>Hermite polynomial</u>

$$\begin{aligned} &H_0(y)=1 \\ &H_1(y)=2y \\ &H_2(y)=4y^2-2 \\ &\ldots \\ &H_{\upsilon+1}=2yH_\upsilon-2\upsilon H_{\upsilon-1} \qquad \text{(recursion relation)} \end{aligned}$$

Normalization factor

$$N_\upsilon = \left(\frac{1}{\alpha\sqrt{\pi}\,2^\upsilon \upsilon!}\right)^{1/2}$$

Orthogonalization:

$$\langle \upsilon | \upsilon' \rangle = \delta_{\upsilon\upsilon'}$$

Energy

$$E_\upsilon = \left(\upsilon + \frac{1}{2} \right) \hbar\omega \qquad \upsilon = 0, 1, \ldots$$

Vibrational frequency

$$\omega = \left(\frac{k}{m} \right)^{1/2}$$

Zero point energy ($\upsilon = 0$)

$$E_0 = \frac{1}{2} \hbar\omega$$

(quantum effect)

Even at 0 K, there is still vibration.

Energy separation

$$\Delta E = E_{\upsilon+1} - E_\upsilon = [(\upsilon + 1 + 1/2) - (\upsilon + 1/2)]\hbar\omega = \hbar\omega$$

(equal separation).

Transition frequency:

$$\nu = \frac{\Delta E}{h} = \frac{\hbar\omega}{h} = \frac{\omega}{2\pi}$$

Example: Calc. zero-point energy and transition frequency for an oscillator with $m = 1.7\times10^{-27}$ kg and $k = 1000$ N/m.

$$\omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{1000N/m}{1.7\times10^{-27}kg}} = 7.7\times10^{14}s^{-1}$$

$$E_0 = \frac{\hbar\omega}{2} = \frac{(1.055\times10^{-34}Js)(7.7\times10^{14}s^{-1})}{2} = 4.06\times10^{-20}J$$

$$\nu = \frac{\omega}{2\pi} = \frac{7.7\times10^{14}s^{-1}}{2\times3.14} = 1.23\times10^{14}s^{-1}$$

<u>Vibrational (infrared) spectrum:</u>

Molecular vibration can be approximated by harmonic oscillator:

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)\hbar\omega$$

with

$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{and} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{(reduced mass)}$$

Selection rules:

- active if vibration changes dipole
- $\Delta\upsilon = \pm1$ ($\Delta\upsilon = \pm2, \pm3, \ldots$ possible but weak)

Transition frequency:

$$\nu = (E_{\upsilon+1} - E_\upsilon)/h = \omega/2\pi$$

For harmonic oscillator, both p and q are to 2nd power.

<u>Ladder operators</u> (2nd quantization)

$$\hat{b} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right), \qquad \hat{b}^{+} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right)$$

so

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{b} + \hat{b}^{+}\right), \qquad \hat{p} = -i\sqrt{\frac{m\omega\hbar}{2}}\left(\hat{b} - \hat{b}^{+}\right)$$

Note: $\hat{b}^{*} = \hat{b}^{+}$.

The operators do not commute:

$$[\hat{b}, \hat{b}^{+}] = \frac{m\omega}{2\hbar}\left[\hat{x} + \frac{i\hat{p}}{m\omega}, \hat{x} - \frac{i\hat{p}}{m\omega}\right]$$

$$= \frac{m\omega}{2\hbar}\left\{[\hat{x}, \hat{x}] - \left[\hat{x}, \frac{i\hat{p}}{m\omega}\right] + \left[\frac{i\hat{p}}{m\omega}, \hat{x}\right] - \left[\frac{i\hat{p}}{m\omega}, \frac{i\hat{p}}{m\omega}\right]\right\}$$

$$= \frac{i}{\hbar}[\hat{p}, \hat{x}] = 1$$

That is

$$\hat{b}\hat{b}^{+} - \hat{b}^{+}\hat{b} = 1, \text{ or } \quad \hat{b}\hat{b}^{+} = 1 + \hat{b}^{+}\hat{b}$$

Reexpress $\hat{H}$:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2}$$
$$= \frac{1}{2m}\left(-\frac{m\omega\hbar}{2}\right)\left(\hat{b} - \hat{b}^+\right)^2 + \frac{m\omega^2}{2}\frac{\hbar}{2m\omega}\left(\hat{b} + \hat{b}^+\right)^2$$
$$= \frac{\hbar\omega}{2}\left(\hat{b}\hat{b}^+ + \hat{b}^+\hat{b}\right)$$

where $\left(\hat{b} \pm \hat{b}^+\right)^2 = \hat{b}^2 + \hat{b}^{+2} \pm \hat{b}\hat{b}^+ \pm \hat{b}^+\hat{b}$.

$$\hat{H} = \frac{\hbar\omega}{2}\left(\hat{b}\hat{b}^+ + \hat{b}^+\hat{b}\right) = \frac{\hbar\omega}{2}\left(1 + \hat{b}^+\hat{b} + \hat{b}^+\hat{b}\right) = \hbar\omega\left(\hat{b}^+\hat{b} + \frac{1}{2}\right)$$

Since

$$\hat{b}^+\hat{b} = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}$$

It is easy to see that the eigenstate of $\hat{H}$ is also an eigenstate of $\hat{b}^+\hat{b}$. Specifically:

$$\hat{b}^+\hat{b}|\upsilon\rangle = \upsilon|\upsilon\rangle$$

In other words, $\hat{b}^+\hat{b}$ is a <u>number operator</u>!

Let's look at $\hat{b}^+|\upsilon\rangle$ and $\hat{b}|\upsilon\rangle$:

$$\hat{b}^+\hat{b}(\hat{b}^+|\upsilon\rangle) = \hat{b}^+(1+\hat{b}^+\hat{b})|\upsilon\rangle = (1+\upsilon)(\hat{b}^+|\upsilon\rangle)$$

$$\hat{b}^+\hat{b}(\hat{b}|\upsilon\rangle) = (\hat{b}\hat{b}^+ - 1)\hat{b}|\upsilon\rangle = \hat{b}\hat{b}^+\hat{b}|\upsilon\rangle - \hat{b}|\upsilon\rangle = (\upsilon - 1)(\hat{b}|\upsilon\rangle)$$

which means

$$\hat{b}^+|\upsilon\rangle \propto |\upsilon+1\rangle, \qquad \text{or} \qquad \hat{b}^+|\upsilon\rangle = c|\upsilon+1\rangle$$
$$\hat{b}|\upsilon\rangle \propto |\upsilon-1\rangle, \qquad \text{or} \qquad \hat{b}|\upsilon\rangle = c'|\upsilon-1\rangle$$

so, $\hat{b}^+$ and $\hat{b}$ are <u>raising and lowering operators</u>.

Since $\left\langle \upsilon \middle| \hat{b}^+\hat{b} \middle| \upsilon \right\rangle = \upsilon$,

$$\begin{aligned}
\upsilon &= \left\langle \upsilon \middle| \hat{b}^+\hat{b} \middle| \upsilon \right\rangle && \left(\int \psi_\upsilon^* \hat{b}^+\hat{b}\psi_\upsilon dx\right) \\
&= \left\langle \hat{b}\upsilon \mid \hat{b}\upsilon \right\rangle && \left(\int (\hat{b}\psi_\upsilon)^* \hat{b}\psi_\upsilon dx\right) \\
&= c'^* c' \langle \upsilon - 1 \mid \upsilon - 1 \rangle && \left(c'^* c' \int \psi_{\upsilon-1}^* \psi_{\upsilon-1} dx\right) \\
&= |c'|^2
\end{aligned}$$

we have

$$c' = \sqrt{\upsilon}, \qquad c = \sqrt{\upsilon+1}$$

$$\hat{b}|\upsilon\rangle = \sqrt{\upsilon}|\upsilon-1\rangle, \qquad \hat{b}^+|\upsilon\rangle = \sqrt{\upsilon+1}|\upsilon+1\rangle$$

Properties of the oscillator

Symmetry of eigenfunctions:

$$\langle \upsilon | \hat{x} | \upsilon \rangle = \sqrt{\frac{\hbar}{2m\omega}} \langle \upsilon | \hat{b} + \hat{b}^{+} | \upsilon \rangle$$
$$= \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{\upsilon} \langle \upsilon \,|\, \upsilon - 1 \rangle + \sqrt{\upsilon + 1} \langle \upsilon \,|\, \upsilon + 1 \rangle \right) = 0$$

Spread:

$$\left\langle \upsilon \middle| x^2 \middle| \upsilon \right\rangle = \frac{\hbar}{2m\omega} \left\langle \upsilon \middle| (b + b^{+})^2 \middle| \upsilon \right\rangle$$
$$= \frac{\hbar}{2m\omega} \left\langle \upsilon \middle| bb + b^{+}b^{+} + bb^{+} + b^{+}b \middle| \upsilon \right\rangle$$

As discussed above,

$$\langle \upsilon | bb | \upsilon \rangle = \left\langle \upsilon \middle| b^{+}b^{+} \middle| \upsilon \right\rangle = 0$$
$$\left\langle \upsilon \middle| b^{+}b \middle| \upsilon \right\rangle = \upsilon, \;\; \left\langle \upsilon \middle| bb^{+} \middle| \upsilon \right\rangle = \left\langle \upsilon \middle| b^{+}b + 1 \middle| \upsilon \right\rangle = \upsilon + 1,$$

so

$$\left\langle \upsilon \middle| x^2 \middle| \upsilon \right\rangle = \frac{\hbar}{2m\omega} \left\langle \upsilon \middle| (b + b^{+})^2 \middle| \upsilon \right\rangle$$
$$= \frac{\hbar}{2m\omega} (2\upsilon + 1)$$

$$<\hat{V}> = \left\langle \upsilon \left| \frac{k\hat{x}^2}{2} \right| \upsilon \right\rangle = \left(\upsilon + \frac{1}{2}\right)\left(\frac{\hbar\omega}{2}\right) = \frac{E_\upsilon}{2}$$

$$<\hat{T}> = \left\langle \upsilon \left| \frac{\hat{p}^2}{2m} \right| \upsilon \right\rangle = \frac{E_\upsilon}{2}$$

$$<\hat{V}> = <\hat{T}>$$

<u>Virial theorem:</u> If $V(x) = ax^\beta$, then

$$2 <\hat{T}> = \beta <\hat{V}>$$

For quadratic potential (harmonic oscillator, $\beta = 2$)

III. Rotational motion

Schrödinger eqn. of **2D rotors:**

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi$$

Use polar coordinate system ($x = r\cos\phi, y = r\sin\phi$)

$$-\frac{\hbar^2}{2I}\frac{d^2\Psi}{d\phi^2} = E\Psi \qquad\qquad (r \text{ fixed, or rigid rotor})$$

with moment of inertia: $I = mr^2$.

General solution:

$$\Psi_m(\phi) = \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi}, \qquad m = \pm\left(\frac{2IE}{\hbar^2}\right)^{1/2}$$

Cyclic boundary condition:

$$\Psi(\phi) \;=\; \Psi(\phi + 2\pi)$$

So,

$$\Psi(\phi+2\pi) = Ne^{im(\phi+2\pi)} = Ne^{i2m\pi}e^{im\phi}$$
$$= N(e^{i\pi})^{2m}e^{im\phi} = (-1)^{2m}\Psi(\phi)$$

$2m$ has to be even integers, i.e.

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

Quantization

$$E_m = \frac{m^2\hbar^2}{2I} \qquad \text{(2D)}$$

Angular momentum:

$l_z = m\hbar$ quantized angular momentum

Angular momentum operator

$$\hat{l}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$
$$= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

Ψ is an eigenfunction of both $\hat{H}$ and $\hat{l}_z$:

$$\hat{l}_z\Psi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\left[\left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi} \right] = im\frac{\hbar}{i}\left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi} = m\hbar\Psi$$

$$\hat{H}\Psi = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\left[\left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi} \right] = \frac{(m\hbar)^2}{2I}\Psi$$

3D free rotors:

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

In the spherical coordinates:

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}$$

3D Hamiltonian becomes:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2I}\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]$$

Schrödinger eqn. for rigid rotor:

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\Psi = E\Psi$$

The solution is separable:

$$\Psi(\theta,\phi) = \Theta(\theta)\Phi(\phi) = P_l^m(\cos\theta)\left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi}$$

$P_l^m(\cos\theta)$: associated Legendre function.
$Y_{l,m}(\theta,\phi) = \Phi_m(\phi)\Theta_l(\theta)$: spherical harmonics (orthonormal)

Two quantum numbers:

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

Rotational energy (3D)

$$E_l = \frac{l(l+1)\hbar^2}{2I}$$

Since E is independent of m, each l level is $2l + 1$ degenerate.

<u>Angular momentum operators</u>

Angular momentum (Classical Mechanics)

$$\vec{l} = l_x \vec{e}_x + l_y \vec{e}_y + l_z \vec{e}_z$$
$$l^2 = l_x^2 + l_y^2 + l_z^2$$

where the components are

$$l_x = yp_z - zp_y, \qquad l_y = zp_x - xp_z, \quad l_z = xp_y - yp_x$$

Quantum operators:

$$\hat{l}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) = -\frac{\hbar}{i}\left(\sin\phi \frac{\partial}{\partial \theta} + \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right)$$

$$\hat{l}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) = -\frac{\hbar}{i}\left(-\cos\phi \frac{\partial}{\partial \theta} + \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right)$$

$$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 = -\hbar^2 \left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta} \right) \right]$$

As discussed above:

$$\hat{l}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m}$$

because

$$\hat{H}Y_{l,m} = \frac{\hat{l}^2}{2I}Y_{l,m} = \frac{l(l+1)\hbar^2}{2I}Y_{l,m}$$

We have further

$$\hat{l}_z Y_{l,m} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\left[P_l^m(\cos\theta)\sqrt{\frac{1}{2\pi}}e^{im\phi} \right] = m_l \hbar Y_{l,m}$$

In bra-ket notation, we have

$$\hat{l}^2 \left| l,m \right\rangle = l(l+1)\hbar^2 \left| l,m \right\rangle$$
$$\hat{l}_z \left| l,m \right\rangle = m\hbar \left| l,m \right\rangle$$

Commutation relations:

$$[\hat{l}_z, \hat{l}_x] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}\hat{p}_z - \hat{z}\hat{p}_y] = i\hbar\hat{l}_y$$

In general:

$$[\hat{l}_i, \hat{l}_j] = i\hbar\hat{l}_k, \qquad i, j, k = x, y, z$$

and

$$[\hat{l}_x, \hat{l}^2] = [\hat{l}_y, \hat{l}^2] = [\hat{l}_z, \hat{l}^2] = 0$$

Conclusions:

- $\hat{l}^2$ commutes with each component, they share eigenfunctions (spherical harmonics: $|l, m\rangle = Y_{l,m}$).
- The components of $\vec{l}$ do not mutually commute. Only one (l_z) is needed to specify the direction of $\vec{l}$

Quantization of $\vec{l}$ includes two aspects:

i. quantization of the magnitude of $\vec{l}$: $|\vec{l}| = \sqrt{l(l+1)}\hbar$

ii. quantization of the orientation of $\vec{l}$: $l_z = m\hbar$

Only certain directions of $\vec{l}$ are allowed.

<u>Vector model</u>: (l = 1, m_l = 0, ±1)

The (2l+1) degeneracy can be removed by external fields.

<u>Ladder operators:</u>

$$\hat{l}_{\pm} = \hat{l}_x \pm i\hat{l}_y$$

It can be proven

$$[\hat{l}_+, \hat{l}_z] = \hat{l}_+\hat{l}_z - \hat{l}_z\hat{l}_+ = -\hbar\hat{l}_+$$

so

$$\begin{aligned}\hat{l}_z\left(\hat{l}_+|l,m\rangle\right) &= \hat{l}_+\hat{l}_z|l,m\rangle + \hbar\hat{l}_+|l,m\rangle \\ &= m\hbar\hat{l}_+|l,m\rangle + \hbar\hat{l}_+|l,m\rangle \\ &= (m+1)\hbar\left(\hat{l}_+|l,m\rangle\right)\end{aligned}$$

or

$$\hat{l}_+|l,m\rangle = c^+_{l,m}|l,m+1\rangle \qquad \text{raising operator}$$
$$\hat{l}_-|l,m\rangle = c^-_{l,m}|l,m-1\rangle \qquad \text{lowering operator}$$

Coefficients:

$$\begin{aligned}
\left\|\hat{l}_+|l,m\rangle\right\|^2 &= \left[\hat{l}_+|l,m\rangle\right]^* \hat{l}_+|l,m\rangle \\
&= \left\langle l,m\middle|\hat{l}_-\hat{l}_+\middle|l,m\right\rangle \\
&= \left\langle l,m\middle|(\hat{l}_x - i\hat{l}_y)(\hat{l}_x + i\hat{l}_y)\middle|l,m\right\rangle \\
&= \left\langle l,m\middle|\hat{l}_x^2 + i\hat{l}_x\hat{l}_y - i\hat{l}_y\hat{l}_x + \hat{l}_y^2\middle|l,m\right\rangle \\
&= \left\langle l,m\middle|\hat{l}^2 - \hat{l}_z^2 - \hbar\hat{l}_z\middle|l,m\right\rangle \\
&= l(l+1)\hbar^2 - m(m+1)\hbar^2
\end{aligned}$$

Noting $\hat{l}_\pm = \hat{l}_\mp^*$ and $[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$.

Since $|l,m\rangle$ is normalized, we have

$$c^+_{l,m} = \hbar\sqrt{l(l+1) - m(m+1)}$$
$$c^-_{l,m} = \hbar\sqrt{l(l+1) - m(m-1)}$$

or

$$\hat{l}_\pm|l,m\rangle = \hbar\sqrt{l(l+1) - m(m\pm 1)}\,|l,m\pm 1\rangle$$

with $\hat{l}_+|l,l\rangle = \hat{l}_-|l,-l\rangle = 0$.

Rotational (microwave) spectrum:

Selection rules:

- active if molecule has permanent dipole
- $\Delta J = \pm 1$ (strict)

Transition frequency for linear rotor:

$$h\nu = (E_{J+1} - E_J)$$
$$= \frac{[(J+1)(J+2) - J(J+1)]\hbar^2}{2I} = \frac{(J+1)h^2}{4\pi^2 I}$$

$$\nu = (J+1)\frac{h}{4\pi^2 I}$$

Rotational spectra consist of equal-distant lines separated by $\frac{h}{4\pi^2 I}$.

Other molecules have more rotational quantum numbers.

Spin

Particles (electrons, nucleus) have internal angular momentum: spin, **S** and $\mathbf{S_z}$. Both are quantized.

$$\hat{S}^2|s,m_s\rangle = s(s+1)\hbar^2|s,m_s\rangle$$
$$\hat{S}_z|s,m_s\rangle = m_s\hbar|s,m_s\rangle$$

Fermion: half-integer spin, electron, proton, etc.

Boson: integer spin, photon, deuterium, etc.

Spin is a relativistic effect, has not functional basis.

For e^-, the spin angular momentum quantum numbers are:

$s = 1/2$

$m_s = 1/2$ (α electron) $\quad |\alpha\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle$

-1/2 (β electron) $\quad |\beta\rangle = \left|\frac{1}{2},-\frac{1}{2}\right\rangle$

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1,$$

$$\langle\alpha|\beta\rangle = 0$$

Matrix representations:

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\Omega_{m_s, m_s'} = \langle s, m_s | \hat{\Omega} | s, m_s' \rangle$$

$$\hat{s}_z = \hbar \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \text{diagonal}$$

$$\hat{s}_z |\beta\rangle = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} |\beta\rangle$$

Ladder operators:

$$\hat{s}_\pm = \hat{s}_x \pm i\hat{s}_y$$
$$\hat{s}_\pm |s, m_s\rangle = \sqrt{s(s+1) - m_s(m_s \pm 1)}\hbar |s, m_s \pm 1\rangle$$

$$\hat{s}_+ |\beta\rangle = \hbar \sqrt{\frac{1}{2}\left(1 + \frac{1}{2}\right) - \left(-\frac{1}{2}\right)\left[1 + \left(-\frac{1}{2}\right)\right]} |\alpha\rangle = \hbar |\alpha\rangle$$

$$\hat{s}_- |\alpha\rangle = \hbar |\beta\rangle$$

$$\hat{s}_+ |\alpha\rangle = \hat{s}_- |\beta\rangle = 0$$

Matrix representation:

$$\hat{s}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad \hat{s}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix},$$

$$\hat{s}_+|\beta\rangle = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar|\alpha\rangle$$

Spin in magnetic field (Zeeman effect):

$$E = g m_s \mu_B B \quad \text{with} \quad g = 2.0023$$

Bohr magneton: $\mu_B = e\hbar / 2m_e$.

Stern-Gerlach experiment: