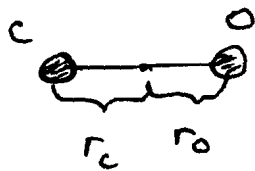


Classical mechanics:

$$K_t = \frac{p^2}{2m} \leftarrow \text{kinetic energy of translational motion}$$



$$K_r = \frac{L^2}{2I} \leftarrow \text{kinetic energy of rotational motion}$$

↑
moment of inertia

$$I_{co} = m_c r_c^2 + m_o r_o^2$$

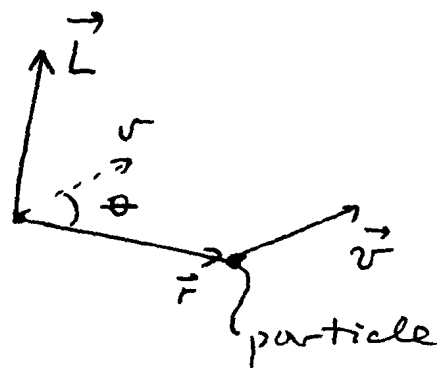
$$I = \sum_i m_i r_i^2$$

↑
sum over all particles making the system

Angular momentum

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

↑
vector product



$$|\vec{L}| = r p \sin \theta$$

if \vec{r} is parallel to \vec{v} , $\vec{L} = 0$, angular momentum is responsible for rotational motion

$$\vec{L} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \vec{i} \underbrace{(y p_z - z p_y)}_{L_x} + \vec{j} \underbrace{(z p_x - x p_z)}_{L_y} + \vec{k} \underbrace{(x p_y - y p_x)}_{L_z}$$

↑
determinant

Conservation of \vec{L} : $\frac{d\vec{L}}{dt} = 0$

7-2

↓ in quantum mechanics

$$[\hat{H}, \hat{L}_x] = 0 \quad \leftarrow \quad [\hat{H}, \hat{L}] = 0$$

$$[\hat{H}, \hat{L}_y] = 0$$

$$[\hat{H}, \hat{L}_z] = 0$$

commutators with all projections of \vec{L} must be equal to zero

Commutation algebra for \vec{L}

In order to establish which components of \vec{L} can be measured simultaneously, one needs commutation relations

Useful rule to remember:

$$[AB, C] = A[B, C] + [A, C]B$$

$$[L_x, L_y] = [y p_z - z p_y, z p_x - x p_z] =$$

$$= [y p_z, z p_x] - [z p_y, z p_x] - [y p_z, x p_z] + [z p_y, x p_z]$$

$$= y [p_z, z] p_x + x [z, p_z] p_y =$$

$$= \frac{\hbar}{i} (y p_x - x p_y) = i\hbar L_z$$

all remaining relations can be obtained by circular permutation of indexes:

$$[x, y] = z \quad \rightarrow \quad [L_y, L_z] = i\hbar L_x$$

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

Each of the components of \vec{L} commutes with the L^2 ; 7-3

$$\begin{aligned} [L_z, L_x^2 + L_y^2 + L_z^2] &= [L_z, L_x^2] + [L_z, L_y^2] = \\ &= L_x [L_z, L_x] + [L_z, L_x] L_x + [L_z, L_y] L_y + \\ &+ L_y [L_z, L_y] = +i\hbar L_y L_x + i\hbar L_x L_y - i\hbar L_x L_y - \\ &- i\hbar L_y L_x = 0 \end{aligned}$$

L^2 and any component of \vec{L} can be measured simultaneously and can have the same set of eigenvectors. We choose

$$L^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle$$

parameter (quantum number)
that characterizes L^2

$$L_z |l, m\rangle = \hbar m |l, m\rangle$$

dimension of $\vec{r} \times \vec{p}$ quantum number for L_z

Values of l, m :

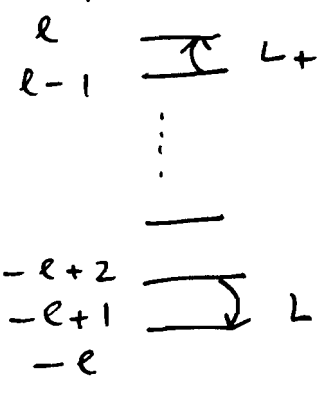
$$l = 0, 1, 2, \dots$$

for each l :

$$m = -l, -l+1, \dots, 0, 1, \dots, l$$

(see p. 123 for proof)

L_{\pm} operators raise and lower the z -projection of the angular momentum operator



They do not change the quantum number l !

l describes the magnitude of \vec{L} : the length of vector \vec{L} is $|\vec{L}| = \hbar \sqrt{l(l+1)}$

! Born was wrong about angular momentum quantization, it does not scale as the integer number of \hbar

$|\vec{L}| = n\hbar \leftarrow$ Born approximation
 $n = 1, 2, \dots$

$|\vec{L}| = \hbar \sqrt{l(l+1)}, \quad l = 0, 1, \dots$
 \curvearrowright actual quantization

Eigenvalue of L_{+} :

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

$\langle l, m | L_{+} L_{-} | l, m \rangle = \hbar^2 l(l+1) - \hbar^2 m^2 + \hbar^2 m$

$\langle L_{-} l, m | L_{-} l, m \rangle = c_{-}(l, m)^2$

$c_{-}(l, m) = \hbar \sqrt{l(l+1) - m^2 + m}$

$c_{+}(l, m) = \hbar \sqrt{l(l+1) - m^2 - m}$

$\left. \begin{array}{l} m_{\min} = -l \\ m_{\max} = +l \end{array} \right\}$

Example

7-6

7-7. A system is described by the Hamiltonian

$$H = \frac{L^2}{2I} + \alpha L_z$$

What is the energy spectrum?

$$\langle H \rangle = \sum_{l,m} E_{l,m} P_{l,m}, \quad \sum_{l,m} = \sum_{l=0}^{\infty} \sum_{m=-l}^l$$

↑
eigenvalues characterized
by a set of quantum
numbers

$$H |l,m\rangle = \underbrace{\left(\frac{\hbar^2 l(l+1)}{2I} + \alpha m \right)}_{E_{l,m}} \underbrace{|l,m\rangle}_{\text{eigenvector}}$$

The spectrum is characterized by two quantum numbers, l and m :

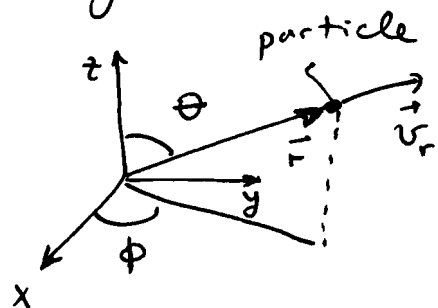
$$E_{l,m} = \frac{\hbar^2 l(l+1)}{2I} + \alpha m$$

So far $|l, m\rangle$ is a quantum state without specification of how one might determine its functional form, i.e. the wave function.

The logic of quantum mechanics then suggests that one has to choose a representation for the quantum state $|l, m\rangle$.

$\langle x, y, z | l, m \rangle$ would result in a function that depends on the Cartesian coordinates x, y, z .

It turns out that this representation involves too much information since the angular momentum is insensitive to a motion along the radius vector \vec{r} .



This type of motion with $\vec{v}_r = \dot{\vec{r}}$ generates zero \vec{L} .

It turns out to be sufficient to determine two spherical angles θ and ϕ and that sets up the angular representation of $|l, m\rangle$ known as spherical harmonic

$$Y_{lm}(\theta, \phi) = \langle \theta, \phi | l, m \rangle$$

Completeness relation for angular states:

$$\int d\Omega |\theta, \phi\rangle \langle \theta, \phi| = 1$$

↑
integration over angles'

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \dots$$

Orthogonality relation: $\langle \theta', \phi' | \theta, \phi \rangle = \frac{1}{\sin\theta} \delta(\theta - \theta') \delta(\phi - \phi')$

Polar coordinate representation:

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

$$\langle \theta, \phi | L_z | \ell, m \rangle = \hbar m \langle \theta, \phi | \ell, m \rangle = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \langle \theta, \phi | \ell, m \rangle$$

From this, $\langle \theta, \phi | \ell, m \rangle = F(\theta) e^{im\phi}$

$$F(\theta) = C_{\ell, m} P_{\ell}^m(\cos\theta)$$

↑
normalization
constant

↑ associated Legendre
polynomials (polynomials
in powers of $\cos\theta$)

Spherical Harmonics

7-9

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

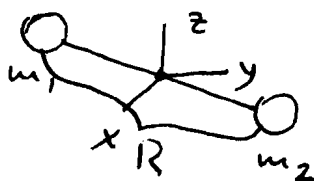
$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta \quad (m=0)$$

$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} e^{i\phi} \sin \theta \quad Y_{1,-1} = -\sqrt{\frac{3}{8\pi}} e^{-i\phi} \sin \theta$$

(see p. 127 for a more complete table)

The rigid rotator (not in the text)

Rigid rotator:



This problem appears in describing states of molecules (diatomics).

rotational

reduced mass

Hamiltonian:

$$\hat{H} = \frac{\hat{L}^2}{2I}$$

$$I = MR^2,$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

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

↑
eigenfunctions
of the Hamiltonian
operator

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

The rotational constant

$$B = \frac{\hbar^2}{2I}$$

is of the order of a few wavenumbers

$$B = 4 \text{ cm}^{-1} = \frac{4}{8065} \text{ eV} = 5 \times 10^{-4} \text{ eV}$$

$k_B T$ is about 200 cm^{-1} and that means that rotational states are typically populated at the room temperature

What is the typical shape of rotational spectra?

Boltzmann distribution of populations

$$\frac{n_l}{n_0} = \frac{g_l}{g_0} \frac{e^{-E_l/k_B T}}{e^{-E_0/k_B T}}$$

number of molecules in state with $l=0$ degeneracy of the rotational state

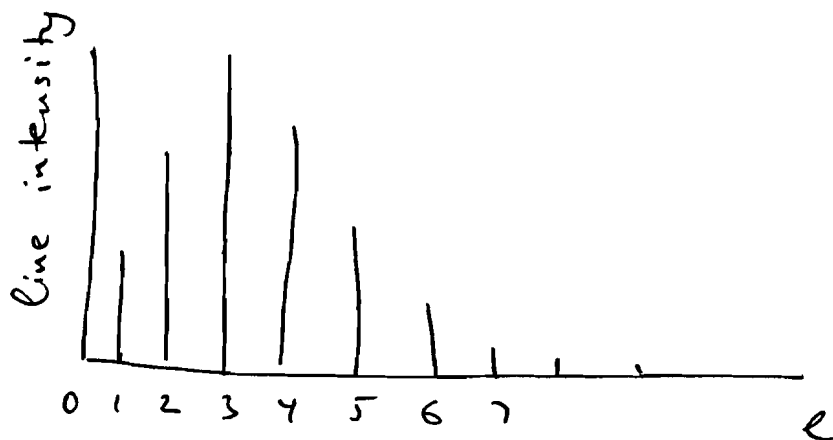
Degeneracy of the rotational state

$$\text{degeneracy} = 2l + 1$$

since $m = -l, \dots, l$ and all states with different m have the same energy E_l

$$\frac{n_e}{n_0} = (2\ell + 1) e^{-B\ell(\ell+1)/k_B T}$$

||
 this is proportional to spectral intensity



This type of rotational spectra is observed for diatomics cooled down in molecular beams.