

# Lecture 7

## Harmonic Oscillator & Rigid Rotor

Recap:

- separation of variables for solving Schrödinger equation

We have solved for the 1D particle in a box and found that many possible solutions exist, of which the ones as per the Born interpretation are admissible. Born interpretation is important since it provides physical meaning in terms of the fact that only the square of wavefunction makes sense as it represents the probability of finding the particle. Even within the Born interpretation more than one wavefunctions can be admissible. We have already seen superposition of wavefunctions in the 1D potential when we mentioned that there left moving wavefunction simultaneously was present with the right moving wavefunction resulting in standing wave solutions.

So, in general  $\Psi = a_1\phi_1 + a_2\phi_2 + \dots$  where  $a_1, a_2, \dots$  are the coefficients of the superposing wavefunctions  $\phi_1, \phi_2, \dots$  and would represent their respective contribution or weightage to the total wavefunction.

We know for normalized total wavefunction  $\Psi$ , we have  $|\Psi|^2 = 1$ .

Similarly, two wavefunctions are orthogonal if the integral of their product vanishes, i.e.,  $\int \Psi_i^*(x)\Psi_j(x)dx = 0$ .

**In general, wavefunctions corresponding to different energies are orthogonal.**

Thus, for an orthonormal set, we have:  $1 = |\Psi|^2 = |a_1|^2 + |a_2|^2 + \dots, \therefore \text{all } a_i^*a_j = 0$

Square of the coefficients, therefore, represent the contribution of the individual wavefunctions to the total wavefunction.

- SHO is one of the few cases where the Schrödinger equation  $\hat{H}\Psi = E\Psi$  can be solved exactly.

### Harmonic Oscillator Problem

The Hamiltonian operator for this system is given by

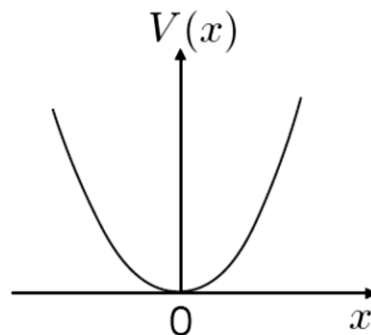
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

and the Schrödinger equation is given by

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

The energy is quantized:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, \dots, \quad \omega = \sqrt{\frac{k}{m}}$$



The exact wavefunction solutions are of the form:

$$\psi_n(x) = N_n H_n(\alpha x) e^{-\alpha^2 x^2 / 2}$$

The same problem can be looked at as a problem with two particles of masses  $m_1$  and  $m_2$  attached together with a massless vibrating spring. Let these particles be confined to move along the x-axis only.

Their positions are taken as  $x_1$  and  $x_2$  and the relative displacement is

$$x = x_1 - x_2 .$$

The Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} + V(|x_1 - x_2|)$$

can be transformed to

$$\hat{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V(|x|)$$

where the center of mass coordinate  $X$  is given by

$$X = \frac{m_1 x_1 + m_2 x_2}{M}$$

with

$$M = m_1 + m_2$$

and

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

See below for details. In the above, we have converted the motion of two particles into a problem of motion of center of mass and relative motion.

The above can be arrived as follows:

$$\frac{\partial}{\partial x_1} = \left( \frac{\partial X}{\partial x_1} \right) \frac{\partial}{\partial X} + \left( \frac{\partial x}{\partial x_1} \right) \frac{\partial}{\partial x} = \frac{m_1}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial x_2} = \left( \frac{\partial X}{\partial x_2} \right) \frac{\partial}{\partial X} + \left( \frac{\partial x}{\partial x_2} \right) \frac{\partial}{\partial x} = \frac{m_2}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

Then,

$$\begin{aligned} \frac{1}{m_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial x_2^2} &= \frac{1}{m_1} \left( \frac{m_1}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x} \right)^2 + \frac{1}{m_2} \left( \frac{m_2}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial x} \right)^2 \\ &= \frac{1}{M} \frac{\partial^2}{\partial X^2} + \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial x^2} \\ &= \frac{1}{M} \frac{\partial^2}{\partial X^2} + \frac{1}{\mu} \frac{\partial^2}{\partial x^2} \end{aligned}$$

## Vibrations of Diatomic Molecules

Let us consider the vibrational motion of a diatomic molecule. If we consider the potential of motion as harmonic and that the molecule is confined along the the  $x$ -axis, then using the relations derived in Appendix-1, we can write

$$\hat{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$$

where  $M$  is the total mass,  $X$  is the center of mass, and the reduced mass

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

Here  $x$  is the relative motion, which is

$$x = R - R_e$$

where  $R$  is some bond distance and  $R_e$  is the equilibrium bond distance. In the above Hamiltonian, the first term corresponds to the center of mass motion and the second term corresponds to the relative motion between the atoms.

Since we are only interested in the vibrational motion, which is the relative motion of two atoms, we can ignore the first term. Then,

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(|x|)$$

(Note the usage of  $d/dx$  instead of  $\partial/\partial x$ ).

The above Hamiltonian is identical to the Hamiltonian of the 1-dimensional harmonic oscillator that we have solved, instead  $m$  is substituted with  $\mu$ . Then the vibrational energy levels of the diatomic molecules are

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega, \quad \omega = \sqrt{\frac{k}{\mu}}, \quad n = 0, 1, \dots$$

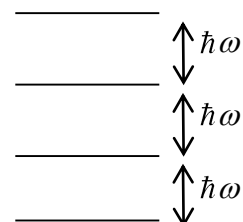
The zero-point vibrational energy of a diatomic molecule is thus  $E_0 = \frac{1}{2}\hbar\omega$ . We can show that vibrational transitions occur when there are energy transitions between two such energy states. However, as mentioned in the last class for SHO:

Spacing of energy levels is Constant

$$\Delta E = E_{n+1} - E_n = \hbar\omega = h\nu \quad (\omega = 2\pi\nu)$$

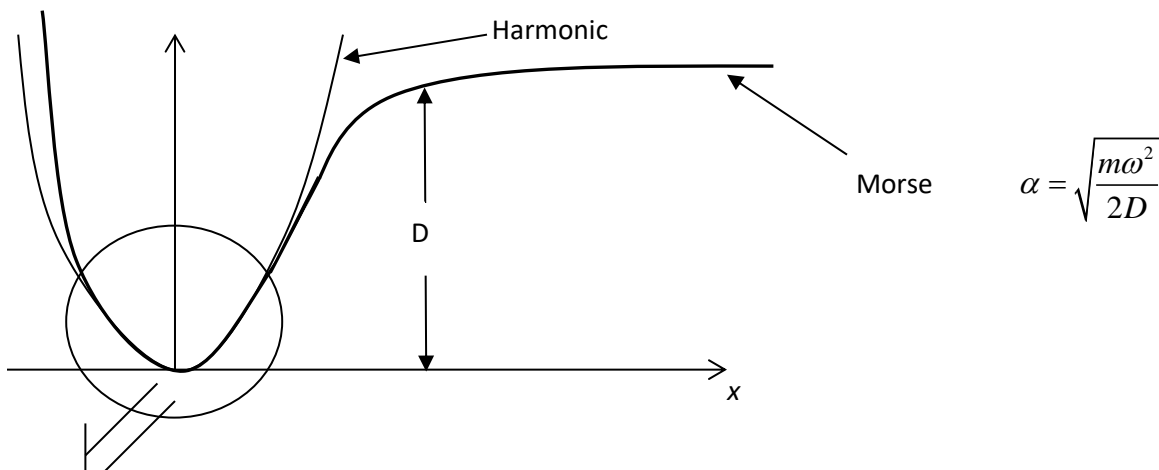
which is not like the real case of vibrating molecules.

With enough energy provided, molecules are bound to break, which



cannot happen with such a simple harmonic oscillator model of molecules. SHO could be valid approximately near equilibrium or at the bottom of the potential.

The Morse Potential, which is of the form:  $V(x) = D(1 - e^{-\alpha x})^2$  is a more realistic form of the vibration for the quantum treatment of the SHO—simple harmonic oscillator.



Bottom of the potential is in good agreement with Harmonic potential, so SHO approximation is valid near equilibrium.

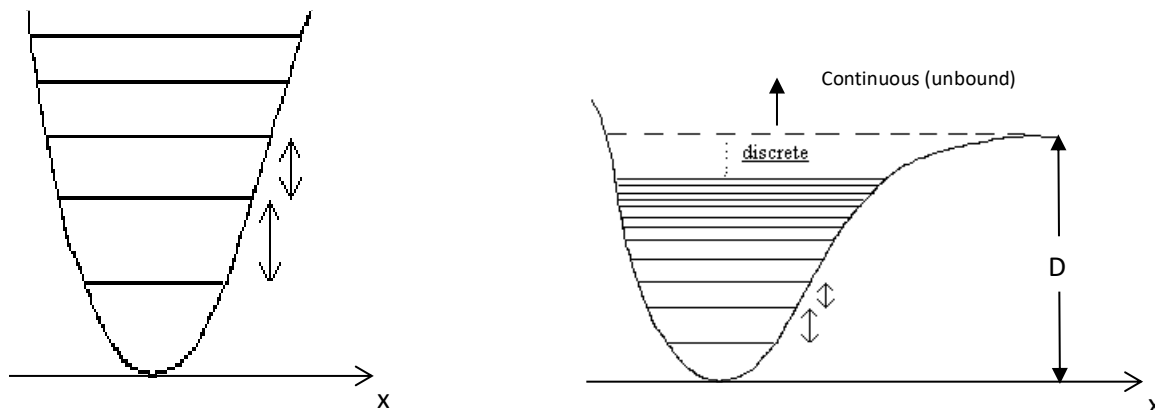
However, beyond some  $x_{\max}$  the “spring” breaks.

One can still solve the Schrodinger Eqn. using  $\hat{H} = \frac{1}{2m} \hat{p}_x \hat{p}_x + \frac{1}{2} D(1 - e^{-\alpha \hat{x}})^2$ , however,  $\Psi$  is complicated.

The energy levels (below  $D$ ) are still discrete and are of the form:

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega - \tilde{x} \left( n + \frac{1}{2} \right)^2, \text{ where } \tilde{x} : \text{Anharmonicity factor (or deviations from harmonicity)}$$

It is important to note that in this case there is a finite number of Quantum Numbers:  $n = 0, 1, 2, \dots, n_{\max}$ . Such a potential (Morse Potential) models many molecular vibrations successfully as the energy spacing also decrease with increasing energy.



Above the value of D (dissociation energy), the energy levels are continuous.

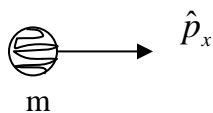
The Morse potential equation  $V(x) = D[1 - e^{-\alpha x}]^2$  can be written about the equilibrium position,  $x = 0$ , as:  $V(x) = [D\alpha^2 x^2 + \text{higher order terms in } x]$ . Comparing this to harmonic oscillator problem of

$$V(x) = \frac{1}{2}kx^2, \text{ we get: } k = 2D\alpha^2 \quad \text{or} \quad \omega = \sqrt{\frac{2D\alpha^2}{m}}, \text{ i.e., } \alpha = \sqrt{\frac{m\omega^2}{2D}}$$

Spectroscopists often use wavenumbers ( $\text{cm}^{-1}$ ) as the preferred choice for the unit of energy and in that case the Morse Potential will have the form:  $V(x) = D_1hc[1 - e^{-\alpha x}]^2$  when  $D_1$  is in  $\text{cm}^{-1}$ . A proper choice of unit is very critical and the most useful unit is the one which requires minimum number independent parameters. Thus, for waves, e.g., its Energy is a better unit than its wavelength since wavelength is medium dependent value unlike Energy. Molecules have translational & internal motions. Among the internal motions this model study has been on vibrations.

Next, we study the rotational motion. First let us look at the close correspondence between linear and angular motion in 1-dim.

Linear



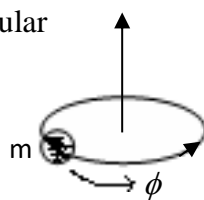
$$\hat{p}_x = -i\hbar \frac{d}{dx}$$

$$\text{Kinetic energy} = \frac{1}{2m} p_x^2$$

$(p_x, x)$  are conjugate

uncertainty  $\Delta x \Delta p_x$

Angular



angular motion

generated by  $L_z$  (ang. mom)

$$KE = \frac{L_z^2}{2I} = \frac{1}{2} I \omega^2$$

$(L_z, \phi)$  are conjugate

uncertainty  $\Delta \phi \Delta L_z$

So, in analogy, we can write:  $\hat{L}_z \rightarrow -i\hbar \frac{d}{d\phi}$ . The dimensionality of this angular momentum

operator  $L.MLT^{-1} = ML^2T^{-1} = \text{dimension of } \hbar$ . Also,  $I$  is the moment of inertia, about axis of rotation. If the particle is rotating at a fixed distance ( $R$ ) from center then  $I = \text{constant} = mR^2$ .

$\therefore$  Hamiltonian operator,  $\hat{H} = \frac{1}{2I} \hat{L}_z \hat{L}_z = \frac{-\hbar^2}{2I} \frac{d^2}{d\phi^2}$  and the quantum state is:  $\psi(\phi)$ , where  $\phi$  is the angular variable.

The equivalent approach to look at this problem is to consider this as a particle in a ring problem which can be formulated as follows:

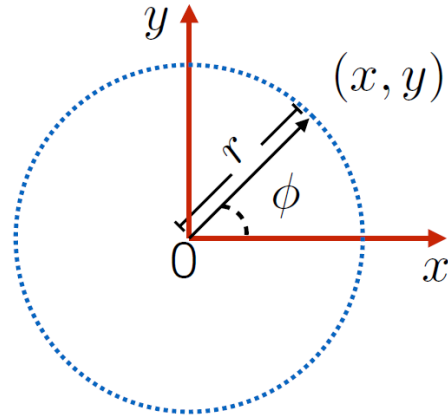
Let us consider a particle confined to move in a ring of radius  $r$ , lying in the  $x - y$  plane. Let us also consider that no potential is acting on the system. The Hamiltonian operator of the system is

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

The boundary condition for this problem is

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

Thus it is convenient to work in polar coordinate (where  $\phi$  is part of the coordinate) system than in Cartesian coordinates system. In polar coordinate system,



$$x = r \cos \phi, \quad y = r \sin \phi$$

where  $r = \sqrt{x^2 + y^2}$ . Also,

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right)$$

As  $r$  is fixed for our problem, the first two terms in the R.H.S of the above expression can be dropped. Thus,

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2mr^2} \frac{d^2}{d\phi^2} \\ &= -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \end{aligned}$$

where the moment of inertia  $I = mr^2$ . Schrödinger equation for the problem is

$$\begin{aligned} -\frac{\hbar^2}{2I} \frac{d^2 \psi}{d\phi^2} &= E\psi(\phi) \\ \frac{d^2 \psi}{d\phi^2} &= -\frac{2IE}{\hbar^2} \psi(\phi) \end{aligned}$$

As we have seen before, the general solution for this problem is of the form:

$$\psi(\phi) = Ae^{im\phi} + Be^{-im\phi}$$

Boundary condition is

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

Substituting the general solution to the differential equation, we get:

$$Ae^{im\phi} + Be^{-im\phi} = Ae^{2\pi im}e^{im\phi} + Be^{-2\pi im}e^{-im\phi}$$

The two terms in the L.H.S. and the R.H.S can only be same if  $m = 0, \pm 1, \pm 2, \dots$ . Since the first two terms only differ in the sign of  $m$ , and thus, we consider only the first term.

$$\psi_m(\phi) = Ae^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots$$

Now, the constant  $A$  can be obtained as,

$$\begin{aligned} \int_0^{2\pi} d\phi \psi_m(\phi)^* \psi_m(\phi) &= 1 \\ A^2 \int_0^{2\pi} d\phi e^{-im\phi} e^{im\phi} &= 1 \\ \Rightarrow A &= \frac{1}{\sqrt{2\pi}} \end{aligned}$$

Thus, the wave function is

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots$$

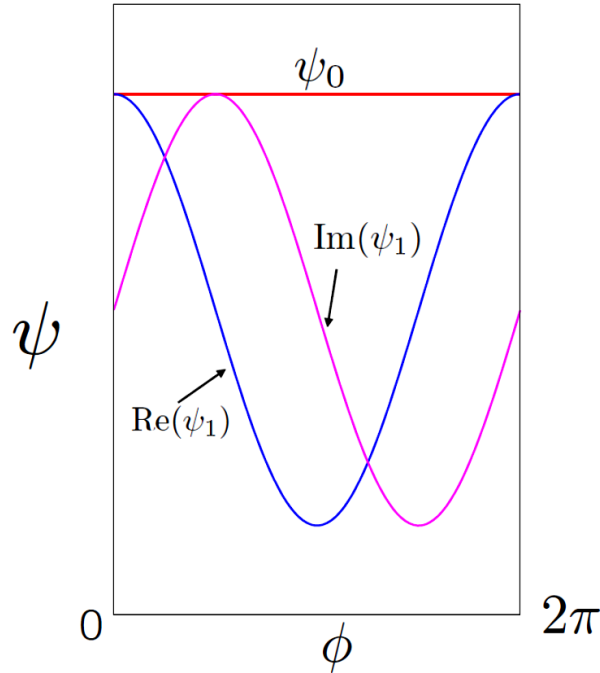
Energy of the system is given by

$$E_m = \frac{m^2 \hbar^2}{2I}, \quad m = 0, \pm 1, \pm 2, \dots$$

The degeneracy of all the excited state levels is 2. Note that the energy gap between the two neighboring levels

$$E \propto \frac{1}{I}$$

Here, the wave function is complex, one could plot the real and the imaginary parts separately.



Note that wave function strictly is localized along the ring in the  $x - y$  plane (as the particle is moving strictly along the ring).

Angular momentum operator (as discussed before) is:

$$\hat{L}_z = -i\hbar \frac{d}{d\phi}$$

Thus the wave function is an eigenfunction of  $\hat{L}_z$ , and the eigenvalues are  $+m\hbar$  or  $-m\hbar$ . Thus  $m > 0$  and  $m < 0$  represents angular rotation in different directions (clock wise or anti clockwise about the  $z$ -axis).

Probability density

$$\psi^*(\phi)\psi(\phi) = \frac{1}{2\pi}$$

is independent of  $\phi$  and thus probability of finding the particle somewhere on the ring is independent of  $\phi$ . Due to this reason, finding the particle is indefinite. This can be expected as angular momentum is certain for the particle. The zero point energy of the



system is zero, but the wave function is still acceptable since the angular position of the particle is uncertain.