

Lecture 6
Third stage



The Harmonic Oscillator

by

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Quantum Harmonic Oscillator

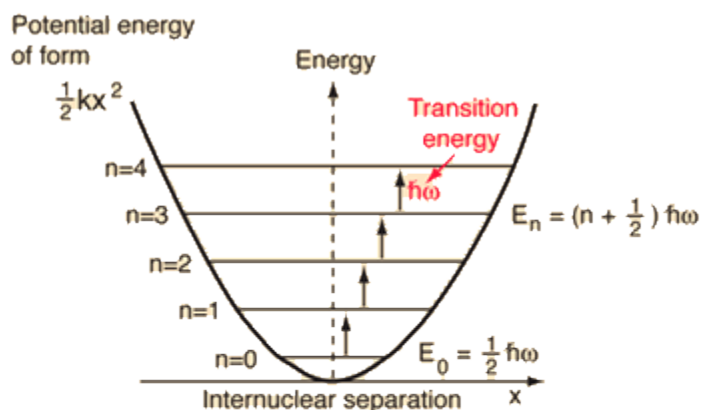
A diatomic molecule vibrates somewhat like two masses on a spring with a potential energy that depends upon the square of the displacement from equilibrium. But the energy levels are quantized at equally spaced values.

The energy levels of the quantum harmonic oscillator are

$$E_n = (n + \frac{1}{2}) \hbar\omega \quad n = 0, 1, 2, 3 \dots$$

$$\omega = 2\pi \cdot \text{frequency}$$

$$\hbar = \text{Planck's constant} / 2\pi$$



and for a diatomic molecule the natural frequency is of the form

$$\omega = \sqrt{\frac{k}{m_r}} \quad \begin{array}{l} k = \text{bond force constant} \\ m_r = \text{reduced mass} \end{array}$$

where the reduced mass is given by

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

This form of the frequency is the same as that for the classical simple harmonic oscillator. The most surprising difference for the quantum case is the so-called "zero-point vibration" of the $n=0$ ground state. This implies that molecules are not completely at rest, even at absolute zero temperature.

The quantum harmonic oscillator has implications far beyond the simple diatomic molecule. It is the foundation for the understanding of complex modes of vibration in larger molecules, the motion of atoms in a solid lattice, the theory of heat capacity, etc. In real systems, energy spacings are equal only for the lowest levels where the potential is a good approximation of the "mass on a spring" type harmonic potential. The anharmonic terms which appear in the potential for a diatomic molecule are useful for mapping the detailed potential of such systems.

Quantum Harmonic Oscillator: Schrodinger Equation

The Schrodinger equation for a harmonic oscillator may be obtained by using the classical spring potential

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2 \quad \omega = \sqrt{\frac{k}{m}} = \text{angular frequency}$$

$$\omega = 2\pi \cdot \text{frequency}$$

The Schrodinger equation with this form of potential is

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

Since the derivative of the wave function must give back the square of x plus a constant times the original function, the following form is suggested:

$$\Psi(x) = Ce^{-\alpha x^2/2}$$

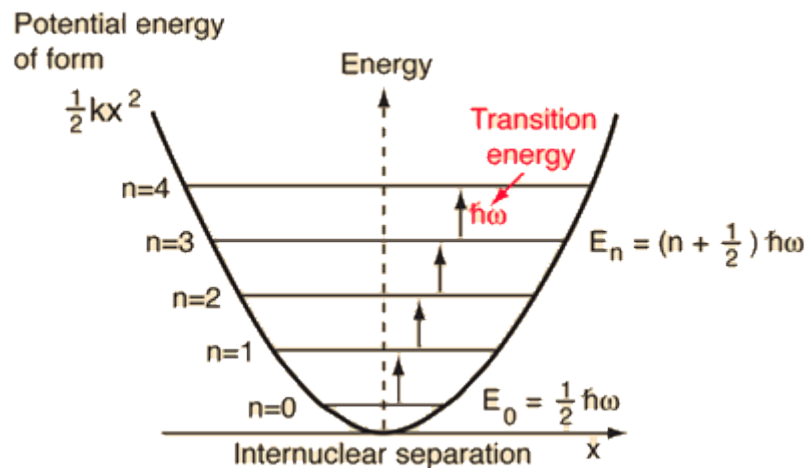
Note that this form (a Gaussian function) satisfies the requirement of going to zero at infinity, making it possible to normalize the wave function.

Substituting this function into the Schrodinger equation and fitting the boundary conditions leads to the ground state energy for the quantum harmonic oscillator:

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

While this process shows that this energy satisfies the Schrodinger equation, it does not demonstrate that it is the lowest energy. One interesting way to show that is to demonstrate that that it is the lowest energy allowed by the uncertainty principle.

The general solution to the Schrodinger equation leads to a sequence of evenly spaced energy levels characterized by a quantum number n .



The wavefunctions for the quantum harmonic oscillator contain the Gaussian form which allows them to satisfy the necessary boundary conditions at infinity. In the wavefunction associated with a given value of the quantum number n , the Gaussian is multiplied by a polynomial of order n called a Hermite polynomial. The expressions are simplified by making the substitution

$$y = \sqrt{\alpha} x \quad \text{where} \quad \alpha = \frac{m\omega}{\hbar}$$

The general formula for the normalized wave functions is

$$\Psi_n(y) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(y) e^{-y^2/2}$$

$H_n(y)$ = Hermite polynomial

The quantum harmonic oscillator is one of the foundation problems of quantum mechanics. It can be applied rather directly to the explanation of the vibration spectra of diatomic molecules, but has implications far beyond such simple systems. It is the foundation for the understanding of complex modes of vibration in larger molecules, the motion of atoms in a solid lattice, the theory of heat capacity, etc. In real systems, energy spacings are equal only for the lowest levels where the potential is a good approximation of the "mass on a spring" type harmonic potential. The anharmonic terms which appear in the potential for a diatomic molecule are useful for mapping the detailed potential of such systems.

The solution of h.o. in the position representation :

The Hamiltonian for the harmonic oscillator in one dimension is

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$$

where ω is the angular frequency and m is the mass of the oscillator. The time-independent Schrödinger equation takes the form

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

Typically, dimensionless parameters are introduced for the position

$$u = \sqrt{\frac{m\omega}{\hbar}}x, \quad \varepsilon = \frac{2E}{\hbar\omega}$$

coordinate and the energy

The Schrödinger equation can then be rewritten as

$$\frac{d^2\psi}{du^2} + (\varepsilon - u^2)\psi = 0$$

where $\psi = \psi(u)$. Solutions to this equation can be obtained using the series method; we simply summarize them here. They are a product of an

$$\psi_n(u) = H_n(u) e^{-u^2/2}$$

exponential and a Hermite polynomial

In terms of the position coordinate, the solution takes the form

$$\psi_n(x) = A_n H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right) e^{-m\omega x^2/2\hbar}$$

Here A_n is a normalization constant.

* Normalization of the Hermite Polynomials

The normalization of the wave functions comes from that of the Hermite polynomials. The orthonormality of the Hermite polynomials is written as:

$$\int_{-\infty}^{\infty} H_m(u) H_n(u) e^{-u^2} du = \sqrt{\pi} 2^n n! \delta_{mn}$$

Using this relationship, we can normalize the wave functions by integrating with the normalization constant

$$\begin{aligned} \int_{-\infty}^{\infty} A_n^2 \psi_n^2 du &= A_n^2 \int_{-\infty}^{\infty} H_n^2(u) e^{-u^2} du \\ &= A_n^2 \left(\sqrt{\frac{\hbar}{m\omega}} \right) \int_{-\infty}^{\infty} H_n^2 \left(\sqrt{\frac{m\omega}{\hbar}} x \right) e^{-m\omega x^2/\hbar} dx \\ &= A_n^2 \left(\sqrt{\frac{\hbar}{m\omega}} \right) \sqrt{\pi} 2^n n! \end{aligned}$$

To have a normalized wave function, this must be equal to unity and so we have

$$A_n^2 = \frac{1}{\sqrt{\pi} 2^n n!} \sqrt{\frac{m\omega}{\hbar}}, \quad \Rightarrow A_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{\frac{1}{4}}$$

We can then write the normalized wave function as

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{\frac{1}{4}} H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right) e^{-m\omega x^2/2\hbar}$$

The energy is found from the series solution technique applied to the Schrödinger equation. The termination condition for this solution dictates that the energy of state n is given by

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

Helpful recursion relationships exist that can be used to derive higher-order Hermit polynomials. These include

$$\begin{aligned} H_{n+1}(u) &= 2u H_n(u) - 2n H_{n-1}(u) \\ \frac{dH_n}{du} &= 2n H_{n-1}(u) \end{aligned}$$

The first few Hermit polynomials are given by

$$H_0(u) = 1$$

$$H_1(u) = 2u$$

$$H_2(u) = 4u^2 - 2$$

$$H_3(u) = 8u^3 - 12u$$

The recursion relations can be useful for determining expectation values.

1. For the harmonic oscillator system, the solution of the Schrödinger equation leads to the quantized energy $E_v = (V + \frac{1}{2}h\nu)$.

A. Define the zero-point energy of the system.

The zero-point energy (ZPE) for a quantum mechanical system is defined as the lowest possible energy allowed. In the case of the harmonic oscillator, the energy depends on the quantum number v , and $v = 0, 1, 2, 3, \dots$

Thus,
$$ZPE = E_0 = (0 + \frac{1}{2}h\nu) = \frac{1}{2}h\nu.$$

B. Determine the energy gap between state $v + 1$ and state v .

The energy gap between the state $v + 1$ and v can be calculated as

$$E_{v+1} - E_v = (V + 1 + \frac{1}{2})h\nu - (V + \frac{1}{2})h\nu = h\nu.$$

It is worth noting that the energy gap is related to the frequency of molecular vibration (see Unit 7, Section 3 later).

2. For the harmonic oscillator, the solution of the Schrödinger equation leads to the ground state wave function $\Psi_0(x) = (\frac{\alpha}{\pi})^{1/4} e^{-\alpha x^2/2}$.