Chapter 5 (Lecture 8)
Quantum harmonic oscillator

The harmonic oscillator is extremely useful in molecular physics as a model for the vibrational motion in a diatomic molecule. Polyatomic molecules can be modeled by coupled harmonic oscillators. The atoms are viewed as point masses which are connected by bonds which act (approximately) like springs obeying Hooke’s law. In these lecture notes we will review the classical harmonic oscillator problem and then discuss the quantum harmonic oscillator.

The **quantum harmonic oscillator** is the quantum mechanical analog of the classical harmonic oscillator. Because an arbitrary potential can be approximated as a harmonic potential at the vicinity of a stable equilibrium point, it is one of the most important model systems in quantum mechanics.

For the sake of simplicity let us consider one dimensional simple harmonic oscillator potential:

\[ V = \frac{1}{2} m \omega^2 x^2 \]

In classical physics we obtain motion of the oscillator by solving Newton’s equation

\[ \ddot{x} + \omega^2 x = 0; \text{where } \omega = \frac{k}{m_0} \]

One can obtain

\[ x = x_0 \cos(\omega t + \delta) \]

And energy is given by

\[ E = \frac{1}{2} m \omega^2 x_0^2 \]

Energy of the classical oscillator is depending on the maximum amplitude of the oscillation.

Now let us turn our attention to the quantum harmonic oscillator. For one dimensional oscillation we can write

\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2; \text{and } H\psi = E\psi \]

It is convenient to introduce a dimensionless variable \( x \rightarrow \frac{m_\omega}{\hbar} x \) then Schrödinger equation takes the form

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

There are various methods to solve this type equations. In the case of diatomic molecule (or two mass connected together with a spring) instead of \( m_0 \) reduced mass to be used:

\[ \mu = \frac{m_1}{m_1 + m_2}; \text{or } \mu = \frac{m_1 m_2}{m_1 + m_2} \]

In this course we will solve the Schrödinger equation including Harmonic oscillator potential by using

1. **Series Method**

2. **Operator method**.

The analysis of wave function: when \( x \rightarrow \pm \infty; \psi \rightarrow 0 \), since there is no particle at \( \pm \infty \).

Leads to guess the wave function to be in the form

\[ \psi = e^{-\frac{x^2}{\sigma^2}} f(x) \]

Then we substitute
Into the Schrödinger equation we obtain

\[
\frac{d^2\psi}{dx^2} = -xe^{-x^2} f' + e^{-x^2} f''
\]

\[
\frac{d^2\psi}{dx^2} = -e^{-x^2} f + x^2 e^{-x^2} f' - xe^{-x^2} f' - xe^{-x^2} f' + e^{-x^2} f''
\]

This equation is known as the Hermite equation and can be solved by using series method. Let

\[
f = \sum_{n=0}^{\infty} a_n x^n; \quad f' = \sum_{n=0}^{\infty} n a_n x^{n-1}; \quad f'' = \sum_{n=0}^{\infty} n(n-1) a_n x^{n-2}
\]

Then

\[
\sum_{n=0}^{\infty} n(n-1)a_n x^{n-2} - \sum_{n=0}^{\infty} 2na_n x^n + \sum_{n=0}^{\infty} (2\epsilon - 1)a_n x^{n-1}
\]

Shifting limits of the first term \(n \to n + 2\)

\[
\sum_{n=0}^{\infty} [(n + 2)(n + 1)a_{n+2} - 2na_n + (2\epsilon - 1)a_n]x^n = 0
\]

Therefore we obtain the relation between coefficients

\[
a_{n+2} = \frac{2n + 1 - 2\epsilon}{(n + 1)(n + 2)} a_n.
\]

For a few values of \(n\) the coefficients are given by:

\[
n = 0; \quad a_2 = \frac{(2)(0) + 1 - 2\epsilon}{(1)(2)} a_0
\]

\[
n = 2; \quad a_4 = \frac{(2)(0) + 1 - 2\epsilon}{(1)(2)} \frac{(2)(2) + 1 - 2\epsilon}{(3)(4)} a_0
\]

\[
n = 4; \quad a_6 = \frac{(2)(0) + 1 - 2\epsilon}{(1)(2)} \frac{(2)(2) + 1 - 2\epsilon}{(3)(4)} \frac{(2)(4) + 1 - 2\epsilon}{(5)(6)} a_0
\]

It is obvious that when \(\epsilon = n + \frac{1}{2}\) then \(m \geq n, a_m = 0\). We obtain discrete eigenvalues. One can easily obtain the coefficients for odd values of \(n\) using the same analogy.

The function \(f\) are given by

\[
n = 0; \quad \epsilon = \frac{1}{2}; \quad f = a_0
\]

\[
n = 2; \quad \epsilon = \frac{5}{2}; \quad f = a_0(1 - 2x^2)
\]

\[
n = 4; \quad \epsilon = \frac{9}{2}; \quad f = a_0(1 - 4x^2 + \frac{4}{3}x^4)
\]

General solution of the equation are given by Hermite polynomials, then our solution is given by

\[
\psi = Ne^{-x^2} H_n(x)
\]

Normalization constant \(N\) can be calculated using
For first few values, Hermite polynomials are given by:

<table>
<thead>
<tr>
<th>n</th>
<th>Polynomial</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>-2 + 4x^2</td>
</tr>
<tr>
<td>4</td>
<td>12 - 48x^2 + 16x^4</td>
</tr>
<tr>
<td>6</td>
<td>-120 + 720x^2 - 480x^4 + 64x^6</td>
</tr>
<tr>
<td>8</td>
<td>1680 - 13440x^2 + 13440x^4 - 3584x^6 + 256x^8</td>
</tr>
<tr>
<td>1</td>
<td>2x</td>
</tr>
<tr>
<td>3</td>
<td>-12x + 8x^3</td>
</tr>
<tr>
<td>5</td>
<td>120x - 160x^3 + 32x^5</td>
</tr>
<tr>
<td>7</td>
<td>-1680x + 3360x^3 - 1344x^5 + 128x^7</td>
</tr>
<tr>
<td>9</td>
<td>30240x - 80640x^3 + 48384x^5 - 9216x^7 + 512x^9</td>
</tr>
</tbody>
</table>

Thus we have obtained solution of the Harmonic oscillator problem. Figure shows plot of the wave function(left), square of wave function(right), potential and eigenvalues.

At this point it is worth to discuss two topic:

Uncertainty and zero point energy

In fact we can use the uncertainty relation $\Delta x \Delta p_x \approx \frac{\hbar}{2}$, in order to estimate the lowest energy of the harmonic oscillator. We can write

$$\Delta p_x = m_0 \Delta v_x = m_0 \omega \Delta x$$

we have

$$\Delta x \Delta p_x = m_0 \omega (\Delta x)^2 \approx \frac{\hbar}{2} \Rightarrow \Delta x \sim \sqrt{\frac{\hbar}{2 m_0 \omega}} \text{ and } \Delta p_x \sim \sqrt{\frac{m_0 \omega \hbar}{2}}$$

Total energy can be written as:

$$E = \frac{(\Delta p)^2}{2m_0} + \frac{1}{2} m_0 \omega^2 (\Delta x)^2$$

$$E = \frac{m_0 \omega \hbar}{2 m} + \frac{1}{2} m_0 \omega^2 \frac{\hbar}{2 m_0 \omega} = \frac{1}{2} \hbar \omega$$

We can obtain the same result by minimizing energy of an quantum oscillator. Total energy of an oscillator in terms of uncertainty of momentum and position can be written as
Using uncertainty principle $\Delta p = \frac{h}{2\Delta x}$, we obtain

$$E = \frac{(\Delta p)^2}{2m} + \frac{1}{2}m_\omega \omega^2 (\Delta x)^2$$

In order to obtain minimum energy we minimize energy by taking the derivative of it w.r.t $\Delta x$:

$$\frac{dE}{d\Delta x} = 0$$

Solving for $\Delta x$ gives that

$$\Delta x = \sqrt{\frac{h}{2m_\omega \omega}}$$

Substitute this value into the energy equation we obtain:

$$E = \frac{1}{2}h\omega$$

**Planck’s Black-body oscillators**

Einstein realized that, in terms of Rayleigh’s electromagnetic standing waves, Planck’s blackbody radiation curves have a simple interpretation: the average energy in an oscillator of frequency $\nu$ at temperature $T$ is

$$\bar{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

As we mentioned before Planck’s work made plausible that this same quantization held for the material oscillators in the walls. Planck made a radical assumption, a black body includes oscillators and the oscillators emit *mean* energy in the form of quanta $E = nh\nu$. It is shown that at absolute zero average energy tends to zero.

Then in 1913, using this formula as a basis, Albert Einstein and Otto Stern published a paper of great significance in which they suggested for the first time the existence of a residual energy that all oscillators have at absolute zero. They called this residual energy *Nullpunktenergie* (German), which later was translated literally as *zero-point energy*. They carried out an analysis of the specific heat of hydrogen gas at low temperature, and concluded that the data are best represented if the vibrational energy is

$$\bar{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{h\nu}{2}$$

According to this expression, an atomic system at absolute zero retains an energy of $\frac{1}{2}h\nu$.

This is a very significant physical result because it tells us that the energy of a system described by a harmonic oscillator potential cannot have zero energy. Physical systems such as atoms in a solid lattice or in polyatomic molecules in a gas cannot have zero energy even at absolute zero temperature. The energy of the ground vibrational state is often referred to as "zero point vibration". The zero point energy is sufficient to prevent liquid helium-4 from freezing at atmospheric pressure, no matter how low the temperature.

**Operator Formalism and Harmonic oscillator**

In the previous chapters we have focused on properties of wave function. We have obtained solution of the Schrodinger equation for infinite well potential. Before begin to solve Schrodinger equation, in this chapter we will summarize properties of wave function and introduce vector notations.

**Space of the Wavefunction: Hilbert Space**
Note that **wave function live in the Hilbert space.** In this space the functions will be square integrable such that:

$$\int_{-\infty}^{\infty} \psi^* \psi dx < \infty$$

In the Hilbert space the wave function has vector properties. We define the vectors:

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi dx \quad \langle \psi | = \int_{-\infty}^{\infty} \psi^* dx$$

$$\langle \phi | \psi \rangle = \int_{-\infty}^{\infty} \phi^* \psi dx$$

where \( \langle ... | \) is called bra and \(| ... \rangle \) is called ket vector. The notation is known ans Bra-ket or Dirac notation.

Expectation values of an operator can be expressed as

$$\langle O \rangle = \langle \phi | O | \psi \rangle = \int_{-\infty}^{\infty} \phi^* O \psi dx$$

As an example of application of the notation, let us consider the operators \(a\) and \(a^*\) acting on the state \(|n\rangle\) (here the state corresponding to wave function \(\psi_n \to |n\rangle\), \(n\) is a quantum number), such that

$$a|n\rangle = \sqrt{n}|n-1\rangle \text{ and } a^*|n\rangle = \sqrt{n+1}|n+1\rangle$$

Using the properties we can calculate expectation values of the operators, \(\langle a\rangle, \langle aa^*\rangle, \langle a^2a^*\rangle\) etc.

$$\langle a \rangle = \langle n | a | n \rangle = \langle n | \sqrt{n} | n - 1 \rangle = \sqrt{n} \langle n | n - 1 \rangle = 0$$

because of the states ortogonality of the states.

$$\langle aa^* \rangle = \langle n | aa^* | n \rangle = \langle n | a \sqrt{n+1} | n + 1 \rangle = \langle n \sqrt{n+1} | n + 1 \rangle = (n+1) \langle n | n \rangle = (n+1)$$

Again using properties of the given operators we can obtain commutation relation between them. As an example, let us calculate \([a, a^*]\):

$$[a, a^*] = aa^* - a^*a = a a^* |n\rangle - a^* a |n\rangle = (n + 1) |n\rangle - n |n\rangle = |n\rangle$$

$$[a, a^*] = 1$$

**Uncertainty Principle**

Without further discussion (see text book for its proof) uncertainty between two operator is given by

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

The simple interpretation is if two operator commute then the corresponding observables can be measured separately without any uncertainty.

The whole of quantum mechanics can be expressed in terms of a small set of postulates. This chapter introduces the postulates and illustrates how they are used.

*This lecture notes collected from the references given below*

An introduction to Quantum Mechanics COURSE NOTES by: Paolo BONIFACIO

Quantum Mechanics Demystified (Mcgraw-HILL) DAVID McMahon