

## Chapter 3 (Lecture 7-9)

### 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:

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

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

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

One can obtain

$$x = x_0 \cos(\omega t + \delta)$$

And energy is given by

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

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

### Classical probability density

The probability ( $dP$ ) of finding the particle in  $dx$  is then proportional to the time it spends there is  $dP = P(x)dx = 2dt/T$ , where  $T$  is the period of oscillation. (Twice in a complete oscillation).

Using definition of velocity and energy equation:

$$v = \frac{dx}{dt}; E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = \frac{1}{2}kA^2$$
$$P(x)dx = \frac{1}{\pi\sqrt{A^2 - x^2}}dx$$

where  $P(x)$  is called probability density and given as:

$$P(x) = \frac{1}{\pi\sqrt{A^2 - x^2}}$$

### Quantum Harmonic oscillator

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

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

It is convenient to introduce a dimensionless variable  $x \rightarrow \sqrt{\frac{m\omega}{\hbar}}x$  and  $\epsilon = \frac{E}{\hbar\omega}$ , then Schrödinger equation takes the form

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

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  $m$  reduced mass to be used:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}; \text{ or } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

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  $x \rightarrow \mp\infty$ ;  $\psi \rightarrow 0$ , since there is no particle at  $\mp\infty$ .

Leads to guess the wave function to be in the form

$$\psi = e^{-\frac{x^2}{2}} f(x)$$

Then we substitute

$$\begin{aligned} \frac{d\psi}{dx} &= -xe^{-\frac{x^2}{2}} f + e^{-\frac{x^2}{2}} f' \\ \frac{d^2\psi}{dx^2} &= -e^{-\frac{x^2}{2}} f + x^2 e^{-\frac{x^2}{2}} f - xe^{-\frac{x^2}{2}} f' - xe^{-\frac{x^2}{2}} f' + e^{-\frac{x^2}{2}} f'' \end{aligned}$$

Into the Schrodinger equation we obtain

$$\frac{d^2 f}{dx^2} - 2x \frac{df}{dx} + (2\epsilon - 1)f = 0$$

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

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

Then

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

Shifting limits of the first term  $n \rightarrow n + 2$

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

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:

$$\begin{aligned} n = 0; a_2 &= \frac{(2)(0) + 1 - 2\epsilon}{(1)(2)} a_0 \\ n = 2; a_4 &= \left( \frac{(2)(0) + 1 - 2\epsilon}{(1)(2)} \right) \left( \frac{(2)(2) + 1 - 2\epsilon}{(3)(4)} \right) a_0 \\ n = 4; a_6 &= \left( \frac{(2)(0) + 1 - 2\epsilon}{(1)(2)} \right) \left( \frac{(2)(2) + 1 - 2\epsilon}{(3)(4)} \right) \left( \frac{(2)(4) + 1 - 2\epsilon}{(5)(6)} \right) a_0 \end{aligned}$$

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

$$n = 0; \epsilon = \frac{1}{2}; f = a_0$$

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

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

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

$$\psi = Ne^{-\frac{x^2}{2}}H_n(x)$$

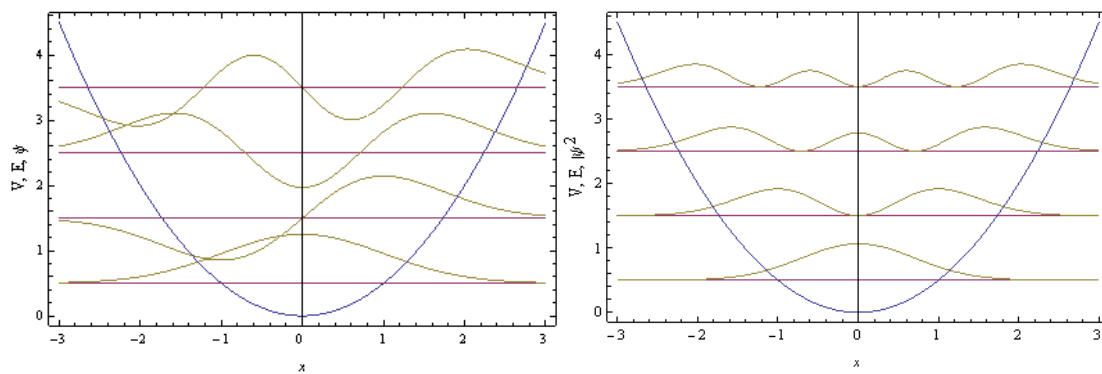
Normalization constant  $N$  can be calculated using

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1 \Rightarrow N = \frac{1}{\sqrt{\pi 2^n n!}}$$

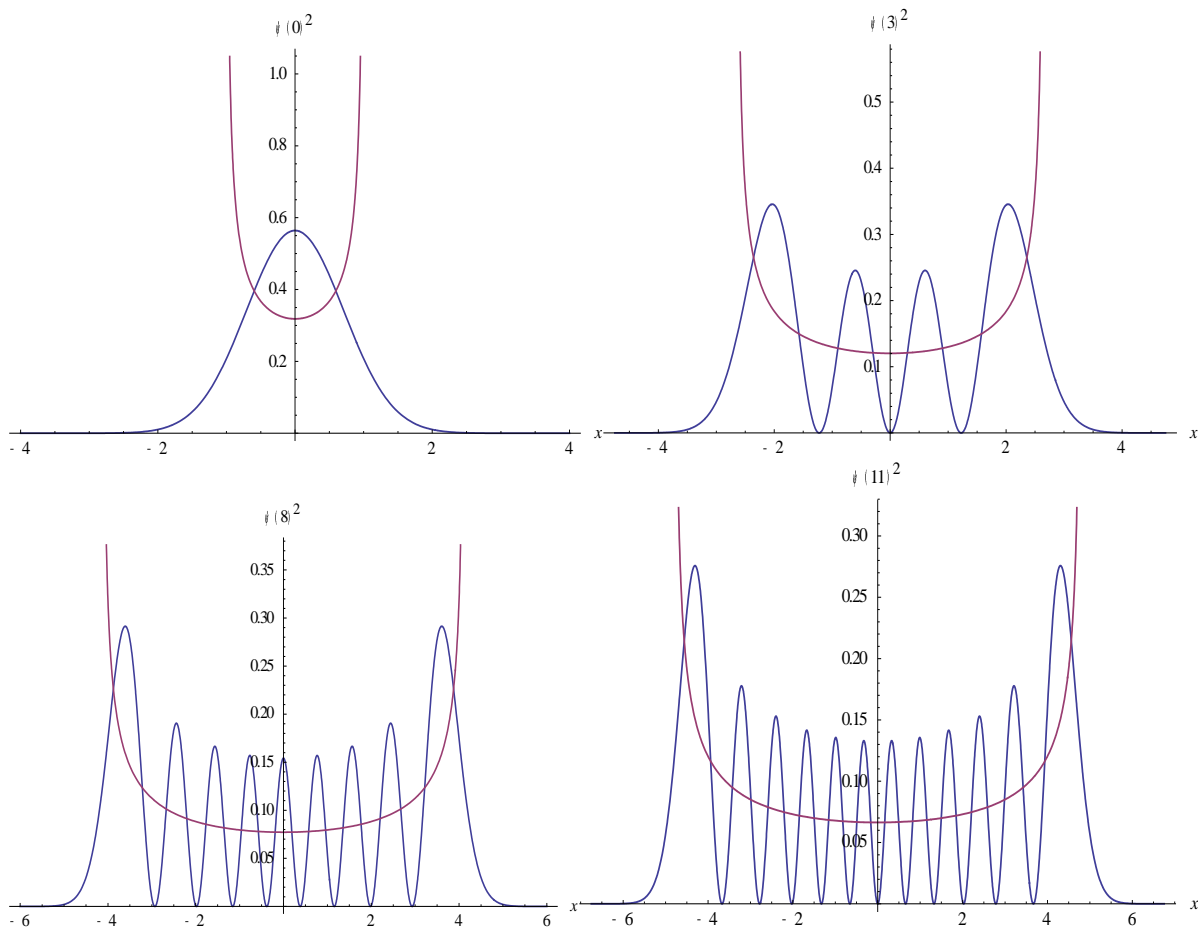
For first few  $n$  values, Hermite polynomials are given by:

0	1
2	$-2 + 4x^2$
4	$12 - 48x^2 + 16x^4$
6	$-120 + 720x^2 - 480x^4 + 64x^6$
8	$1680 - 13440x^2 + 13440x^4 - 3584x^6 + 256x^8$
1	$2x$
3	$-12x + 8x^3$
5	$120x - 160x^3 + 32x^5$
7	$-1680x + 3360x^3 - 1344x^5 + 128x^7$
9	$30240x - 80640x^3 + 48384x^5 - 9216x^7 + 512x^9$

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.



The following figure shows the probability density distribution for finding the quantum harmonic oscillator in its  $n=0, 3, 5$  and  $11$ th quantum state. The red curve shows the probability density distribution of a classical oscillator with the same energy.



**Exercise.** The  $H_2$  molecule can be approximated by a simple harmonic oscillator having spring constant  $k=1.1 \times 10^3 \text{ N/m}$ . Find (a) the energy levels and (b) the possible wavelengths of photons emitted with the  $H_2$  molecule decays from the third excited state eventually to the ground state.

**Exercise.** The HCl diatomic molecule consists of one chlorine atom and one hydrogen atom. Because the chlorine atom is 35 times more massive than the hydrogen atom, the vibrations of the HCl molecule can be quite well approximated by assuming that the Cl atom is motionless and the H atom performs harmonic oscillations due to an elastic molecular force modeled by Hooke's law. The infrared vibrational spectrum measured for hydrogen chloride has the lowest-frequency line centered at  $f=8.88 \times 10^{13} \text{ Hz}$ . What is the spacing between the vibrational energies of this molecule? What is the force constant  $k$  of the atomic bond in the HCl molecule?

### Solution

The energy spacing is

$$\Delta E = hf = (4.14 \times 10^{-15} \text{ eV} \cdot \text{s})(8.88 \times 10^{13} \text{ Hz}) = 0.368 \text{ eV}$$

The force constant is

$$k = m\omega^2 = m(2\pi f)^2 = (1.67 \times 10^{-27} \text{ kg})(2\pi \times 8.88 \times 10^{13} \text{ Hz})^2 = 520 \text{ N/m}.$$

### Significance

The force between atoms in an HCl molecule is surprisingly strong. The typical energy released in energy transitions between vibrational levels is in the infrared range. As we will see later, transitions in between vibrational energy levels of a diatomic molecule often accompany transitions between rotational energy levels.

**Exercise.** The vibrational frequency of the hydrogen iodide HI diatomic molecule is  $6.69 \times 10^{13} \text{ Hz}$ .

- What is the force constant of the molecular bond between the hydrogen and the iodine atoms? (295 N/m)
- What is the energy of the emitted photon when this molecule makes a transition between adjacent vibrational energy levels? (0.277 eV)

**The quantum oscillator differs from the classic oscillator in three ways:**

- First, the ground state of a quantum oscillator is  $E_0 = \frac{1}{2}\hbar\omega$ , not zero. In the classical view, the lowest energy is zero. The nonexistence of a zero-energy state is common for all quantum-mechanical systems because of omnipresent fluctuations that are a consequence of the Heisenberg uncertainty principle. If a quantum particle sat motionless at the bottom of the potential well, its momentum as well as its position would have to be simultaneously exact, which would violate the Heisenberg uncertainty principle. Therefore, the lowest-energy state must be characterized by uncertainties in momentum and in position, so the ground state of a quantum particle must lie above the bottom of the potential well.
- Second, a particle in a quantum harmonic oscillator potential can be found with nonzero probability outside the interval  $-A \leq x \leq +A$ . In a classic formulation of the problem, the particle would not have any energy to be in this region. The probability of finding a ground-state quantum particle in the classically forbidden region is about 16%.
- Third, the probability density distributions  $|\psi_n(x)|^2$  for a quantum oscillator in the ground low-energy state,  $|\psi_0(x)|^2$ , is largest at the middle of the well ( $x=0$ ). For the particle to be found with greatest probability at the center of the well, we expect that the particle spends the most time there as it oscillates. This is opposite to the behavior of a classical oscillator, in which the particle spends most of its time moving with relative small speeds near the turning points.

**Exercise.** Find the expectation value of the position for a particle in the ground state of a harmonic oscillator using symmetry. (ans:  $\langle x \rangle = 0$ .)

At this point it is worth to discuss two topic:

**Uncertainty and zero point energy**

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

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

we have

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

Total energy can be written as:

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

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

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

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

Using uncertainty principle  $\Delta p = \frac{\hbar}{2\Delta x}$ , we obtain

$$E = \frac{\hbar^2}{2m_0(4(\Delta x)^2)} + \frac{1}{2}m_0\omega^2(\Delta x)^2$$

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

$$\frac{dE}{dx} = 0$$

Solving for  $\Delta x$  gives that

$$\Delta x = \sqrt{\frac{\hbar}{2m_0\omega}}$$

Substitute this value into the energy equation we obtain:

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

### Planck's Black-body oscillators (Optional)

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.

### Three Dimensional harmonic oscillator

The 3D harmonic oscillator can be separated in Cartesian coordinates. For the case of a

$$V = \frac{1}{2}m\omega^2r^2 = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)$$

central potential, this problem can also be solved nicely in spherical coordinates using rotational symmetry. The cartesian solution is easier and better for counting states though.

The Hamiltonian of this system can be written as:

$$H = \frac{p^2}{2m_0} + \frac{1}{2}m\omega^2r^2$$

$$H = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 + \frac{p_y^2}{2m} + \frac{1}{2}m\omega^2 y^2 + \frac{p_z^2}{2m} + \frac{1}{2}m\omega^2 z^2$$

It is obvious that Hamiltonian is separable and its solution is the same as one dimensional oscillator.

The problem separates nicely, giving us three independent harmonic oscillators. Energy of the 3D oscillator are given by:

$$E = \left( n_x + n_y + n_z + \frac{3}{2} \right) \hbar\omega$$

And wavefunction is

$$\psi_{n_x, n_y, n_z} = e^{-\frac{1}{2}(x^2+y^2+z^2)} H_{n_x}(x) H_{n_y}(y) H_{n_z}(z)$$

**Example.** For a harmonic oscillator, what is the energy of the highest occupied level in the ground state for a systems of 10 noninteracting particles?

**Solution**

In this case we assume that the particles are spinless, then:

Energy	$n_x n_y n_z$	#particle
3/2	000	1
5/2	001, 010, 100	3
7/2	011, 101, 110, 002, 020, 200	6

Note that all higher energy levels are what is called “**degenerate**”; there is more than one eigenfunction that produces that energy.

For example, in the quantum mechanics of molecules, chemical bonds often select among nonunique theoretical solutions those that best fit the given conditions. The nonuniqueness arises from the fact that:

Linear combinations of eigenfunctions at the same energy level produce alternative eigenfunctions that still have that same energy level.

**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 Schrödinger 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:

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

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

where  $\langle \dots |$  is called bra and  $| \dots \rangle$  is called ket vector. The notation is known as 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  $\psi_n \rightarrow |n\rangle$ ,  $n$  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,  $\langle a \rangle$ ,  $\langle aa^+ \rangle$ ,  $\langle a^2 a^{+2} \rangle$  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 orthogonality of the states.

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

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

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

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

We can relate the consider the operators  $a$  and  $a^+$  with the harmonic oscillator Hamiltonian by expressing them

$$a = \sqrt{\frac{\hbar}{2m\omega}} \frac{d}{dx} + \sqrt{\frac{m\omega}{2\hbar}} x$$

$$a^+ = -\sqrt{\frac{\hbar}{2m\omega}} \frac{d}{dx} + \sqrt{\frac{m\omega}{2\hbar}} x$$

Then product of the operators  $a^+a$  gives us:

$$\begin{aligned} a^+a &= -\frac{\hbar}{2m\omega} \frac{d^2}{dx^2} + \frac{m\omega}{2\hbar} x^2 - \frac{1}{2} \frac{d}{dx} x + \frac{1}{2} x \frac{d}{dx} \\ &= -\frac{\hbar}{2m\omega} \frac{d^2}{dx^2} + \frac{m\omega}{2\hbar} x^2 - \frac{1}{2} \end{aligned}$$

Multiply and divide the equation by  $\hbar\omega$ , and remember harmonic oscillator Hamiltonian  $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega x^2$ , we obtain

$$a^+a = \frac{H}{\hbar\omega} - \frac{1}{2} \text{ or } H = \left( a^+a + \frac{1}{2} \right) \hbar\omega$$

The eigenvalue equation:

$$H|n\rangle = E|n\rangle$$



Leads to the energy

$$E = \left(n + \frac{1}{2}\right) \hbar\omega$$

**Example:**

Show that the the wavefunction as a function of  $x$  can be obtained by using operators.

Solution: Action of the operator on the state:

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

Ground state wave function  $\psi_0 \rightarrow |0\rangle$  ( $n = 0$ ) then we can express

$$a|0\rangle = 0 \text{ or } \left(\sqrt{\frac{\hbar}{2m\omega}} \frac{d}{dx} + \sqrt{\frac{m\omega}{2\hbar}} x\right) |0\rangle = 0$$

Solution of first order DE gives us

$$|0\rangle = C e^{-\frac{m\omega}{\hbar} x^2} = \psi_0$$

Exercise: Show that 1<sup>st</sup>, 2<sup>nd</sup>, ... excited state wavefunctions can be obtained by using action of the operator  $|1\rangle = a^+|0\rangle$ ,  $|2\rangle = a^+|1\rangle$ , ... so on.

Example: Find expectation values of  $x$  and  $x^2$  using operator method.

Solution: Functional representation of the operators are:

$$a = \sqrt{\frac{\hbar}{2m\omega}} \frac{d}{dx} + \sqrt{\frac{m\omega}{2\hbar}} x \text{ and } a^+ = -\sqrt{\frac{\hbar}{2m\omega}} \frac{d}{dx} + \sqrt{\frac{m\omega}{2\hbar}} x$$

When we add the operators we obtain

$$a + a^+ = 2\sqrt{\frac{m\omega}{2\hbar}} x \text{ or } x = \sqrt{\frac{\hbar}{2m\omega}} (a + a^+)$$

Then expectation values of  $x$  is

$$\langle x \rangle = \sqrt{\frac{\hbar}{2m\omega}} \langle n|(a + a^+)|n\rangle = \sqrt{\frac{\hbar}{2m\omega}} \langle n|(a)|n\rangle + \sqrt{\frac{\hbar}{2m\omega}} \langle n|(a^+)|n\rangle = 0$$

Similarly  $x^2 = \sqrt{\frac{\hbar}{2m\omega}} (a + a^+) \sqrt{\frac{\hbar}{2m\omega}} (a + a^+) = \frac{\hbar}{2m\omega} (a^2 + aa^+ + a^+a + a^{+2})$ , gives us:

$$\langle x^2 \rangle = \frac{\hbar}{2m\omega} (\langle n|a^2|n\rangle + \langle n|aa^+|n\rangle + \langle n|a^+a|n\rangle + \langle n|a^{+2}|n\rangle)$$

$$\langle x^2 \rangle = \frac{\hbar}{2m\omega} (0 + (n+1) + n + 0) = \frac{\hbar}{m\omega} \left(n + \frac{1}{2}\right)$$

**Exercise:** Find expectation values of  $p_x$  and  $p_x^2$ .

## 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.

Note that uncertainties can also be estimated from wavefunction or state vector. The uncertainty in the quantity  $A$  is given by

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

Where  $\langle A^2 \rangle$  and  $\langle A \rangle$  are expectation values of  $A^2$  and  $A$  respectively.

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.

**Exercise:** Show that uncertainty between position  $x$  and momentum  $p_x$  in harmonic oscillator is given by:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} (2n + 1)$$

\*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