Lecture 8

Properties of Quantum Harmonic Oscillator

Study Goal of This Lecture

- Energy level and vibrational states
- Expectation values

8.1 Energy Levels and Wavefunctions

We have "solved" the quantum harmonic oscillator model using the operator method. Again, the mathematics is not difficult but the "logic" needs some effort to get used to it. Think it through. Now we are ready to examine the rules. The quantum harmonic oscillator model yields.

Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2,\ \omega = \sqrt{\frac{k}{\mu}}, \tag{8.1}$$

k is force constant which related to bond energy and the μ is reduced mass for diatomics.

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

Schrödinger Equation:

$$\hat{H}\psi_n = E_n\psi_n. \tag{8.2}$$

Energy:

$$E_n = (n + \frac{1}{2})\hbar\omega, \ \ n = 0, 1, 2, 3, \cdots . \tag{8.3}$$

Wavefunctions:

$$\psi_0(x) = (\frac{\mu\omega}{\pi\hbar})^{\frac{1}{4}} \cdot e^{-\frac{\mu\omega}{2\hbar}x^2}, \ \ \psi_n(x) = \Big[\frac{1}{\sqrt{2}}(\sqrt{\frac{\mu\omega}{\hbar}}x - \sqrt{\frac{\hbar}{\mu\omega}}\frac{d}{dx})\Big]^n \cdot \psi_0(x). \tag{8.4}$$

Energy levels and stationary wave functions:

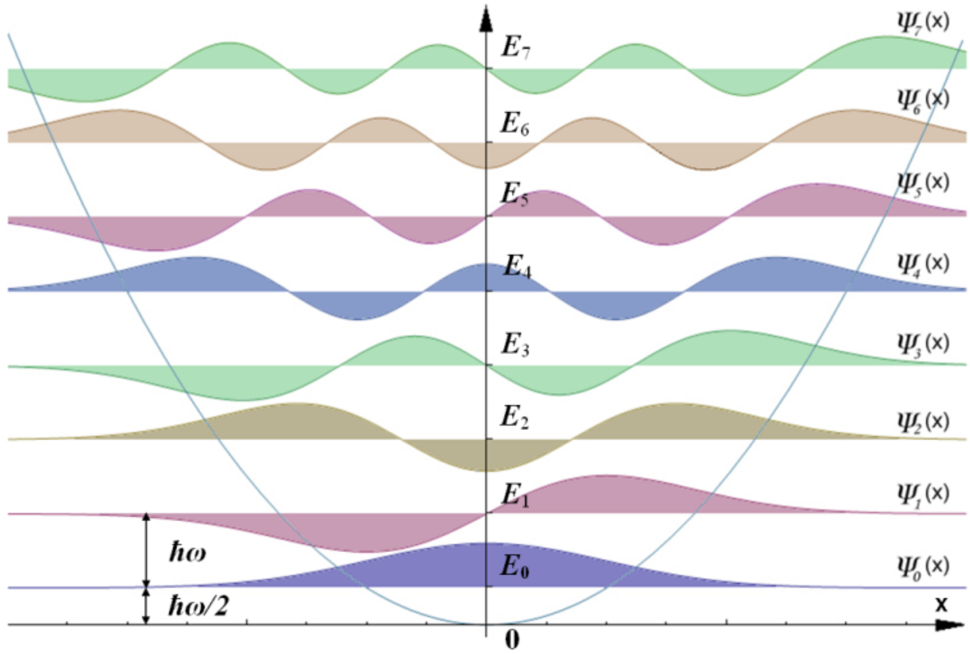

Figure 8.1: Wavefunctions of a quantum harmonic oscillator. Figure's author: AllenMcC.

The features of harmonic oscillator:

1. $\psi_0(x)$ is non-degenerate, all levels are non-degenerate.

2. Energy levels are equally spaced. The vibrational quanta $= \hbar\omega$ and n is the number of vibrational energy in the oscillator. The zero point energy $= \frac{1}{2}\hbar\omega$.

3. Wave function can be constructed by considering number of nodes.

4. At classical turning points: kinetic energy $= 0$,

$$V(x_t) = E_n \Rightarrow \frac{1}{2}\mu\omega^2 x_t^2 = (n + \frac{1}{2})\hbar\omega, \tag{8.5}$$

$$x_t^{(n)} = \sqrt{\frac{2\hbar}{\mu\omega}(n+\frac{1}{2})}. \tag{8.6}$$

Still, $|\psi_n(x > x_t^n)|^2 > 0$, there is pobability of finding the particle in the classical forbidden region $\Rightarrow$ quantum tunneling.

5. Vibrational spectrum (IR/Raman) from transition between nearest vibrational levels.

$$\therefore \Delta E = \hbar\omega = h\nu,\ \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}},$$

note $\nu \propto \sqrt{\frac{k}{\mu}}$, for stronger bond: $\nu \uparrow$ and for larger mass: $\nu \downarrow$. This related to isotope effect. (See Exercise)

8.2 Expectation Values

In addition to thest properties of energy levels and wave functions, we can also quantitative calculate any expectation values of observables using the results we have so far. Let's recall the properties of ladder operators:

$$\begin{aligned}
\hat{a} &= \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} + i\frac{\hat{p}}{m\omega}),\ \text{lowing operator},\\
\hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} - i\frac{\hat{p}}{m\omega}),\ \text{raising operator},\\
\hat{x} &= \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a}),\\
\hat{p} &= i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}^\dagger - \hat{a}),\\
[\hat{a}, \hat{a}^\dagger] &= 1,\\
\hat{a}^\dagger\psi_n &= \sqrt{n+1}\psi_{n+1},\\
\hat{a}\psi_n &= \sqrt{n}\psi_{n-1}.
\end{aligned}$$

These results allow us to rewrite any observable in terms of $\hat{a}$ and $\hat{a}^\dagger$, then we can calculate expectation values easily!

Let's calculate the position and momentum expectation values for the vibrational states first. Before we start, note that $\{\psi_n\}$ form a orthonormal set

$$\therefore \int \psi_n^* \hat{a}\psi_n d\tau = \int \psi_n^*(\sqrt{n+1})\psi_{n+1} d\tau = \sqrt{n+1}\int \psi_n^*\psi_{n+1} d\tau = 0. \tag{8.7}$$

Similarly,

$$\therefore \int \psi_n^* \hat{a}^\dagger \psi_n d\tau = 0. \tag{8.8}$$

Expectation value of position

The expectation value of position of wavefunction with n quantum number.

$$\begin{aligned}
\langle \hat{x} \rangle_n &= \int \psi_n^*(x) \hat{x} \psi_m(x) dx \\
&= \int \psi_n^*(x) \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a}) \psi_n(x) dx \\
&= \sqrt{\frac{\hbar}{2m\omega}} \int \psi_n^*(x) \cdot [\ \sqrt{n+1}\psi_{n+1}(x) + \sqrt{n}\psi_{n-1}(x)\ ] dx = 0.
\end{aligned} \tag{8.9}$$

$$\begin{aligned}
\langle \hat{x}^2 \rangle &= \int \psi_n^*(x) \frac{\hbar}{2m\omega} (\hat{a}^\dagger + \hat{a}^2) \psi_n(x) dx \\
&= \frac{\hbar}{2m\omega} \int \psi_n^*(x) \{ (\hat{a}^\dagger + \hat{a}) [\sqrt{n+1}\psi_{n+1}(x) + \sqrt{n}\psi_{n-1}(x)] \} dx \\
&= \frac{\hbar}{2m\omega} \int \psi_n^*(x) \{ \sqrt{(n+1)(n+2)}\psi_{n+2}(x) + n\psi_n(x) + \\
&\quad (n+1)\psi_n(x) + \sqrt{n(n-1)}\psi_{n-2}(x) \} dx \\
&= \frac{\hbar}{2\mu\omega}(2n+1) = \frac{1}{\mu\omega^2} \hbar\omega(n+\frac{1}{2}) = \frac{E_n}{\mu\omega^2}.
\end{aligned} \tag{8.10}$$

Notice that only the term which the number of $\hat{a}$ and $\hat{a}^\dagger$ match will contribute.(or saying nonzero)

With these result, we obtain the potential energy:

$$\langle \hat{V} \rangle_n = \langle \frac{1}{2}\mu\omega^2 \hat{x}^2 \rangle_n = \frac{1}{2}\mu\omega^2 \langle \hat{x}^2 \rangle_n = \frac{1}{2} E_n. \tag{8.11}$$

We find that it is half the total energy $\to$ make sense!

Try to explain why it is one half the total energy in your own language!

The expectation value of momentum

Since the potential energy is known, the kinetic energy can be determined easily:

$$\langle \hat{T} \rangle_n = E_n - \langle \hat{V} \rangle_n = \frac{1}{2} E_n. \tag{8.12}$$

So the expectation value of momentum square:

$$\therefore \langle \frac{\hat{p}^2}{2\mu} \rangle_n = \langle \hat{T} \rangle_n,\ \langle \hat{p}^2 \rangle_n = 2\mu \cdot \frac{1}{2} E_n = \mu\hbar\omega(n+\frac{1}{2}). \tag{8.13}$$

The above fomula can be checked using the same trick of ladder operator. Expectation value of momentum can be calculated too and one will find it is is zero ($\langle \hat{p} \rangle_n = 0$).

Uncertainty of harmonic oscillator

Recall that for any phycial observable $\hat{A}$, the uncertainty is

$$(\Delta\hat{A})^2 = \langle(\hat{A} - \langle A\rangle)^2\rangle = \langle\hat{A}^2\rangle - \langle A\rangle^2, \tag{8.14}$$

so for the uncertainty of position and momentum:

$$\Delta\hat{x} = \sqrt{\langle\hat{x}^2\rangle - \langle x\rangle^2} = \sqrt{\frac{\hbar}{2\mu\omega}}, \tag{8.15}$$

$$\Delta\hat{p} = \sqrt{\langle\hat{p}^2\rangle - \langle p\rangle^2} = \sqrt{\frac{\mu\hbar\omega}{2}}. \tag{8.16}$$

Multiply them, we obtain

$$\Delta\hat{x}\Delta\hat{p} = \frac{\hbar}{2}. \tag{8.17}$$

This is the minimal possible value allowed by the Heisenberg uncertainty principle.

This is a special property of the ground state of the harmonic osillator model. It is also called a "minimal uncetainty wavefunction", "coherent state", $\cdots$. We will show what's special about it when we discuss time-evolution of it. The key for calculating the expectation value of quantum harmonic oscillator is to use $\hat{a}$ and $\hat{a}^\dagger$.

8.2.1 Evaluate the Expectation Value of Superposition State

The above calculation is not restricted to eigenstate. Since $\hat{H}\psi_n = E_n\psi_n$, $\{\psi_n\}$ form a complete orthonormal set, any wavefunction can be written as superposition of $\{\psi_n\}$:

$$\Psi(x) = \sum_n C_n\psi_n, \text{ where } C_n = \int \psi_n^*\Psi(x)dx. \tag{8.18}$$

Then any $\hat{A}(x,p)$ can be evaluated:

$$\langle\hat{A}\rangle = \int \Psi^*(x)\cdot\hat{A}(\hat{x},\hat{p})\cdot\Psi(x)dx. \tag{8.19}$$

Let's consider an example, for:

$$\Psi = \frac{1}{\sqrt{2}}(\psi_0 + \psi_1), \tag{8.20}$$

then the energy will be

$$\langle E\rangle = \int \Psi^*\hat{H}\Psi d\tau = \frac{1}{2}\int(\psi_0^* + \psi_1^*)\hat{H}(\psi_0 + \psi_1)d\tau. \tag{8.21}$$

Since $\hat{H}(\psi_0 + \psi_1) = \hat{H}\psi_0 + \hat{H}\psi_1 = E_0\psi_0 + E_1\psi_1$

$$\begin{aligned}
\langle E \rangle &= \int \Psi^* \hat{H} \Psi d\tau = \frac{1}{2} \int (\psi_0^* + \psi_1^*)(E_0\psi_0 + E_1\psi_1) d\tau \\
&= \frac{1}{2} [\ E_0 \int \psi_0^* \psi_0 d\tau + E_1 \int \psi_0^* \psi_1 d\tau + E_0 \int \psi_1^* \psi_0 d\tau + E_1 \int \psi_1^* \psi_1 d\tau\ ] \\
&= \frac{1}{2}(E_0 + E_1) \leftarrow \text{averaged energy!}
\end{aligned} \tag{8.22}$$

and for the position:

$$\begin{aligned}
\langle x \rangle &= \frac{1}{2} \int (\psi_0^* + \psi_1^*) \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a})(\psi_0 + \psi_1) d\tau \\
&= \frac{1}{2} \sqrt{\frac{\hbar}{2m\omega}} \int (\psi_0^* + \psi_1^*)(\psi_1 + \sqrt{2}\psi_2 + \psi_0) d\tau \\
&= \frac{1}{2} \sqrt{\frac{\hbar}{2m\omega}} \neq 0.
\end{aligned} \tag{8.23}$$

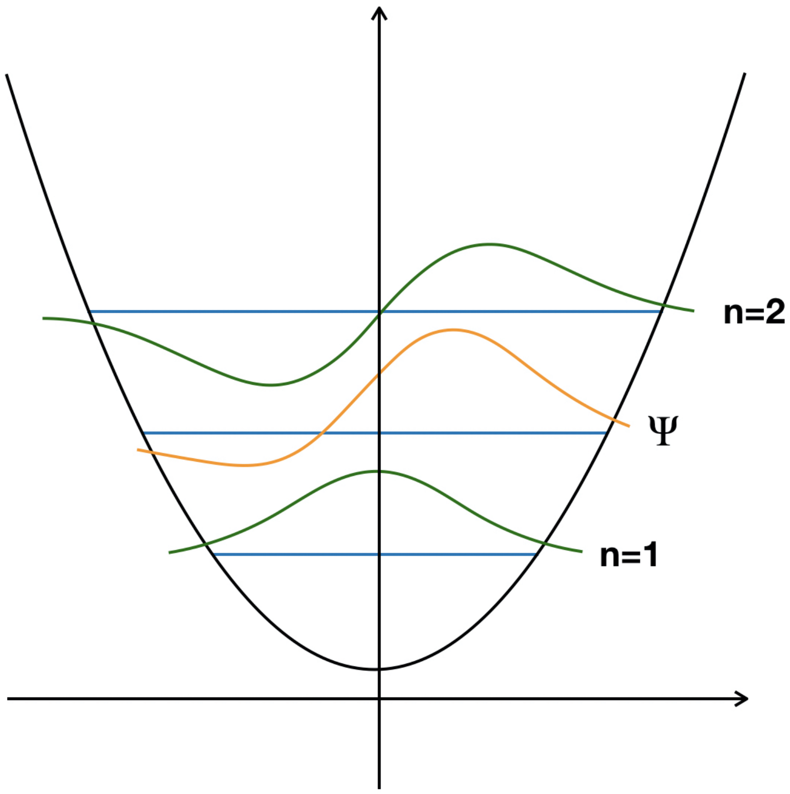

Figure 8.2: $\Psi = \frac{1}{\sqrt{2}}(\psi_0 + \psi_1)$. This state can exist but it is not a stationary state.