Lecture #11 Supplement: Nonstationary States of Quantum Mechanical Harmonic Oscillator

Last time

$$\hat{\tilde{x}} = \left[\frac{\mu\omega}{\hbar}\right]^{1/2} \hat{x}$$

$$\hat{\tilde{p}} = [\hbar\mu\omega]^{-1/2}\, \hat{p}$$

$$\hat{\mathbf{a}} = 2^{-1/2}\left(i\hat{\tilde{p}} + \hat{\tilde{x}}\right)$$

$$\widehat{\mathbf{a}^{\dagger}} = 2^{-1/2}\left(-i\hat{\tilde{p}} + \hat{\tilde{x}}\right)$$

$$\hat{\tilde{x}} = 2^{-1/2}\left(\hat{\mathbf{a}}^{\dagger} + \hat{\mathbf{a}}\right)$$

$$\hat{\tilde{p}} = 2^{-1/2}\, i\left(\hat{\mathbf{a}}^{\dagger} - \hat{\mathbf{a}}\right)$$

$$\hat{x} = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2}\left(\hat{\mathbf{a}}^{\dagger} + \hat{\mathbf{a}}\right)$$

$$\hat{p} = \left(\frac{\hbar\mu\omega}{2}\right)^{1/2} i\left(\hat{\mathbf{a}}^{\dagger} - \hat{\mathbf{a}}\right)$$

$$\hat{\mathbf{a}}\psi_v = [v]^{1/2}\,\psi_{v-1}\ \text{, e.g. } \hat{\mathbf{a}}^3\psi_v = [v(v-1)(v-2)]^{1/2}\,\psi_{v-3}$$

$$\hat{\mathbf{a}}^{\dagger}\psi_v = [v+1]^{1/2}\,\psi_{v+1}\ \text{, e.g. } \widehat{\mathbf{a}^{\dagger}}^{10}\psi_v = [(v+10)\ldots(v+1)]^{1/2}\,\psi_{v+10}$$

What is so great about $\hat{\mathbf{a}},\hat{\mathbf{a}}^{\dagger}$?
Born with *selection rule* and *values* of all integrals attached!

$$\int dx\psi_{\mathrm{v}}^{*}(\hat{\mathbf{a}}^{\dagger})^{m}(\hat{\mathbf{a}})^{n}\,\psi_{v+n-m} = \Big[\underbrace{(v+n-m)(v+n-m-1)\ldots(v-m+1)}_{n\text{ terms}}\underbrace{(v-m+1)\ldots(v-1)(v)}_{m\text{ terms}}\Big]^{1/2}$$

$$(\hat{\mathbf{a}}^{\dagger})^{m}(\hat{\mathbf{a}})^{n} \rightarrow v_f - v_i = m - n$$

Suppose you want $\int dx\psi_{\mathrm{v}+2}^{*}\mathbf{Op}\psi_{\mathrm{v}} \neq 0$? Then **Op** could be $\hat{\mathbf{a}}^{\dagger 2}$ or $\hat{\mathbf{a}}^{\dagger 3}\hat{\mathbf{a}}$ (in any order).

Suppose you have $\hat{p}^3$ and want $\psi_{\mathrm{v}+3}\hat{p}^3\psi_{\mathrm{v}}$ integral? Only a total of 3 multiplicative $\hat{\mathbf{a}}$ or $\hat{\mathbf{a}}^{\dagger}$ factors possible, therefore you need only keep $\hat{\mathbf{a}}^{\dagger 3}$ term.

<u>Today</u> A taste of Wavepacket Dynamics.

- Coherent superposition state
  dephasing
  rephasing: partial or complete rephasing
- $\langle x \rangle_t, \langle p \rangle_t$ Ehrenfest's Theorem — "center" of wavepacket follows Newton's laws.
- Tunneling through a barrier

All of this is very qualitative, but forms a transparent basis for intuition.

Imagine, at $t = 0$, a state of the system is created that is not an eigenstate of $\widehat{H}$.

* Half harmonic oscillator
* Gaussian wavepacket (velocity = 0) transferred by photon excitation from one potential energy curve to another electronic state potential curve at a value of x where $\frac{dV_{\text{excited}}}{dx} \neq 0$
* molecule created in "wrong" vibrational state (i.e. a vibrational eigenstate of the neutral molecule is not a vibrational eigenstate of the ion) by sudden photoionization

What happens?

Insights come from a special class of problem where the energy levels have the special property:

$$E_n = (\text{integer})E_{\text{common factor}}$$

particle in box $\quad E_n = E_1 n^2$

harmonic oscillator $\quad E_n = E_0 + n\hbar\omega = \underbrace{\frac{\hbar\omega}{2}}_{E_0}(2n+1)$

$$\Psi(x,0) = \sum_n c_n \psi_n(x)$$

expand in complete basis set, where $\{\psi_n\}$ are eigenfunctions of $\widehat{H}$. WHY is this convenient and instructive?

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$$

assume all $\{\psi_n\}$ and $\{c_n\}$ are real

The probability density is

$$P(x,t) \equiv \Psi^*(x,t)\Psi(x,t) = \sum_{n,m} c_n c_m \psi_n \psi_m \left(e^{-i(E_n-E_m)t/\hbar}\right)$$

$$= \sum_n c_n^2 \psi_n^2 + \sum_{n\neq m} c_n c_m \psi_n \psi_m \left(e^{-i(E_n-E_m)t/\hbar}\right)$$

$$= \sum_n \underbrace{c_n^2 \psi_n^2}_{\substack{\text{static}\\ \text{term}}} + \sum_{n>m} \underbrace{2c_n c_m \psi_n \psi_m \cos\omega_{nm} t}_{\text{oscillating term "coherence"}}$$

all real, not complex

positive at all x

regions of + and – vs. x

P(x,t) must be ≥ 0 and real at *all x* for *all t*. Why?
Normalization:

$$\int dx \Psi^* \Psi = \sum_n c_n^2 = 1$$

No time dependences, Ψ is normalized, and ψ_n, ψ_m are orthogonal. Normalization is conserved.

Note, we get rid of all x information only when we integrate over x. For example, the energy

$$\langle \widehat{H} \rangle = \langle E \rangle = \int dx \Psi^* \widehat{H} \Psi = \sum_n c_n^2 E_n$$

$$\begin{cases}\text{No time dependence of } \langle E \rangle \\ \text{E is conserved.}\end{cases}$$

Look at P(x,t) probability distribution.

What are some *special times*?

$$\cos\omega t = 1, \quad 0, \quad -1$$

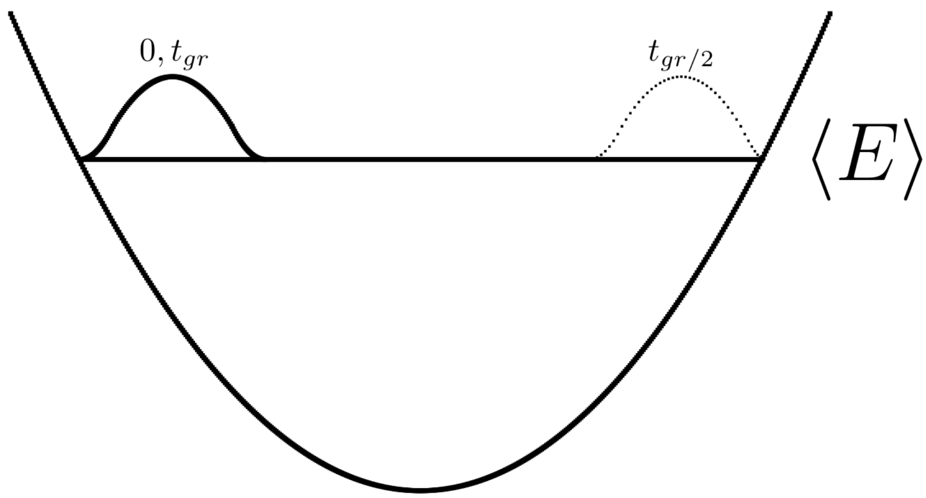
$\boxed{\omega t = 2n\pi}$ $\quad$ $\boxed{\omega t = (2n+1)\frac{\pi}{2}}$ $\quad$ $\boxed{\omega t = (2n+1)\pi}$

If all ω_{nm} are multiples of a common factor, call it ω_{gr} (gr = "grand rephasing")

when $t_{gr} = \dfrac{2n\pi}{\omega}$ $\quad \Psi(x,t_{gr}) = \Psi(x,0)$

when

$\underbrace{t_{agr}}_{\text{anti-grand rephasing}} = \dfrac{(2n+1)\pi}{\omega}$, most of the coherence terms have opposite sign to what they had at $t = 0$. Usually this means that wavepacket is localized at the other side of center.



At $\dfrac{t_{gr} + t_{agr}}{2} = \dfrac{\pi}{2\omega} + \dfrac{2n\pi}{\omega}$, all $\psi_n\psi_m$ cross terms are = 0, the only surviving terms are ψ_n^2, and these are + everywhere, thus the probability is distributed over the entire region.

This is the "dephased" situation. The evolution is sequential: phased up, dephased, phased "down", repeat.

Suppose you compute $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$.

Non-Lecture

$$\Psi(x,t) = \sum_{n=0}^{n_{\max}} c_n \psi_n e^{-iE_n t/\hbar}$$

$$\Psi^*\Psi = \sum_{n=0}^{n_{\max}} \sum_{m=0}^{m_{\max}} c_n c_m \psi_n \psi_m e^{-i\omega_{nm}t}$$

$$= \sum_{n=0}^{n_{\max}} c_n^2 \psi_n^2 + \sum_{n,m>n}^{m_{\max}} c_n c_m \psi_n \psi_m \left[e^{-i\omega_{mn}t} + e^{i\omega_{mn}t}\right]$$

$(x_{nn} = 0)$

$$= \sum_{n=0}^{n_{\max}} c_n^2 \psi_n^2 + \sum_{m>n}^{m_{\max}} c_n c_m \psi_n \psi_m \left(2\cos\omega_{mn}t\right)$$

$$\langle \hat{x} \rangle_t = \int dx \Psi^* \hat{x} \Psi = 0 + \sum_{n=0} 2 c_n c_{n+1} \cos\omega t \int dx \psi_n \hat{x} \psi_{n+1}$$

$$\int dx \psi_n \hat{x} \psi_{n+1} = \left(\frac{\hbar}{2\mu\omega}\right)^{1/2} [n+1]^{1/2}$$

$$\langle \hat{x} \rangle_t = 2\left(\frac{\hbar}{2\mu\omega}\right)^{1/2} \cos\omega t \left[\sum c_n c_{n+1} (n+1)^{1/2}\right]$$

$$= A\cos\omega t$$

A similar analysis for $\langle \hat{p}_x \rangle_t$ gives $B \sin \omega t$.

For HO, there are especially simple selection rules for $\hat{x}$ and $\hat{p}$: the $\psi^*_{v_f}\psi_{v_i}$ integrals follow the $\Delta v = \pm 1$ selection rule.

Before integration over x, only need to keep the terms $\left.\begin{matrix}\psi_v\psi_{v+1}\cos\omega t \\ \psi_v\psi_{v-1}\cos\omega t\end{matrix}\right)$ Phase convention for ψ_v chosen so that these products are
+ at x near x_+
– at x near x_-

There is no variation of ω with *E* for Harmonic Oscillator.

All of the coherence terms in HO give

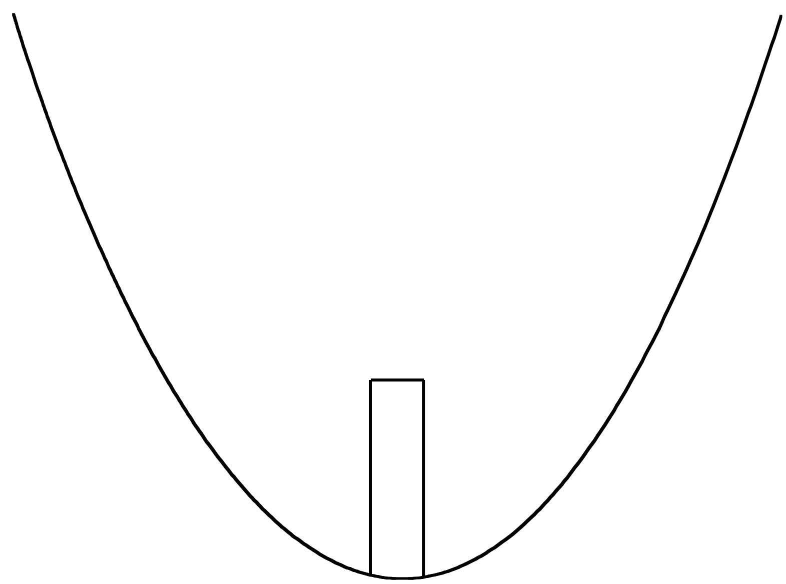
$\langle x \rangle_t \propto \text{A} \cos \omega t$
$\langle p \rangle_t \propto \text{B} \sin \omega t$

Does this look familiar?
Just like classical HO

$$\left.\begin{aligned} \frac{d}{dt}\langle x \rangle &= \frac{1}{m}\langle p_x \rangle \\ v &= p / m \\ \frac{d}{dt}\langle p_x \rangle &= -\langle \nabla V(x) \rangle \\ ma &= F \end{aligned}\right] \text{Ehrenfest's Theorem} \qquad \begin{pmatrix} \text{here, } v \text{ is velocity, not} \\ \text{vibrational quantum number} \end{pmatrix}$$

Center of wavepacket moves according to Newton's equations!

Tunneling

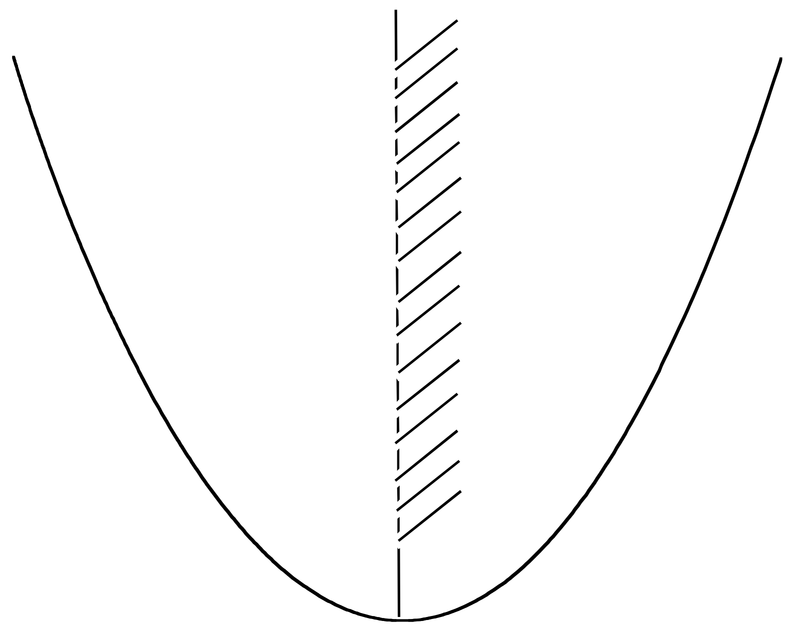


For a thin barrier, all ψ_v with node in middle (odd v) hardly feel barrier. They are shifted to higher E only <u>very</u> slightly.

The ψ_v with a maximum at $x = 0$ (even v) all feel the barrier very strongly. They are shifted up almost to the energy of next higher level, if the energy of HO ψ_v lies below top of barrier.

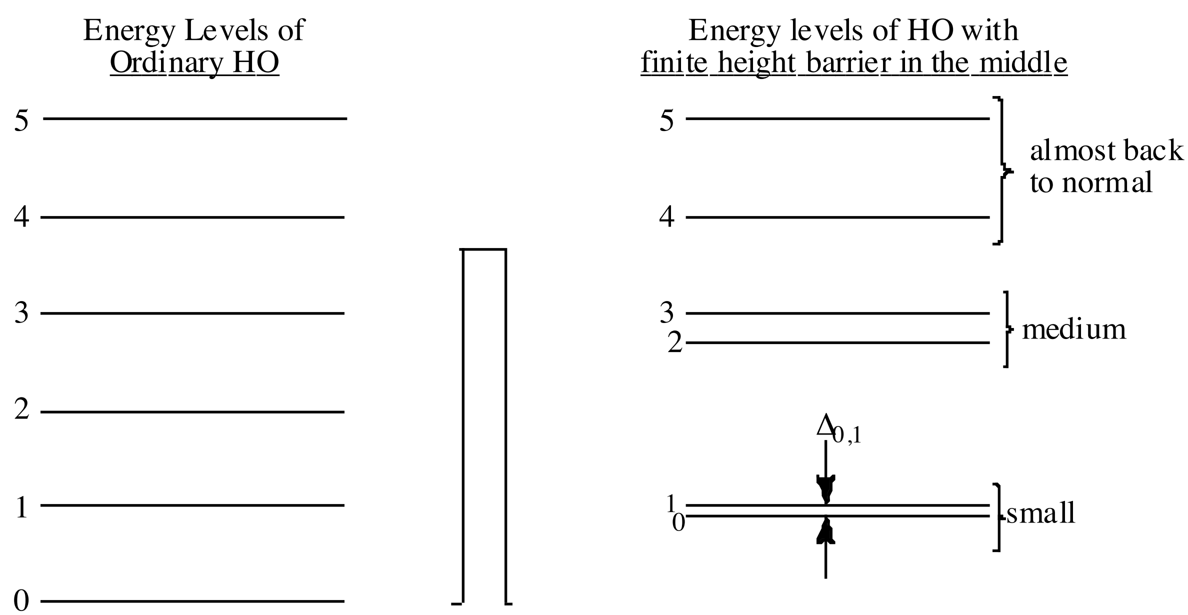
Why do I say that the barrier causes all HO energy levels to be shifted up?
[We will return to this problem once we have discovered non-degenerate perturbation theory.]

We see some evidence for this difference in energy shifts for odd vs. even-v levels by thinking about ½ HO.



This half-HO oscillator only has levels at E_1, E_3 of the full oscillator so $v = 0$ of ½ oscillator is at the energy of v = 1 of the full oscillator.

So a barrier causes even-v levels to shift up a lot relative to the next higher odd-v level.

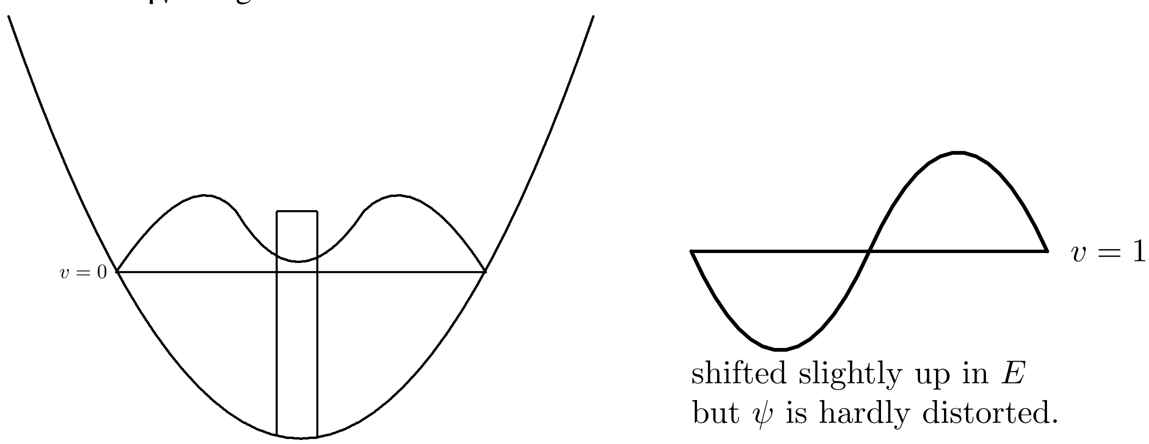


Suppose we make ψ_1, ψ_0 two-state superposition.

$$\Psi^*(x,t)\Psi(x,t) = c_0^2\psi_0^2 + c_1^2\psi_1^2 + 2c_1c_2\psi_0\psi_1\cos\Delta_{01}t$$

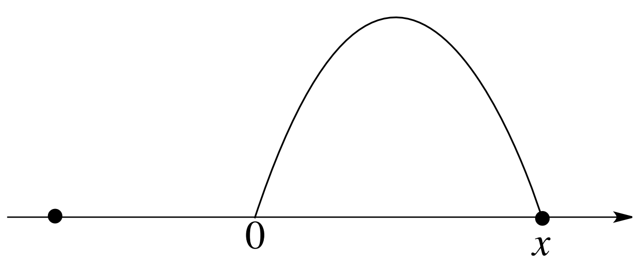
$$\Delta_{0,1} = \frac{E_1 - E_0}{\hbar} \qquad (\Delta_{0,1} \text{ is small})$$

What does ψ_v=0 eigenstate look like?



Zero nodes (tried but barely fails to have one node). It resembles the v = 1 state of no-barrier oscillator.

$\Psi_{1,0}(x,0) = 2^{-1/2}\left[\psi_1(x) + \psi_0(x)\right]$ looks like this at $t = 0$



$$\Psi_{1,0}^*(x,t)\Psi_{1,0}(x,t) = \frac{1}{2}\psi_0^2 + \frac{1}{2}\psi_1^2 + \psi_1\psi_0\cos\Delta_{0,1}t$$

We get oscillation of nearly perfectly localized wavepacket right – left – right *ad infinitum*.

* $\Delta_{0,1}$ is small so period of oscillation is long (it is the energy difference between the $v = 0$ and $v = 1$ *eigenstates* of the harmonic plus barrier potential)

Similarly for 3,2 wavepacket.

* left/right localization is less perfect
* oscillation is faster because $\Delta_{2,3}$ is larger

MESSAGE: As you approach top of barrier, tunneling gets faster.

Tunneling is slow (small splittings of consecutive pairs of levels) for high barrier, thick barrier, or at E far below top of barrier.

Can use pattern of energy levels ($\Delta_{0,1}$ and $\Delta_{2,3}$) observed in a spectrum (frequency-domain) to learn about time-domain phenomena (tunneling).

"Dynamics in the frequency-domain."