Lecture #11: Wavepacket Dynamics for Harmonic Oscillator and PIB

Last time: Time–Dependent Schrödinger Equation

$$\widehat{\mathbf{H}}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Express Ψ in complete basis set of eigenfunctions of time–independent $\widehat{\mathbf{H}}$

$$\{\psi_n(x),\, E_n\}$$
$$\Psi(x,t) = \sum_j c_j e^{-iE_j t/\hbar}\psi_j(x)$$

For 2-state Ψ's, we saw that

1. $|\Psi^\star(x,t)\,\Psi(x,t)|$ moves only if Ψ contains at least 2 different E_j's;
2. $\int dx \Psi^\star\Psi = 1$ for all $\Psi(x,t)$. Conservation of probability.
3. $\langle \hat{x} \rangle_t$ and $\langle \hat{p} \rangle_t$ obey Newton's laws. Motion of "center of wavepacket". Ehrenfest's Theorem.
4. Survival probability $P(t) = \left|\int dx \Psi^\star(x,t)\,\Psi(x,t=0)\right|^2$. How fast does $\Psi(x,t)$ move away from its initial preparation $\Psi(x,0)$. Dephasing, partial recurrence, grand recurrence.
5. Recurrences occur when all ΔE_{ij} are integer multiples of common factor.

TODAY: Some examples of wavepackets in a Harmonic Oscillator or PIB potential well. Mostly pictorial.

We start with the initial condition, $\Psi(x,t=0)$, which I call the "pluck". It is quite analogous to what musicians understand about a wave on a string that is tied down at both ends.

$$\Psi(x,0) = \sum_j c_j\psi_j$$

If we have a "complete set" of $\psi_j(x)$, then we can expand any $\Psi(x,0)$ as a linear combination of $\psi_j(x)$. Like a Fourier series. Once we have $\Psi(x,0)$ it is trivial to put in the t–dependence

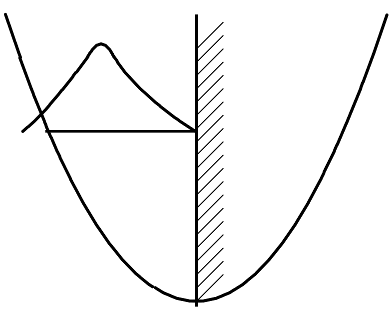
$$\Psi(x,t) = \sum c_j e^{-iE_jt/\hbar}\psi_j(x)$$

because for each known ψ_j there is a known E_j.

We usually like to create a wavepacket localized near a turning point. The more $\psi_j(x)$ wavefunctions we use in describing $\Psi(x,0)$, the sharper we can make the $t = 0$ wavepacket.

There are several experimentally or pictorially simple schemes for creating a wavepacket, which is a superposition of eigenstates of $\widehat{\mathbf{H}}$ that have *different* values of E_j (needed in order to have any motion at all).

Create a non-eigenstate at $t = 0$



Half Harmonic Oscillator, barrier at $x = 0$.
Remove barrier at $t = 0$

To make such a $t = 0$ wavepacket, we can use any of the ψ_{2v+1} (odd) eigenstates that have a node at $x = 0$. But in order to have time dependent $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$ we also need some ψ_{2v} (even) eigenstates in pairs, $c_2\psi_2(0) = -c_0\psi_0(0)$, so that $c_2\psi_2(0) + c_0\psi_0(0) = 0$. Usually, in order to make life simple, we choose only 3 ψ_v to create a $\Psi(x, t = 0)$ with *approximately* the correct shape

$$\Psi(x,0) = c_0\psi_0(x) + c_1\psi_1(x) + c_2\psi_2(x).$$

This will have a node at $x = 0$ and larger probability for $x < 0$ than for $x > 0$.

$$\langle \hat{x} \rangle_t = 2c_0c_1x_{01}\cos\omega t + 2c_1c_2x_{12}\cos\omega t.$$

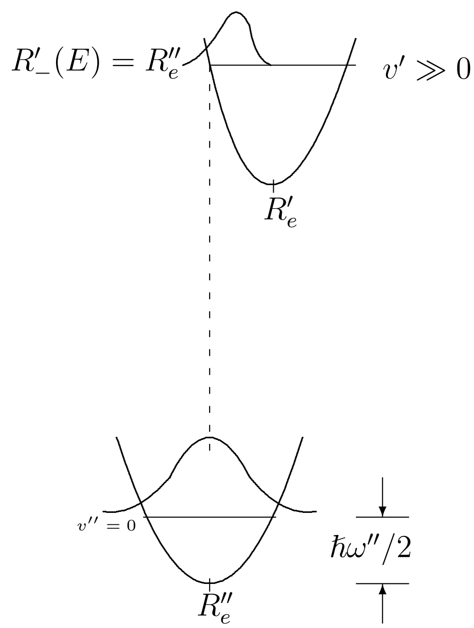
Note that x_{00}, x_{11}, x_{22}, and x_{02}, are all zero because of the Harmonic Oscillator $\Delta v = \pm 1$ selection rule for $\hat{x}$. Note that probability and $\langle \hat{x} \rangle$ sloshes back and forth between the $x < 0$ and $x > 0$ regions at angular frequency ω.

What is $\left\langle \widehat{\mathbf{H}} \right\rangle_t$? Is it t–dependent?

$$\left\langle \widehat{\mathbf{H}} \right\rangle_t = |c_0|^2E_0 + |c_1|^2E_1 + |c_2|^2E_2$$

because the ψ_v are eigenfunctions of $\widehat{\mathbf{H}}$, therefore orthogonality ensures that there are no $c_i c_j$ cross terms, and the pairs of $e^{-iE_v t/\hbar}$ and $e^{+iE_v t/\hbar}$ factors combine to yield 1. Of course, E has to be conserved.

Create a non–eigenstate wavepacket by causing a vertical electronic transition at $t = 0$. The excited state potential energy curve is displaced from that of the electronic ground state.



Notation:
$'$ for upper state
$''$ for lower state

The $v'' = 0$ wavepacket is "transferred" to the excited state. The **Franck–Condon principle** says that, since electrons move much faster than nuclei, the electronic transition is instantaneous as far as the nuclei are concerned. This means that x and p do not change in an electronic transition. So we start out with a wavepacket on the excited state where $\left\langle \widehat{R} \right\rangle_0 = R''_e$, $\langle \hat{p} \rangle_0 = [2\mu\hbar\omega''/2]^{1/2}$. It is clear that the initially formed wavepacket will be localized near the inner turing point of the excited state and will be experiencing a large force in the $+x$ direction. If we approximate $\Psi(x,0)$ as a mixture of $v' = 10$ and $v' = 11$ states

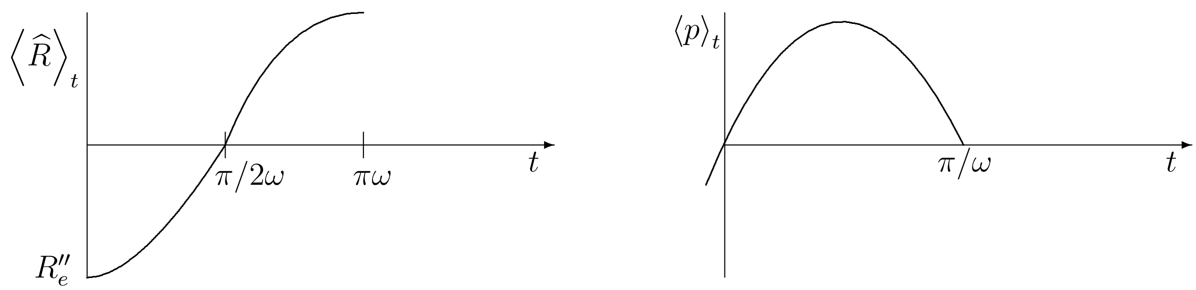
$$\Psi(x,0) = c_{10}\psi_{v'=10}(x) + c_{11}\psi_{11}(x)$$
$$\Psi^\star(x,t)\Psi(x,t) = |c_{10}|^2|\psi_{10}|^2 + |c_{11}|^2|\psi_{11}|^2 + 2c_{10}c_{11}\psi_{10}\psi_{11}\cos\omega t$$

(allowing c_j and ψ_j to be real)

$$\begin{aligned} P(t) &= \left| \langle \Psi^\star(x,t)\Psi(x,0) \rangle \right|^2 \\ &= \left| |c_{10}|^2 e^{i10.5\hbar\omega t/\hbar} + |c_{11}|^2 e^{i11.5\hbar\omega t/\hbar} \right|^2 \\ &= c_{10}^4 + c_{11}^4 + 2c_{10}^2 c_{11}^2 \cos\omega t \end{aligned}$$

At $t = 0$ $P(t)$ is at its maximum value. But there are a series of perfect rephasings at $t = n\frac{2\pi}{\omega}$ and minimum values at $t = (2n+1)\frac{\pi}{\omega}$.

Why does the wavepacket behave in this way?

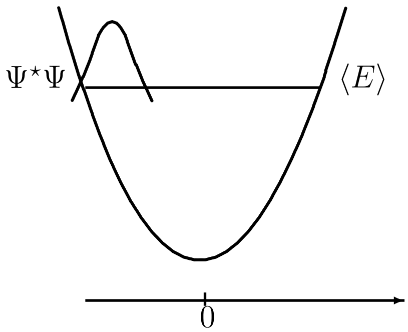


$$\begin{aligned} \left\langle \widehat{R} \right\rangle_t &= c_{10}c_{11}R_{10,11}\cos\omega t \quad (c_{10}c_{11} < 0) \\ \langle \hat{p} \rangle_t &= c_{10}c_{11}p_{10,11}\sin\omega t \quad \text{(the } R_{10,11} \text{ harmonic oscillator integral is positive} \\ &\qquad\qquad \text{and the } P_{10,11} \text{ integral is imaginary)} \end{aligned}$$

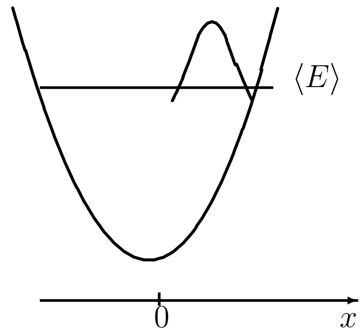
The initial wavepacket moves away from itself faster in momentum space than in coordinate space, so the initial decay of $P(t)$ is predominantly a momentum effect.

Dephasing and Rephasing of a Wavepacket

A favorite kind of wavepacket is one that is localized near a turning point at $t = 0$. It is a particle–like state that we expect will act in a classical mechanical particle-like manner. For a Harmonic Oscillator, all $E_{v'} - E_v$ are integer multiples of $\hbar\omega$. Thus, if the time–dependent part of $\Psi^\star(x,t)\Psi(x,t)$ (the coherence term) is "phased up" at $t = 0$, then it will be "phased down" at $t = \frac{1}{2}\tau = \frac{1}{2}\frac{h}{\hbar\omega}$ because the signs of all the $\Delta v = \pm 1$ coherence terms will be reversed. We expect

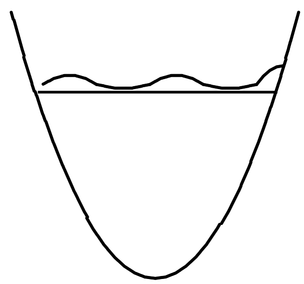


$t = 0$
phased up



$t = \frac{1}{2}\frac{2\pi}{\omega}$
phased down

At in between times, $\Psi^\star\Psi$ is likely to look very un–particle–like. Dephased.



The wavepacket undergoes simple harmonic motion, and appears in all of its simple glory at alternating turning points. Its expectation values $\langle\hat{x}\rangle_t$ and $\langle\hat{p}\rangle_t$ move according to Newton's laws, but the picture of $\Psi^\star(x,t)\Psi(x,t)$ can be more complicated.

Speculate about what you might expect for a wavepacket composed of eigenstates of an anharmonic oscillator, with energy levels $G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$, where $\frac{\omega_e x_e}{\omega_e} \approx 0.02$.

Is the periodic rephasing perfect? Is each successive rephasing only partial? Does the wavepacket eventually lose its particle–like localization? Once this happens, does the localized wavepacket ever re–emerge as a fully rephased entity?

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

All of the coherence terms in HO give

$$\langle x\rangle_t \propto A\cos\omega t$$

$$\langle p\rangle_t \propto B\sin\omega t$$

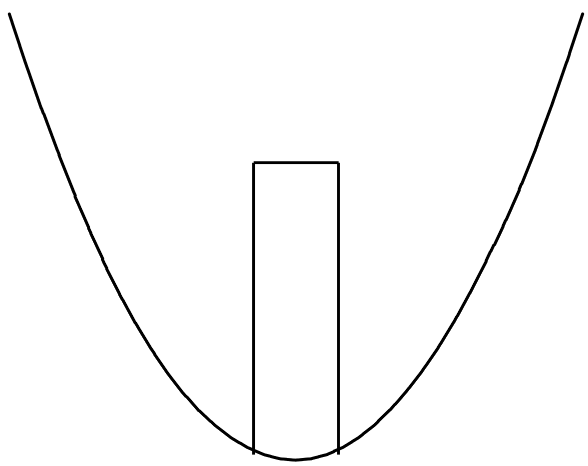
Does this look familiar? Just like classical HO

$$\left.\begin{array}{c} \frac{d}{dt}\langle x\rangle = \frac{1}{m}\langle p_x\rangle \\ v = p/m \\ \frac{d}{dt}\langle p_x\rangle = -\langle \nabla V(x)\rangle \\ ma = F \end{array}\right] \text{Ehrenfest's Theorem}$$

(here, v is velocity, not vibrational quantum number)

Center of wavepacket moves according to Newton's equations!

Tunneling

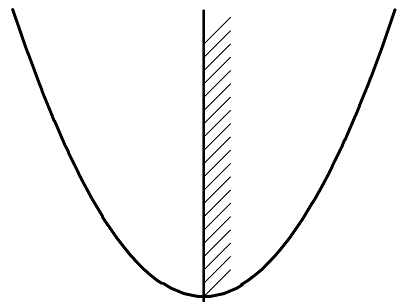


For a thin barrier, all ψ_v with node in middle (odd v) hardly feel the barrier. They are shifted to higher E only very slightly.

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

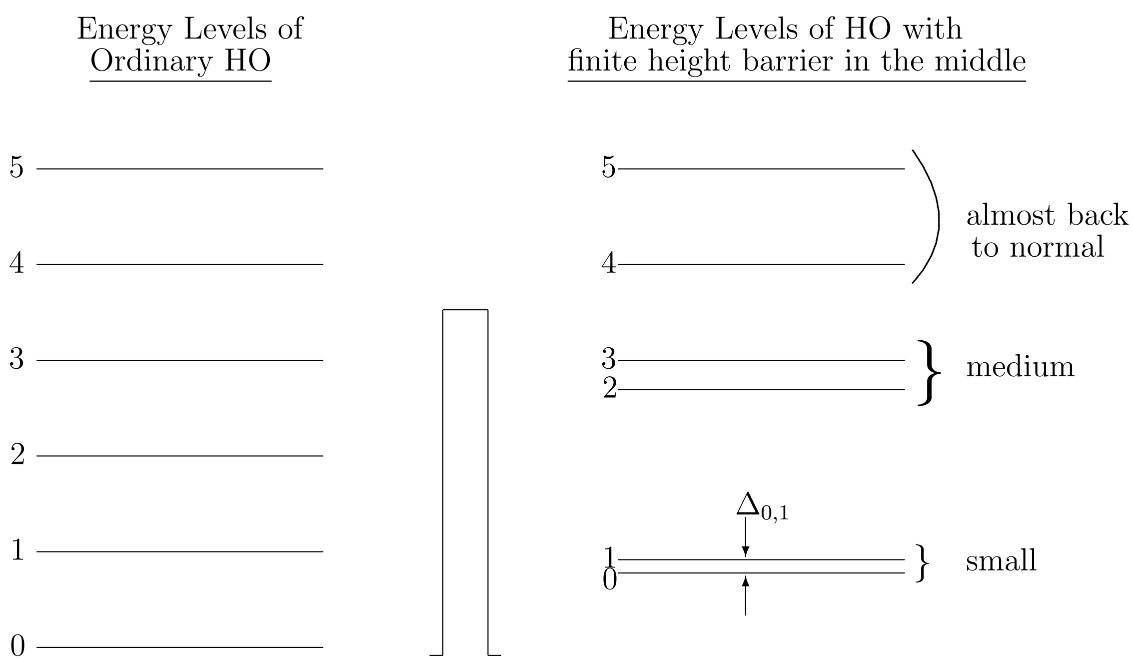
Why do I say that the barrier causes all HO energy levels to be shifted up? [We will return to this problem once we have discovered non-degenerate perturbation theory.]

We see some evidence for this difference in energy shifts for odd vs. even-v levels by thinking about the $\frac{1}{2}$ HO.



This half-HO oscillator only has levels at E_1, E_3 of the full oscillator so $v = 0$ of the $\frac{1}{2}$ oscillator is at the energy of $v = 1$ of the full oscillator.

So a barrier causes even-v levels to shift up a lot and become near-degenerate with the next higher odd-v level. [Can't change energy order because the energy levels are in order of # of nodes.]

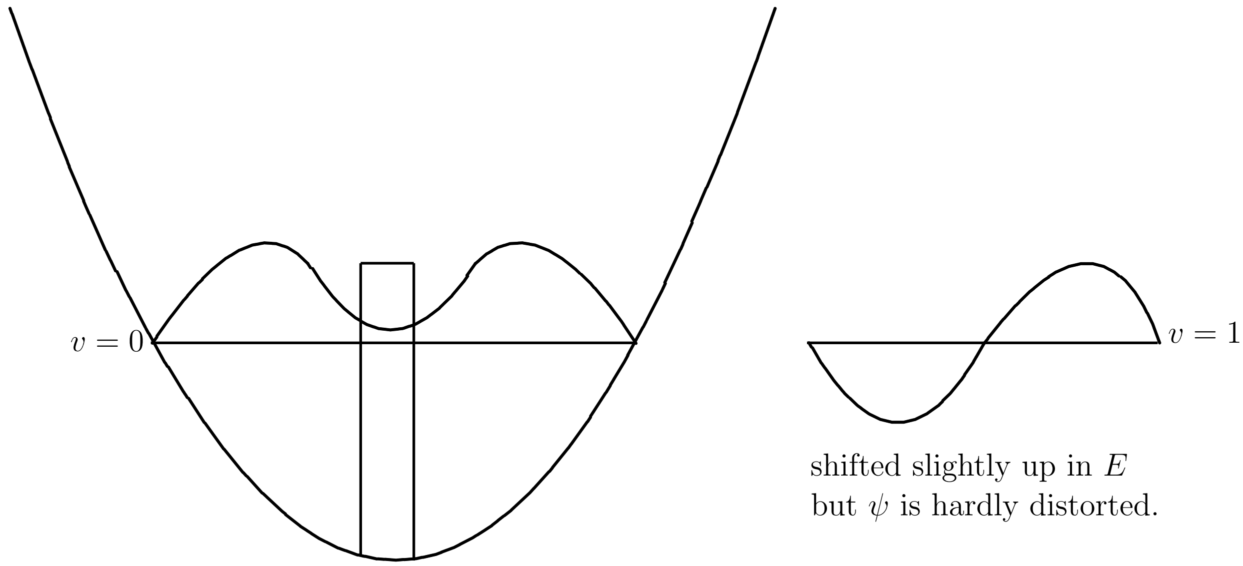


Suppose we make a ψ_1, ψ_0 two-state superposition

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

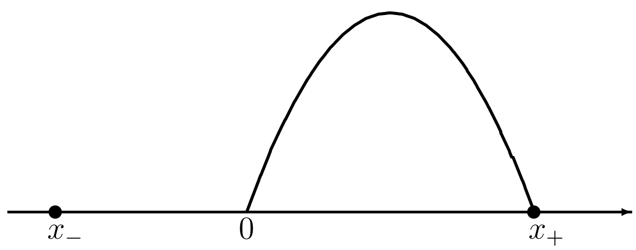
$$\Delta_{0,1} = \frac{E_1 - E_0}{\hbar} \qquad (\Delta_{0,1} \text{ is small})$$

What does the $\psi_v = 0$ eigenstate of the well with barrier in the middle look like?



$v = 0$ has zero nodes (wavefunction tried but barely failed to have one node). It resembles the $v = 1$ state of the no-barrier oscillator.

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



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

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."