Lecture #8: Quantum Mechanical Harmonic Oscillator

Last time

Classical Mechanical Harmonic Oscillator

* $V(x) = \frac{1}{2}kx^2$ (leading term in power series expansion of most V(x) potential energy functions)
* x is displacement from equilibrium ($x = 0$ at equilibrium)
*   angular frequency $\omega = [k/\mu]^{1/2}$
* $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ reduced mass

From $F = ma$ we get $\dfrac{d^2 x}{dt^2} = -\dfrac{k}{m}x$ [we get $x(t)$ from this, not from $\psi(x)$]

$x(t) = A\sin\omega t + B\cos\omega t = C\sin(\omega t + \phi)$

get A,B or C,ϕ from initial conditions of pluck

turning point $x_{\pm}(E) = \pm\left(\dfrac{2E}{k}\right)^{1/2}$ from $E = V(x_{\pm}(E))$

ν, ω, τ

$T(t), \overline{T}$ (kinetic energy)

$V(t), \overline{V}$ (potential energy)

Today

*   simplify Schrödinger Equation to get rid of constant factors
*   solution: Gaussian envelope $\times$ Hermite polynomials
*   pictures
*   semiclassical interpretation (not in most texts): combination of classical mechanics with $\lambda(x) = h/p(x)$ (a unique source of insight)
*   vibrational transition intensities and "selection rules"

Quantum Mechanical Harmonic Oscillator (McQuarrie, Chapters 5.5, 5.8-10)

$$\widehat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k\hat{x}^2$$

$$= -\frac{\hbar^2}{2\mu}\frac{\partial}{\partial x^2} + \frac{1}{2}k\hat{x}^2$$

We can "clean up" this equation by making the substitution

$$\xi = \alpha^{1/2}x \qquad \text{where } \alpha = (k\mu)^{1/2}/\hbar \quad (\xi \text{ is dimensionless,}$$

which makes the equation "universal")

$$\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} = \frac{\hbar^2}{2\mu}\alpha\frac{\partial^2}{\partial\xi^2} = \frac{\hbar}{2}\left(\frac{k}{\mu}\right)^{1/2}\frac{\partial^2}{\partial\xi^2} = \frac{\hbar}{2}\omega\frac{\partial^2}{\partial\xi^2}$$

$$\left[\text{because } \frac{\partial}{\partial x} = \frac{\partial}{\partial\xi}\underbrace{\frac{\partial\xi}{\partial x}}_{\alpha^{1/2}}\right]$$

$$\frac{1}{2}kx^2 = \frac{1}{2}k\left(\frac{1}{\alpha}\right)\xi^2$$

$$= \frac{1}{2}\left(\frac{k}{\mu}\right)^{1/2}\hbar\xi^2 = \frac{1}{2}\hbar\omega\xi^2$$

$$\widehat{H} = \frac{\hbar\omega}{2}\left[-\frac{\partial^2}{\partial\xi^2} + \xi^2\right] \qquad (\text{ much simpler form})$$

$$\widehat{H}\psi(\xi) = E\psi(\xi)$$

$$0 = \left[-\frac{\partial^2}{\partial\xi^2} + \xi^2 - \frac{2E}{\hbar\omega}\right]\psi \qquad \begin{array}{l}(\text{entire differential equation, except}\\ \psi, \text{ is dimensionless})\end{array}$$

One can convert this into the Hermite differential equation by making the substitution $\psi(\xi) = e^{-\xi^2/2}f(\xi)$ and finding a new differential equation for f(ξ). The reason for doing this is that $e^{-\xi^2/2}$ ensures that $\psi \to 0$ as $|\xi| \to \infty$. Note that letting $\xi^2 \to \infty$ means that $2E/\hbar\omega$ is negligible with respect to ξ^2. What is the solution to the differential equation if we ignore the $\frac{2E}{\hbar\omega}$ term?   **Gaussian**

This is a very clean form of the Schrödinger equation because all of the k,μ-specific factors are absorbed into a dimensionless ξ variable. Why would we want this?

The Hermite polynomials (in integer powers of ξ) are solutions to the differential equation

$$\frac{d^2H_n}{d\xi^2} - 2\xi\frac{dH_n}{d\xi} + 2nH_n = 0 . \qquad (\text{Hermite equation})$$

There are very convenient "recursion relations" that relate the H_{n-1} to the H_n, etc.

$$\frac{dH_n}{d\xi} = 2nH_{n-1}(\xi) .$$

This looks like the effect of $\hat{p}$ on H_n (because the leading term in H_n is ξ^n).

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \text{ , rearranging}$$

$$\xi H_n(\xi) = \frac{1}{2}H_{n+1}(\xi) + nH_{n-1}(\xi).$$

This looks like the effect of $\hat{x}$ on H_n. We will use this second recursion relation to compute integrals of the form

$$\int d\xi \; \psi_n^* \xi^m \psi_p \; . \; (n, m, p \text{ are integers}).$$

These recursion relations enable us to evaluate all integrals of the form

$$\int \psi_v \left(\hat{x}^n \hat{p}^m \right) \psi_{v+\ell} dx$$

(we will postpone the actual evaluation until next lecture) and we derive the "selection rule" for nonzero integrals

$$\ell = n + m, n + m - 2, \dots - (n + m)$$

There is also a general expression (Rodrigues formula) for the H_n

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

The Hermite equation is a well known (to mathematicians) differential equation.

The solutions of the Schrödinger equation are

$$\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2} \qquad \xi = \alpha^{1/2}x$$

Gaussian envelope ensures $\psi \to 0$ as $x \to \pm\infty$

$$\psi_v(x) = \frac{1}{\left(2^v v!\right)^{1/2}} \left(\frac{\alpha}{\pi}\right)^{1/4} H_v(\xi) e^{-\xi^2/2}$$

vibrational quantum number $v = 0, 1, 2, \ldots$

N_v Normalization

Hermite polynomials

* Normalized
* $\psi_v(\pm\infty) = 0$
* $\psi_v(0) = 0$ for odd-v (odd function)

$* \left.\dfrac{d\psi_v}{dx}\right|_{x=0} = 0$ for even-v (even function), to be worked out

$E_v = \hbar\omega(v + \tfrac{1}{2})$

What do we know about orthogonality? Based on results derivable from postulates?
Non-degenerate eigenvalues.

$$\int dx\,\psi_v^*\psi_{v'} = \delta_{vv'} \qquad \text{orthonormal}$$

Semi-Classical Picture – applicable to all 1-dimensional problems for insight, prediction, and obtaining $\psi(x)$ *without solving any differential equation*.

Classical: $T(x) = E - V(x) = p(x)^2/2\mu$
            $p(x) = [2m(E - V(x))]^{1/2}$

$p(x)$ is momentum in classical mechanics but just a convenient function in quantum mechanics.

$\oplus$

Quantum: de Broglie $\lambda = \dfrac{h}{p}$

            valid not just for free particle or a piecewise constant potential

$$\boxed{=}$$
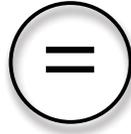
Semi-classical: $\lambda(x) \equiv \dfrac{h}{p_{\text{classical}}(x)}$

* pair of nodes nearest to x are spaced by $\lambda(x)/2$.

Qualitative Shapes of $\psi_v(x)$:

*   exponentially damped envelope, extending into non-classical regions (!!!!)
*   oscillations within classically allowed region with number of internal nodes equal to the quantum number
*   even v, even function, antinode at $x = 0$
*   outer lobes (near x_+ and x_-) are largest [see McQuarrie, page 226, Fig. 5.10 right side]
*   envelope within classically allowed region resembles what you expect from classical mechanics

$$\psi^*(x)\psi(x)dx \propto \frac{dx}{\text{v}_{\text{classical}}} \qquad \text{(slow speed} \leftrightarrow \text{high probability)}$$

$$\text{v}_{\text{classical}} = p_{\text{classical}}/\mu = \frac{1}{\mu}\{2\mu[E - V(x)]\}^{1/2}$$

To get the proportionality constant, consider the fraction of time the particle is found between x and $x + dx$:

$$\frac{\text{time } (x \rightarrow x + dx)}{\text{time } (x_- \text{ to } x_+)} = \left\{ \begin{array}{c} \text{probability of finding particle moving} \\ \text{to right between } x \text{ and } x + dx \end{array} \right\} = \frac{dx/\text{v}_{\text{classical}}(x)}{\tau/2}$$

$$\tau = \frac{1}{\nu} = \frac{2\pi}{\omega} = 2\pi\left(\frac{\mu}{k}\right)^{1/2} \left[\nu = \omega/2\pi, \ \omega = [k/\mu]^{1/2}\right]$$

$$\psi^*(x)\psi(x)dx = \frac{dx}{(\text{v}_{\text{classical}})(\tau/2)} = \frac{dx}{\left\{\frac{2}{\mu}[E - V(t)]\right\}^{1/2}} \frac{1}{\pi}\left(\frac{\mu}{k}\right)^{-1/2} = \left[\frac{k/2\pi^2}{E - V(x)}\right]^{1/2} dx$$

$$\psi^*(x)\psi(x) = \left[\frac{k/2\pi^2}{E - V(x)}\right]^{1/2} \qquad \text{gives the classical average of } \psi^*(x)\psi(x) \text{ near } x$$

(but not the phase). [To get the classical envelope, assume that the maximum value of $\psi^*\psi$ is twice the average value. [This is always a good approximation for a rapidly oscillating always positive function.] Thus the envelope of

$$\psi^*(x)\psi(x) \text{ envelope is } \left[\frac{2k/\pi^2}{E - V(x)}\right]^{1/2}\Bigg].$$

* node spacing

(1)   recall $\lambda = \dfrac{h}{p(x)}$, use classical ideas to *qualitatively* locate nodes,

(2)   nodes are closest together when p is largest (near $x = 0$), envelope and node spacing allows you to sketch $\psi*(x)\psi(x)$ without solving a differential equation.

(3)   or compute a "phase integral" $\dfrac{\Delta x}{\lambda(x)} = \dfrac{1}{2}$ (want to find value of Δx that is equal to $\lambda/2$, the distance between nodes)

replace $\lambda(x)$ by $h/p(x)$. We get

$p(x)\Delta x = \dfrac{h}{2}$ as the distance, Δx, between nodes $\left[\text{more accurately,} \int_{x}^{x+\lambda/2} dx\, p(x) = \dfrac{h}{2} \right]$

phase integral $\dfrac{2}{h}\int_{x_1}^{x_2} p_E(x)\,dx$ tells us *how many nodes* there are between x_1 and x_2 at energy E. This is the same as knowing how many bound energy levels lie at or below E.
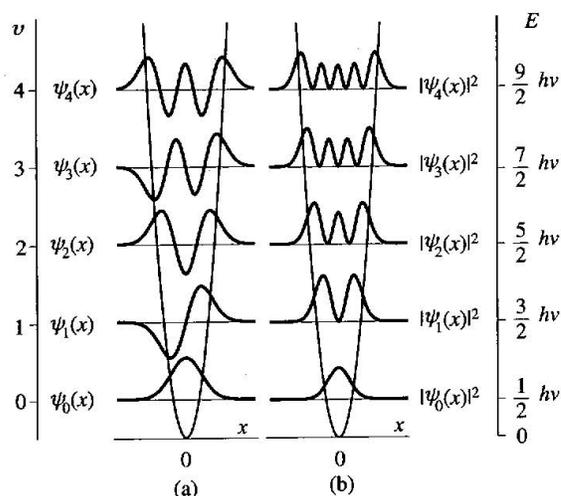
FIGURE 5.10
(a) The normalized harmonic-oscillator wave functions. (b) The probability densities for a harmonic oscillator. As in Figure 5.7, the potential energy is indicated by the parabolas in (a) and (b).

TABLE 5.3
The First Few Hermite Polynomials [a]

$H_0(\xi) = 1$	$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$	$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

a. The variable ξ is equal to $\alpha^{1/2}x$, where $\alpha = (k\mu)^{1/2}/\hbar$.

TABLE 5.4
The First Few Harmonic-Oscillator Wave Functions, Equation 5.44 [a]

$$\psi_0(x) = |0\rangle = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad \psi_2(x) = |2\rangle = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

$$\psi_1(x) = |1\rangle = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2} \qquad \psi_3(x) = |3\rangle = \left(\frac{\alpha^3}{9\pi}\right)^{1/4} (2\alpha x^3 - 3x)e^{-\alpha x^2/2}$$

a. The parameter $\alpha = (k\mu)^{1/2}/\hbar$.

McQuarrie, Donald A. Quantum Chemistry. 2nd ed. Sausalito, CA: University Science Books, 2007. Used with permission.

* non-classical tails [(extend into region where $E < V(x)$]
* x_+ lobe positive by convention
* lobes nearest x_- and x_+ largest
* nodes closest together near $x = 0$
* no zero crossings in classically forbidden region

What about pictures of $\psi^*(x)\psi(x)$?

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Non-Lecture

What do we do with these HO wavefunctions?

      1.   calculate relative intensities of vibrational transitions

2.   Use perturbation theory (Lectures #14, #15 and #18) to compute
      consequences of higher than quadratic terms in V(x)

e.g. for Morse oscillator

$$\frac{E_v}{hc} = \tilde{\omega}(v+1/2) - \widetilde{\omega x}(v+1/2)^2$$

| (˜ means cm^{-1} units) |

"anharmonicity", comes mostly
from x^3 and x^4 terms in V(x)

<u>Spectral intensities</u>

$$I_{f_i} \propto \left| \int dx\, \psi^*_{v_f} \mu(x) \psi_{v_i} \right|^2$$

electric dipole moment
(HCl vs. H_2, N_2, O_2, Cl_2)
(think of radio antenna)

hν v_f v_i

$$\mu(x) = \mu(0) + \frac{d\mu}{dx}x + \frac{1}{2}\frac{d^2\mu}{dx^2}x^2 + \ldots$$

μ_0 μ_1 μ_2

$\Delta v = 0$ $\Delta v = \pm 1$ $\Delta v = 0, \pm 2$
pure rotation   vibrational   vibrational
spectrum   fundamental   overtone

Two contributions to vibrational overtone transitions
   *   mechanical anharmonicity (Morse potential)
   *   electronic anharmonicity (higher derivatives of $\mu(x)$)

In the following we will look only at the electronic anharmonicity contributions.

$$\int dx\, \psi_{v_f}^* \left[\mu_0 + \mu_1 x + \frac{1}{2}\mu_2 x^2 \right] \psi_{v_i} = \mu_0 \int dx\, \underbrace{\psi_{v_f}^* \psi_{v_i}}_{\substack{\text{ortho-}\\ \text{normal}\\ \delta_{v_f v_i}}}$$

$$+\mu_1 \underbrace{\int dx\, \psi_{v_f}^* x \psi_{v_i}}_{\substack{\text{see recursion}\\ \text{relationship}}} + \frac{\mu_2}{2}\int dx\, \psi_{v_f}^* x^2 \psi_{v_i}$$

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi)$$

$$\underbrace{\xi H_n(\xi)}_{x\psi_v} = \frac{1}{2}\underbrace{H_{n+1}(\xi)}_{\psi_{v+1}} + n\underbrace{H_{n-1}(\xi)}_{\psi_{v-1}}$$

selection rule: $\Delta v = \pm 1$

for x^2 term (evaluate in two steps)

$$\xi^2 H_n = \frac{1}{2}\xi H_{n+1} + n\xi H_{n-1}$$

$$= \frac{1}{2}\left(\frac{1}{2}H_{n+2} + (n+1)H_n \right) + n\left(\frac{1}{2}H_n + (n-1)H_{n-2} \right)$$

$$\Delta v = 0, \pm 2$$

Next time: $\mathbf{a}^\dagger, \mathbf{a}$ treatment

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