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 $\omega=\left[k/\mu\right]^{1/2}$
- * $\mu=\frac{m_1 m_2}{m_1+m_2}$ reduced mass

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

$x(t)=A\sin\omega t+B\cos\omega t=C\sin\left(\omega t+\phi\right)$: general solution

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

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

ν,ω,τ definitions and inter-relationships

$$\left.\begin{array}{l} T(t),\bar{T} \text{ (kinetic energy)} \\ V(t),\bar{V} \text{ (potential energy)} \end{array}\right\} \text{overbar means average value}$$

Today

- * simplify Schrödinger Equation to get rid of constant factors
- * solution: Gaussian envelope × Hermite polynomial
- * pictures: at least as important as the mathematical form
- * semiclassical interpretation (not in most texts): combination of classical mechanics with quantum mechanics via $\lambda(x) = h/p(x)$ (a unique and never-ending 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

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

which makes the equation "universal")

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

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

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

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

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

$$\widehat{H}\psi(\xi) = E\psi(\xi) \qquad \left(\text{rearrange and divide by } \frac{\hbar\omega}{2}\right)$$

$$0 = \left[-\frac{\partial^2}{\partial \xi^2} + \xi^2 - \frac{2E}{\hbar\omega}\right]\psi(\xi)$$

(entire differential equation, except ψ, is dimensionless)

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 the $e^{-\xi^2/2}$ factor 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

$$\frac{d^2H_n}{d\xi^2} - 2\xi\frac{dH_n}{d\xi} + 2nH_n = 0\,.$$

(Hermite equation. H_n is a polynomial in ξ.)

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

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

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

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

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

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 when we will also derive the "selection rule" for nonzero integrals):

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

ℓ is an integer and goes from its maximum value of $n + m$ down to its minimum value in steps of 2.

There is also a general expression (Rodrigues formula) for all of 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 harmonic oscillator Schrödinger equation are

$$\underset{\substack{\uparrow\\ \text{vibrational quantum}\\ \text{number}}}{\psi_v(x)} = \underbrace{\frac{1}{(2^v v!)^{1/2}}\left(\frac{\alpha}{\pi}\right)^{1/4}}_{\substack{N_v\\ \text{Normalization}}} \underset{\substack{\uparrow\\ \text{Hermite polynomial}}}{\underbrace{\overset{\substack{\xi=\alpha^{1/2}x\\ \downarrow}}{H_v(\xi)}}}\, e^{\overbrace{-\xi^2/2}^{\substack{\text{Gaussian envelope}\\ \text{ensures } \psi\to 0\\ \text{as } x\to\pm\infty}}}$$

$v = 0, 1, 2, \ldots$ (vee, not nu!)

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

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

$E_v = \hbar\omega(v + ½)$

What do we know about orthogonality? Based on results derivable from postulates? For non-degenerate eigenvalues:

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

Semi-Classical Picture – applicable to *all* 1-dimensional problems as a basis 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.

⊕

Quantum: de Broglie $\lambda = \frac{h}{p}$
valid not just for free particle or a piecewise constant potential

⊜

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 $\psi_{\text{v}}(x)$:

- * exponentially damped envelope, extending into non-classical ($E < \text{V}(x)$) 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

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

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

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

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

τ is the quantum number independent period of the harmonic oscillator.

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

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

$$\psi^*(x)\psi(x) = \left[\frac{k/2\pi^2}{E - V(x)}\right]^{1/2}$$ gives the classical (i.e. nodeless) average of $\psi^*(x)\psi(x)$ 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 $\psi^*(x)\psi(x)$ is $\left[\left[\dfrac{2k/\pi^2}{E - V(x)}\right]^{1/2}\right]$. The envelope is the smooth curve that connects all of the maxima of $\psi^*(x)\psi(x)$ between x_- and x_+.

- * node spacing

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

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

(3) or compute a "phase integral" $\frac{\Delta x}{\lambda(x)} = \frac{1}{2}$ (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

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

The phase integral $\frac{2}{h}\int_{x_1}^{x_2} p_E(x)dx$ 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.

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

Figure removed due to copyright restrictions. See Figure 5.1 in: Merzbacher, Eugen. Quantum Mechanics. Wiley, 1997. ISBN: 9780471887027.

* non-classical tails [(extend into region where $E < V(x)$]
* x_+ lobe positive by convention (x_- lobes alternate sign as -1^v)
* lobes nearest x_- and x_+ largest
* nodes closest together near $x = 0$
* no zero crossings in classically forbidden region

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

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

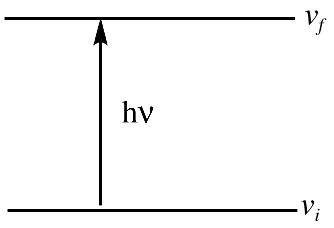
(~ means cm^{-1} units)

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

Spectral intensities

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

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



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

μ_0 μ_1 μ_2

Δv = 0
pure rotation
spectrum

Δv = ±1
vibrational
fundamental

Δv = 0, ±2
vibrational
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.

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

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

Recursion Relationships

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

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

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

for x^2 term selection rules (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