

# Lecture 19 — The Quantum Harmonic Oscillator

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**Reading:** Engel 4th ed., Chapter 7 (Sections 7.1–7.3)

## Learning Objectives

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- Set up the Schrödinger equation for the harmonic oscillator using the reduced mass
  - State the quantized energy levels and explain zero-point energy
  - Sketch the first several wavefunctions and probability densities
  - Compare the quantum and classical probability distributions
  - Connect the harmonic oscillator to real molecular vibrations
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## 1. The Classical Harmonic Oscillator

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A diatomic molecule vibrates like two masses connected by a spring. For small displacements from equilibrium, the potential is:

$$V(x) = \frac{1}{2}kx^2$$

where  $x = r - r_e$  is the displacement from equilibrium and  $k$  is the **force constant** (related to bond stiffness — units: N/m).

The classical frequency of oscillation:

$$\nu_{\text{cl}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where  $\mu$  is the **reduced mass**:

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

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## 2. The Schrödinger Equation for the Harmonic Oscillator

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$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$$

This equation has exact analytical solutions discovered by Hermite. The key results:

## Quantized Energy Levels

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega = \left(v + \frac{1}{2}\right) h\nu, \quad v = 0, 1, 2, \dots$$

where  $\omega = \sqrt{k/\mu}$  is the angular frequency and  $\nu = \omega/(2\pi)$ .

## Key Features

1. **Even spacing:**  $\Delta E = \hbar\omega = h\nu$  between all adjacent levels
2. **Zero-point energy:**  $E_0 = \frac{1}{2}\hbar\omega \neq 0$ 
  - The molecule can never stop vibrating completely
  - Required by the uncertainty principle:  $\Delta x \cdot \Delta p \geq \hbar/2$
3. **Equal spacing** is a unique feature of the harmonic potential
4. **Non-degenerate:** each energy level has exactly one wavefunction

[!NOTE] **Concept Check 19.1** Explain why the harmonic oscillator has a non-zero energy ( $E_0 = \frac{1}{2}\hbar\omega$ ) even in its lowest possible state. How does this result relate to the Heisenberg uncertainty principle?

## 3. Wavefunctions

$$\psi_v(x) = N_v H_v(\alpha x) e^{-\alpha^2 x^2/2}$$

where:

- $\alpha = \left(\frac{\mu\omega}{\hbar}\right)^{1/2} = \left(\frac{\mu k}{\hbar^2}\right)^{1/4}$
- $H_v$  are the **Hermite polynomials**
- $N_v = \left(\frac{\alpha}{\sqrt{\pi} 2^v v!}\right)^{1/2}$  is the normalization constant

### First Few Hermite Polynomials

$v$	$H_v(y)$	$\psi_v(x)$ (unnormalized)
0	1	$e^{-\alpha^2 x^2/2}$

$v$	$H_v(y)$	$\psi_v(x)$ (unnormalized)
1	$2y$	$x e^{-\alpha^2 x^2/2}$
2	$4y^2 - 2$	$(2\alpha^2 x^2 - 1)e^{-\alpha^2 x^2/2}$
3	$8y^3 - 12y$	$(2\alpha^3 x^3 - 3\alpha x)e^{-\alpha^2 x^2/2}$

## Properties of the Wavefunctions

- $\psi_v$  has  $v$  nodes
- **Parity:** Even  $v \rightarrow$  symmetric ( $\psi_v(-x) = \psi_v(x)$ ); Odd  $v \rightarrow$  antisymmetric ( $\psi_v(-x) = -\psi_v(x)$ )
- All wavefunctions decay as Gaussians at large  $|x|$
- The ground state  $\psi_0$  is itself a Gaussian — the minimum-uncertainty wave packet

## Symmetry Classification

In a molecule with symmetry, each vibrational mode belongs to an irreducible representation (from Week 6). The ground vibrational state ( $v = 0$ ) always transforms as the totally symmetric representation (e.g.,  $A_1$  in  $C_{2v}$ ).

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## 4. Classical Turning Points and Tunneling

The classical turning points are where  $E = V(x)$ :

$$x_{\text{tp}} = \pm \sqrt{\frac{2E}{k}} = \pm \sqrt{\frac{(2v+1)\hbar}{\mu\omega}}$$

Classically, the particle cannot exist beyond these points. Quantum mechanically,  $\psi_v$  extends into the classically forbidden region (exponential tail) — **tunneling into the barrier**.

For the ground state ( $v = 0$ ), the probability of finding the particle beyond the classical turning points is approximately **16%**.

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## 5. Classical vs. Quantum Probability

**Classical:** A classical oscillator spends more time near the turning points (where it slows down), so the probability density peaks at the edges.

**Quantum (low  $v$ ):** The ground state probability density peaks at the center — opposite to the classical result.

**Quantum (large  $v$ ):** The quantum probability density averaged over oscillations approaches the classical result — the **correspondence principle**.

[!NOTE] **Concept Check 19.2** Sketch the probability density for a particle in the  $v = 100$  state of a harmonic oscillator (qualitatively). Where is the particle most likely to be found, and how does this compare to the  $v = 0$  case?

## 6. Molecular Vibrational Parameters

Molecule	$\tilde{\nu}$ (cm $^{-1}$ )	$k$ (N/m)	$E_0/hc$ (cm $^{-1}$ )
H <sub>2</sub>	4401	575	2200
HCl	2991	516	1496
HBr	2649	412	1325
CO	2170	1902	1085
N <sub>2</sub>	2359	2294	1180

- Strong bonds  $\rightarrow$  large  $k \rightarrow$  high  $\tilde{\nu}$
- Light atoms (especially H)  $\rightarrow$  small  $\mu \rightarrow$  high  $\tilde{\nu}$

## Key Equations Summary

Equation	Expression
Reduced mass	$\mu = m_1 m_2 / (m_1 + m_2)$
Classical frequency	$\nu = \frac{1}{2\pi} \sqrt{k/\mu}$
Energy levels	$E_v = (v + \frac{1}{2})\hbar\omega$

Equation	Expression
Zero-point energy	$E_0 = \frac{1}{2}\hbar\omega$
Level spacing	$\Delta E = \hbar\omega$
Wavefunctions	$\psi_v = N_v H_v(\alpha x) e^{-\alpha^2 x^2/2}$

## Recent Literature Spotlight

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### "Anharmonic Force Constants Extracted from First-Principles Molecular Dynamics"

O. Hellman, I. A. Abrikosov, S. I. Simak, Physical Review Letters, **2018**, 121, 225902. [DOI](#)

This work introduces a method for extracting anharmonic force constants from ab initio molecular dynamics, enabling the calculation of phonon properties that go beyond the harmonic approximation. The temperature-dependent phonon spectra in diamond illustrate how the parabolic potential  $V = \frac{1}{2}kx^2$  taught in this lecture is only the first term in a more complete description of molecular vibrations.

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## Practice Problems

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- Force constant.** The fundamental vibrational frequency of  ${}^1\text{H}{}^{35}\text{Cl}$  is  $2991\text{ cm}^{-1}$ . Calculate (a) the reduced mass, (b) the force constant, and (c) the zero-point energy in kJ/mol.
  - Isotope effect.** Predict the fundamental frequency of  ${}^2\text{H}{}^{35}\text{Cl}$  (DCl) given that  $\tilde{\nu}(\text{HCl}) = 2991\text{ cm}^{-1}$ . Assume the force constant is unchanged.
  - Classical turning points.** Calculate the classical turning points for the  $v = 0$  and  $v = 5$  states of HCl. Express in pm and compare to the equilibrium bond length of 127.5 pm.
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Next lecture: Harmonic Oscillator Properties & Ladder Operators