

Lecture 19 — The Quantum Harmonic Oscillator

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

Learning Objectives

- 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

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 μ is the **reduced mass**:

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

2. The Schrödinger Equation for the Harmonic Oscillator

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

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

- ψ_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 ψ_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}).

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, ψ_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%**.

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 ₂	4401	575	2200
HCl	2991	516	1496
HBr	2649	412	1325
CO	2170	1902	1085
N ₂	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

"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.

Practice Problems

- Force constant.** The fundamental vibrational frequency of $^1\text{H}^{35}\text{Cl}$ is 2991 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