Lecture 10 — The Uncertainty Principle & Problem-Solving Workshop

Reading: Engel 4th ed., Chapter 3 (Sections 3.7–3.8)

Learning Objectives

- Derive the generalized uncertainty principle from the postulates
- Apply the Heisenberg uncertainty principle to physical problems
- Verify the uncertainty principle using the particle in a box
- Work through representative problems applying the postulates to the PIB

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1. The Generalized Uncertainty Principle

Statement

For any two observables A and B:

$$\boxed{\Delta A \cdot \Delta B \geq \frac{1}{2}\left|\langle[\hat{A}, \hat{B}]\rangle\right|}$$

where $\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}$ is the standard deviation of measurements of A.

Derivation Sketch

1. Define $\hat{\alpha} = \hat{A} - \langle A\rangle$ and $\hat{\beta} = \hat{B} - \langle B\rangle$
2. Consider $I(\lambda) = \int |(\hat{\alpha} + i\lambda\hat{\beta})\Psi|^2\, dx \geq 0$ for all real λ
3. Expand: $I(\lambda) = \langle\hat{\alpha}^2\rangle + \lambda^2\langle\hat{\beta}^2\rangle + i\lambda\langle[\hat{\alpha}, \hat{\beta}]\rangle \geq 0$
4. Since $[\hat{\alpha}, \hat{\beta}] = [\hat{A}, \hat{B}]$, the discriminant condition gives the result

The Heisenberg Uncertainty Principle

For position and momentum: $[\hat{x}, \hat{p}] = i\hbar$

$$\boxed{\Delta x \cdot \Delta p \geq \frac{\hbar}{2}}$$

This is not about limitations of measurement apparatus — it is a fundamental property of nature arising from the wave-like character of matter.

> [!NOTE] **Concept Check 10.1** Is it possible for a particle to be in a state where the uncertainty in its position (Δx) is exactly zero? If so, what does the uncertainty principle predict for the uncertainty in its momentum (Δp)?

Energy-Time Uncertainty

$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$

Here Δt is the time required for a significant change in the system, not an "uncertainty in time measurement." This relation explains:

- Natural linewidths of spectral lines
- Lifetimes of excited states
- Virtual particles in quantum field theory

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2. Verifying Uncertainty with the Particle in a Box

Complete Calculation for the PIB Ground State

For $\psi_1(x) = \sqrt{2/a}\sin(\pi x/a)$:

Position:

$\langle x \rangle = \frac{2}{a}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right)dx = \frac{a}{2}$

$\langle x^2 \rangle = \frac{2}{a}\int_0^a x^2\sin^2\left(\frac{\pi x}{a}\right)dx = a^2\left(\frac{1}{3} - \frac{1}{2\pi^2}\right)$

$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = a\sqrt{\frac{1}{12} - \frac{1}{2\pi^2}} \approx 0.181a$

Momentum:

$\langle p \rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\left(-i\hbar\frac{d}{dx}\right)\sin\left(\frac{\pi x}{a}\right)dx = 0$

$\langle p^2 \rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\left(-\hbar^2\frac{d^2}{dx^2}\right)\sin\left(\frac{\pi x}{a}\right)dx = \frac{\pi^2\hbar^2}{a^2}$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \frac{\pi\hbar}{a}$$

Verification:

$$\Delta x \cdot \Delta p = \pi\hbar\sqrt{\frac{1}{12} - \frac{1}{2\pi^2}} \approx 0.568\,\hbar > \frac{\hbar}{2} \quad \checkmark$$

The PIB ground state satisfies the uncertainty principle, but does *not* saturate the bound (only a Gaussian wave packet achieves exact equality).

> [!NOTE] **Concept Check 10.2** For the $n = 2$ PIB state, would you expect Δx to be larger or smaller than for $n = 1$? What about Δp? (Hint: think about the shape of $|\psi_2|^2$ — it has two peaks vs. one.)

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3. Physical Consequences

Zero-Point Energy from Uncertainty

The uncertainty principle forbids a particle from being simultaneously at rest ($p = 0$) and at a definite position ($\Delta x = 0$). Confined particles always have nonzero kinetic energy — the **zero-point energy**.

Quick estimate for the PIB:

$$\Delta x \sim a, \quad \Delta p \gtrsim \frac{\hbar}{2a}, \quad E_{\text{min}} \sim \frac{(\Delta p)^2}{2m} \sim \frac{\hbar^2}{8ma^2}$$

Compare to the exact ground-state energy: $E_1 = \frac{\pi^2\hbar^2}{2ma^2} = \frac{h^2}{8ma^2}$ — the same order of magnitude!

Stability of Atoms

Classical electrodynamics predicts that an orbiting electron should radiate and spiral into the nucleus. The uncertainty principle prevents this: confining the electron to a smaller region (Δx decreases) increases the momentum (Δp increases), raising the kinetic energy. The atom reaches a stable minimum-energy configuration.

Quick estimate for hydrogen:

$$E(\Delta x) \approx \frac{\hbar^2}{2m_e(\Delta x)^2} - \frac{e^2}{4\pi\epsilon_0\,\Delta x}$$

Minimizing: $\Delta x_{\text{min}} \approx a_0$ (the Bohr radius), $E_{\text{min}} \approx -13.6$ eV. The uncertainty principle gives the correct order of magnitude!

What the Uncertainty Principle Does NOT Say

- ❌ It does NOT say measurements are imprecise due to crude instruments
- ❌ It does NOT say the act of measurement always disturbs the system (though it can)
- ✅ It DOES say that conjugate variables cannot simultaneously have well-defined values
- ✅ It IS a property of the wave nature of quantum states

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4. Compatible and Incompatible Observables

Property	**Compatible ($[\hat{A}, \hat{B}] = 0$)**	**Incompatible ($[\hat{A}, \hat{B}] \neq 0$)**
Simultaneous eigenstates?	Yes	No
Measured simultaneously?	Yes, to arbitrary precision	No; $\Delta A \cdot \Delta B \geq \frac{1}{2}\lvert\langle[\hat{A}, \hat{B}]\rangle\rvert$
Example	$\hat{L}^2$ and $\hat{L}_z$	$\hat{x}$ and $\hat{p}$

PIB connection: The PIB eigenstates are eigenstates of $\hat{H}$ and $\hat{p}^2$ simultaneously (since $\hat{H} = \hat{p}^2/(2m)$ inside the box, so $[\hat{H}, \hat{p}^2] = 0$). But they are *not* eigenstates of $\hat{p}$ or $\hat{x}$ individually.

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5. Problem-Solving Workshop

Worked Problem 1: Eigenvalue Verification

Is $\psi = Axe^{-\alpha x}$ (for $x \geq 0$) an eigenfunction of the kinetic energy operator?

Apply $\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$:

$\frac{d\psi}{dx} = A(1 - \alpha x)e^{-\alpha x}$

$\frac{d^2\psi}{dx^2} = A(-2\alpha + \alpha^2 x)e^{-\alpha x}$

$\hat{T}\psi = -\frac{\hbar^2}{2m}A(\alpha^2 x - 2\alpha)e^{-\alpha x}$

This is NOT proportional to $\psi = Axe^{-\alpha x}$ (additional constant term in the parentheses), so ψ is **not** an eigenfunction of $\hat{T}$.

Worked Problem 2: Commutator Practice

Evaluate $[\hat{x}, \hat{p}^2]$.

Using the identity $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$:

$$[\hat{x}, \hat{p}^2] = [\hat{x}, \hat{p}]\hat{p} + \hat{p}[\hat{x}, \hat{p}] = i\hbar\hat{p} + \hat{p}(i\hbar) = 2i\hbar\hat{p}$$

Worked Problem 3: PIB Transition Wavelength

Conjugated dye molecules can be modeled as a PIB. β-carotene has 11 conjugated double bonds spanning $a \approx 2.4$ nm, with 22 π-electrons filling levels $n = 1$ through $n = 11$. Calculate the wavelength of the lowest-energy electronic transition ($n = 11 \to 12$).

$$\Delta E = (12^2 - 11^2)\frac{h^2}{8m_e a^2} = 23 \cdot \frac{(6.626\times10^{-34})^2}{8(9.109\times10^{-31})(2.4\times10^{-9})^2}$$

$$\Delta E \approx 3.8 \times 10^{-19}\ \mathrm{J}, \quad \lambda = \frac{hc}{\Delta E} \approx 520\ \mathrm{nm}\ (\mathrm{green})$$

This correctly predicts that β-carotene absorbs blue-green light, making it appear orange-red!

Key Equations Summary

Equation	Expression
Generalized uncertainty	$\Delta A \cdot \Delta B \geq \frac{1}{2}\|\langle[\hat{A}, \hat{B}]\rangle\|$
Position-momentum	$\Delta x \cdot \Delta p \geq \hbar/2$
Energy-time	$\Delta E \cdot \Delta t \geq \hbar/2$
Commutator identity	$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$
PIB Δx (ground state)	$a\sqrt{1/12 - 1/(2\pi^2)} \approx 0.181a$
PIB Δp (ground state)	$\pi\hbar/a$

Recent Literature Spotlight

"Fragment Molecular Orbital-Based Variational Quantum Eigensolver for Quantum Chemistry in the Age of Quantum Computing" *H. Yoshida, T. Takahashi, H. C. Watanabe, et al.*, Scientific Reports, **2024**, 14, 2564. DOI

This paper uses the variational principle on a quantum computer to find ground-state energies of molecules. The FMO/VQE algorithm works by minimizing $\langle\Psi_{\text{trial}}|\hat{H}|\Psi_{\text{trial}}\rangle$ with respect to parameterized trial wavefunctions — exactly like our uncertainty-principle-based energy estimation, but using a quantum computer to handle many-electron systems. The uncertainty principle sets the fundamental limits on what can be simultaneously known about these molecular systems.

Practice Problems

1. **Estimation.** Use the uncertainty principle to estimate the ground-state energy of a harmonic oscillator ($V = \frac{1}{2}kx^2$). Compare to the exact result $E_0 = \frac{1}{2}\hbar\omega$.

2. **Spectral linewidths.** An excited state has a lifetime of $\tau = 10^{-8}$ s. Estimate the minimum uncertainty in the energy of the emitted photon and the corresponding natural linewidth $\Delta\nu$.

3. **PIB uncertainty for $n = 2$.** Calculate Δx and Δp for the $n = 2$ PIB state and verify $\Delta x \cdot \Delta p \geq \hbar/2$.

Next lecture: Particle in 2-D and 3-D Boxes — Degeneracy