# Quantum mechanics and atomic physics

GRE undergraduate preparation · local supported objectives

# Quantum mechanics

- Normalise wavefunctions and read probabilities from coefficients.
- Use operators, eigenvalues and expectation values.
- Know the infinite well and harmonic oscillator by heart.
- Decide which observables commute.

# Wavefunctions and normalisation

- Normalise first, then calculate any probability.
- $\psi$ must be continuous; where $V$ is finite, $d\psi/dx$ is continuous too.
- A **wavefunction** multiplied by a constant phase $e^{i\alpha}$ describes the same state.

# Measurement probabilities

- A measurement gives one **eigenvalue 本征值** $E_j$, with probability $|c_j|^2$.
- After the measurement, the state is $\phi_j$; measuring again at once gives $E_j$ again.
- Relative phases between the $c_j$ change position densities, but not these energy probabilities.

# Observables and expectation values

- $\langle A \rangle$ need not be a possible single result.
- Momentum: $\hat{p} = -i\hbar\, d/dx$. Energy: $\hat{H} = \hat{p}^2/2m + V(x)$.

$$\langle A \rangle = \int \psi^* \hat{A}\, \psi \, dx = \sum_j |c_j|^2 a_j$$

# The infinite well

- The lowest energy is not zero: a confined particle always moves. $n = 0$ would give $\psi = 0$, which is not a state.
- Doubling $L$ divides every level by 4.

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \qquad E_n = \frac{n^2 h^2}{8mL^2} = n^2 E_1, \quad n = 1, 2, 3, \ldots$$

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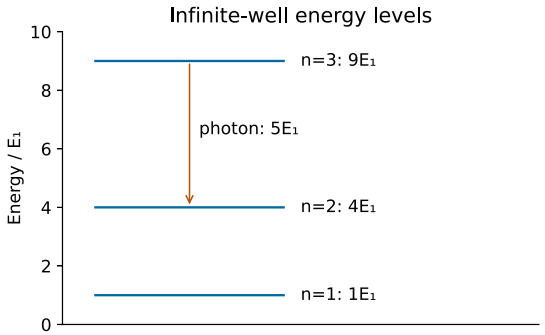
# Figure: The infinite well




- Levels scale as $n^2$, so the $3 \to 2$ photon carries $9E_1 - 4E_1 = 5E_1$
- Read the axes and units first.

# The harmonic oscillator

- The ground state has **zero-point energy 零点能** $\frac{1}{2}\hbar\omega$ and a Gaussian **wavefunction**.
- Its photons all have energy $\hbar\omega$, because neighbouring levels are $\hbar\omega$ apart.

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

# Commutators and uncertainty

- $[x, p] = i\hbar$, which leads to $\Delta x \Delta p \geq \hbar/2$.
- $p$ commutes with $p^2/2m$ but not with $V(x)$, so momentum is conserved only for a free particle.
- $[L_x, L_y] = i\hbar L_z$, but $L^2$ commutes with each component: you can know $L^2$ and $L_z$ together.

# Worked example: a superposition

- Check **normalisation**: $(1^2 + 2^2)/5 = 1$.
- Probabilities: $P(E_1) = 1/5$ and $P(E_2) = 4/5$.
- Average energy: $\langle E \rangle = \frac{1}{5}E_1 + \frac{4}{5}(4E_1) = 3.4\,E_1$, which is not one of the allowed energies.

# Worked example: an electron in a 1 nm box

- Ground state: $E_1 = \dfrac{h^2}{8mL^2} = \dfrac{(6.63\times10^{-34})^2}{8(9.11\times10^{-31})(1.0\times10^{-18})} = 6.0\times10^{-20}$ J $= 0.38$ eV.
- The $3 \to 2$ photon has $5E_1 = 1.9$ eV, so $\lambda = 1240/1.9 = 660$ nm: red light.
- This is roughly why some dye molecules with long chains are coloured.

# Common errors

- Calculating probabilities before normalising.
- Treating $\langle E \rangle$ as a possible measured result.
- Starting the infinite well at $n = 0$, or the oscillator at $n = 1$.

# Common errors (2)

- Mixing $h$ and $\hbar$: $n^2h^2/8mL^2$ and $n^2\pi^2\hbar^2/2mL^2$ are the same, but mixed forms are off by $4\pi^2$.
- Assuming $L_x$ and $L_z$ can both be definite.

# Key terms

- **wavefunction**: The function whose squared size gives the probability density of a particle.
- **normalisation**: Scaling a **wavefunction** so the total probability is one.
- **eigenvalue**: A possible result of measuring an observable.
- **Hermitian**: Equal to its own conjugate transpose, so with real eigenvalues.

# Check yourself

- The width of an infinite well is doubled. What happens to $E_1$?
- A harmonic oscillator has $\hbar\omega = 0.20$ eV. What are its ground-state energy and the energy of its photons?
- Can a measurement give definite values of both $L_x$ and $L_z$?