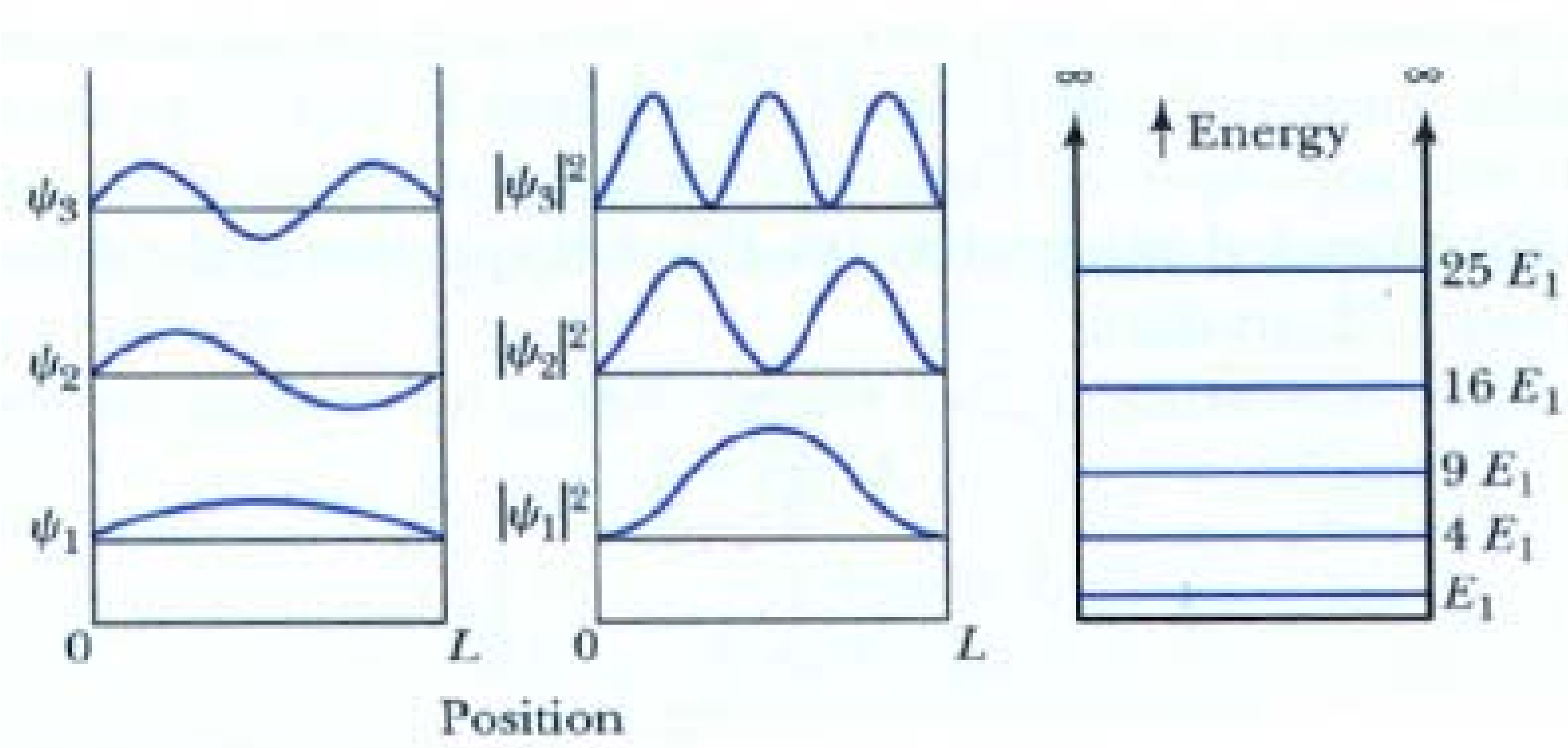
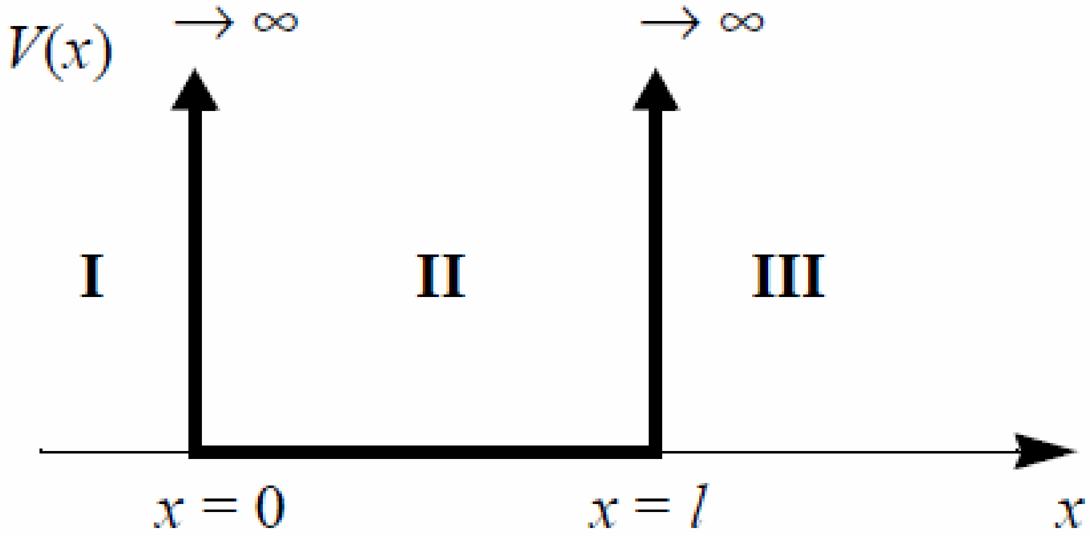
Wavefunctions and Probability Density



- **Think what might happen to the probability density when the quantum number *n* is very high**



$$\psi(x) = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right) \text{ for } 0 \le x \le l;\ \psi(x) = 0 \text{ elsewhere}$$

$$E = \frac{n^2h^2}{8mL^2}, n = 1, 2, 3, \cdots$$

Orthogonality of wavefunctions

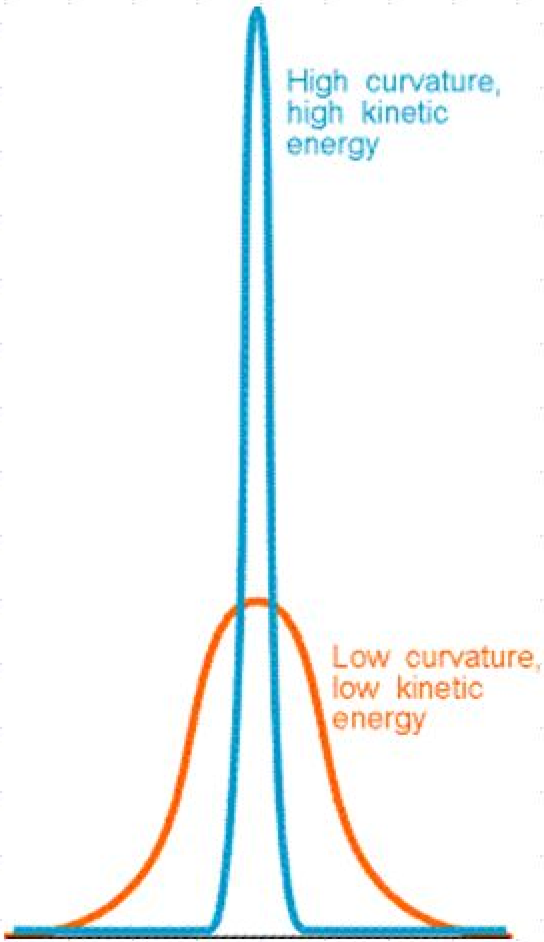
$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \frac{2}{l} \int_0^l \sin\left(\frac{n_i \pi x}{l}\right) \sin\left(\frac{n_j \pi x}{l}\right) dx = \left(\frac{2}{l} \cdot \frac{l}{\pi}\right) \int_0^l \sin(n_i \tau) \sin(n_j \tau) dx \ ,$$

where $\tau = \pi x / l$. As $\sin\alpha \sin\beta = (1/2)[\cos(\alpha - \beta) - \cos(\alpha + \beta)]$, we find

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = 0, \ \ i \neq j \ .$$

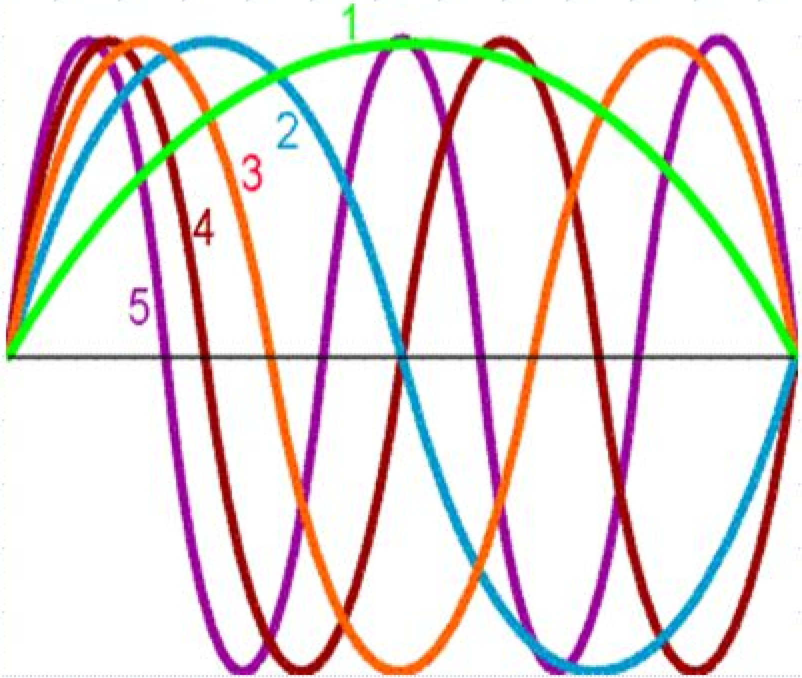
The Curvature of a Wavefunction

- The average kinetic energy of a particle can be ‘determined’ by noting its average curvature.



The Solutions for the Particle in a 'Box'

- The first five normalized wavefunctions of a particle in a box.
- Successive functions possess one more half wave and a shorter wavelength.



Pay attention to the increasing curvatures, this being a reflection of kinetic energy increasing as a function of the quantum number *n*.

The Hamiltonian for the particle inside the box is the kinetic energy operator.

$$\hat{\mathcal{H}} = \frac{-\hbar^2}{2\,m}\,\frac{d^2}{dx^2}$$

Applying the Hamiltonian within the Schrödinger equation implies that we find the energy for the particle-in-a-box by taking the second derivative of the wavefunction and multiplying by some constants.

Recall from calculus that the second derivative is a measure of the curvature of a function. When the wavefunction has the correct energy, i.e., the correct curvature, the boundary conditions are met. Thus looking at the curvature of a particle-in-a-box wavefunction can help in finding correct energy eigenvalues.

Also, since the kinetic energy operator is proportional to the second derivative, the curvature of a particle's wavefunction is a measure of the particle's kinetic energy.

Make sure you know how to find the expectation values as discussed in class!