Physical Chemistry 2

Lecture 4. Particle in a Box

June 30th, 2021

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Topics in Lecture 4

Review on postulates of quantum mechanics

Review on Hermitian operators and Dirac notation

Particle-in-a-Box problem

In Atkins' *Physical Chemistry* (11th ed.),

7D Translational motion

Main Reference for this lecture

Donald A. McQuarrie, John D. Simon
Physical Chemistry: A Molecular Approach (2nd ed.), University Science Books (1997).

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Review

Postulate 1

The state of a quantum-mechanical system is completely specified by a function $\psi(x)$ that depends upon the coordinate of the particle. All possible information about the system can be derived from $\psi(x)$. This function, called the wave function or the state function, has the important property that $\psi^*(x)\psi(x)dx$ is the probability that the particle lies in the interval dx, located at the position x.

Schrödinger equation

$$\hat{H}\psi = E\psi \text{ where } \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

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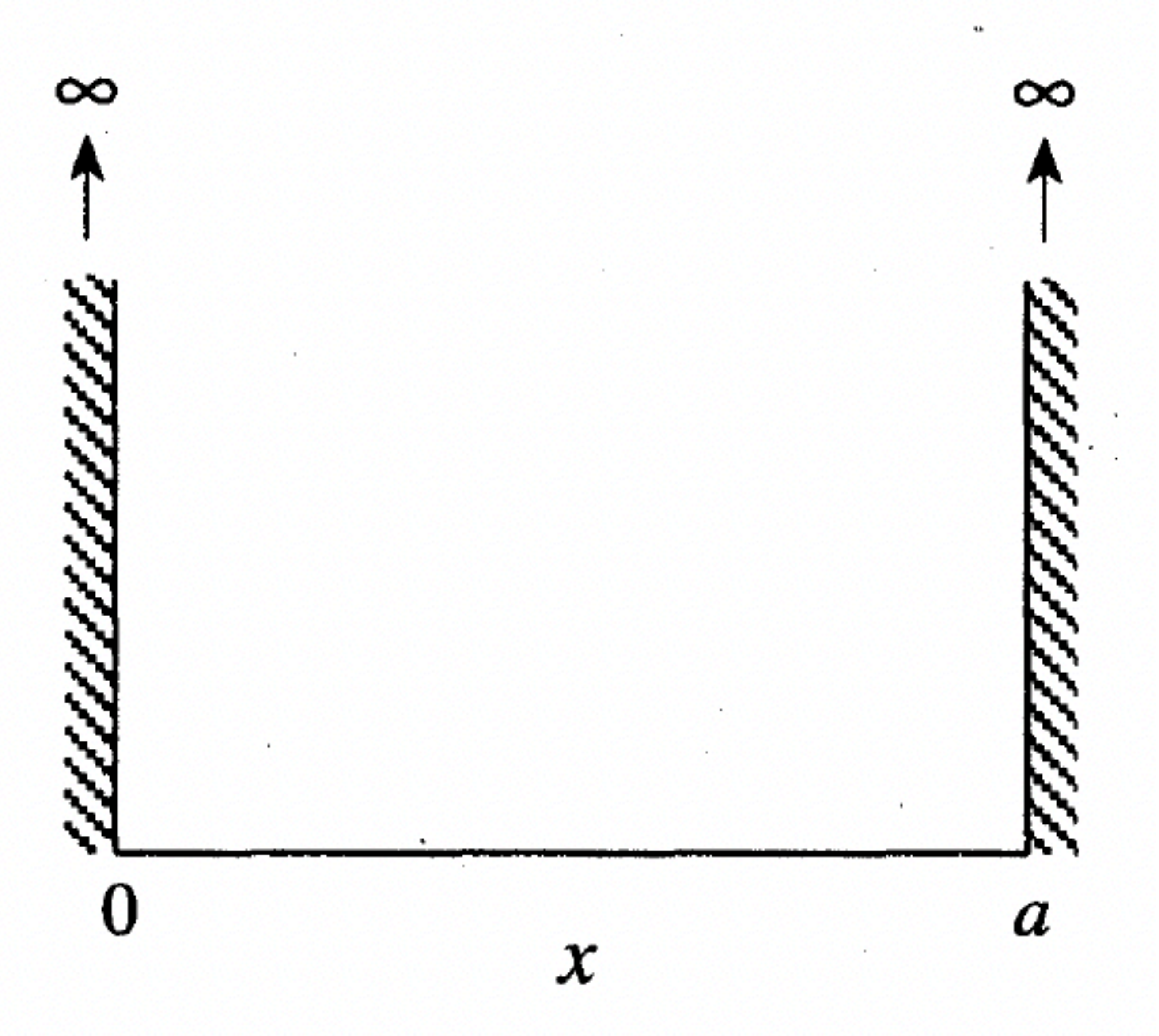
Particle-in-a-box

Consider a free particle of mass m constrained to lie along the x-axis between $0 \leq x \leq L$.
Free particle means that the particle experiences no potential energy.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$$

Precisely, $V(x) = 0$ if $0 \leq x \leq L$, $V(x) = \infty$ otherwise



$$\frac{d^2}{dx^2}\psi(x) = -\frac{2mE}{\hbar^2}\psi(x) = -k^2\psi(x) \text{ where } k^2 = \frac{2mE}{\hbar^2}$$

Special solutions of this differential equation are

$$\sin kx, \ \cos kx$$

Therefore, general solution for this equation is

$$\psi(x) = A\sin kx + B\cos kx$$

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To find the coefficients, we need some *boundary conditions*. Since the particle is restricted inside the box, the probability that the particle is found outside this region is zero. Therefore, wavefunction outside the box should be zero. We have learned that wavefunction should continuous. Therefore,

$$\psi(0) = \psi(L) = 0$$

$$\psi(0) = B\cos 0 = 0 \implies B = 0$$

$$\psi(L) = A\sin kL = 0 \implies kL = n\pi \ (n = 1,2,3,\ldots)$$

$$\psi(x) = A\sin\frac{n\pi x}{L} \ (n = 1,2,\ldots)$$

Normalization

$$1 = \int \psi^*(x)\psi(x)\,dx = |A|^2 \int_0^L \sin^2\frac{n\pi x}{L}\,dx = \frac{|A|^2}{2}\int_0^L 1 - \cos\frac{2n\pi x}{L}\,dx = |A|^2\frac{L}{2} \implies |A| = \sqrt{\frac{2}{L}}$$

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \ (n = 1,2,\ldots)$$

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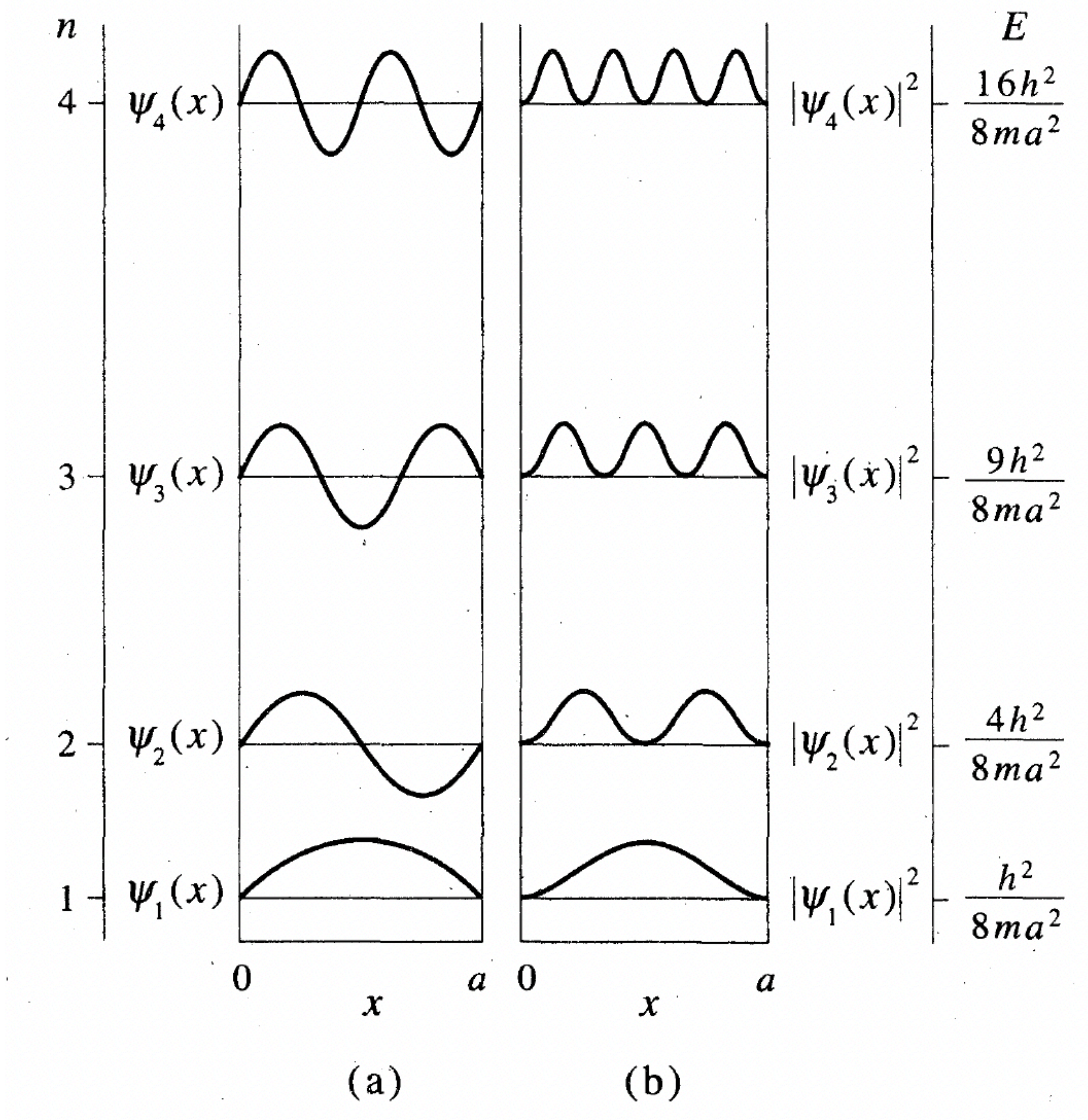
Energy is given by

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \cdot \frac{n^2\pi^2}{L^2} = \frac{n^2 h^2}{8mL^2}$$

We can calculate probability distribution with $|\psi|^2$.



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Expectation values

$$\langle x \rangle = \int \psi^* x \psi \, dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} \, dx = \frac{L}{2}$$

$$\langle x^2 \rangle = \int \psi^* x^2 \psi \, dx = \frac{2}{L} \int_0^L x^2 \sin^2 \frac{n\pi x}{L} \, dx = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\sigma_x = \langle x^2 \rangle - \langle x \rangle^2 = \frac{L}{2\pi n} \left(\frac{\pi^2 n^2}{3} - 2 \right)^{1/2}$$

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

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

$$\sigma_p = \frac{n\pi\hbar}{L}$$

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Uncertainty principle

$$\sigma_x = \left\langle x^2 \right\rangle - \langle x \rangle^2 = \frac{L}{2\pi n}\left(\frac{\pi^2 n^2}{3} - 2\right)^{1/2}, \ \sigma_p = \frac{n\pi\hbar}{L}$$

$$\sigma_x \sigma_p = \frac{\hbar}{2}\left(\frac{\pi^2 n^2}{3} - 2\right)^{1/2} > \frac{\hbar}{2}$$

Properties of wavefunctions

- wavefunctions are alternately even and odd.
- As energy increase, each state has one more node.
- Wavefunctions are mutually orthogonal.

$$\int \psi_m^* \psi_n \, dx = \left\langle \psi_m \,|\, \psi_n \right\rangle = \delta_{mn}$$

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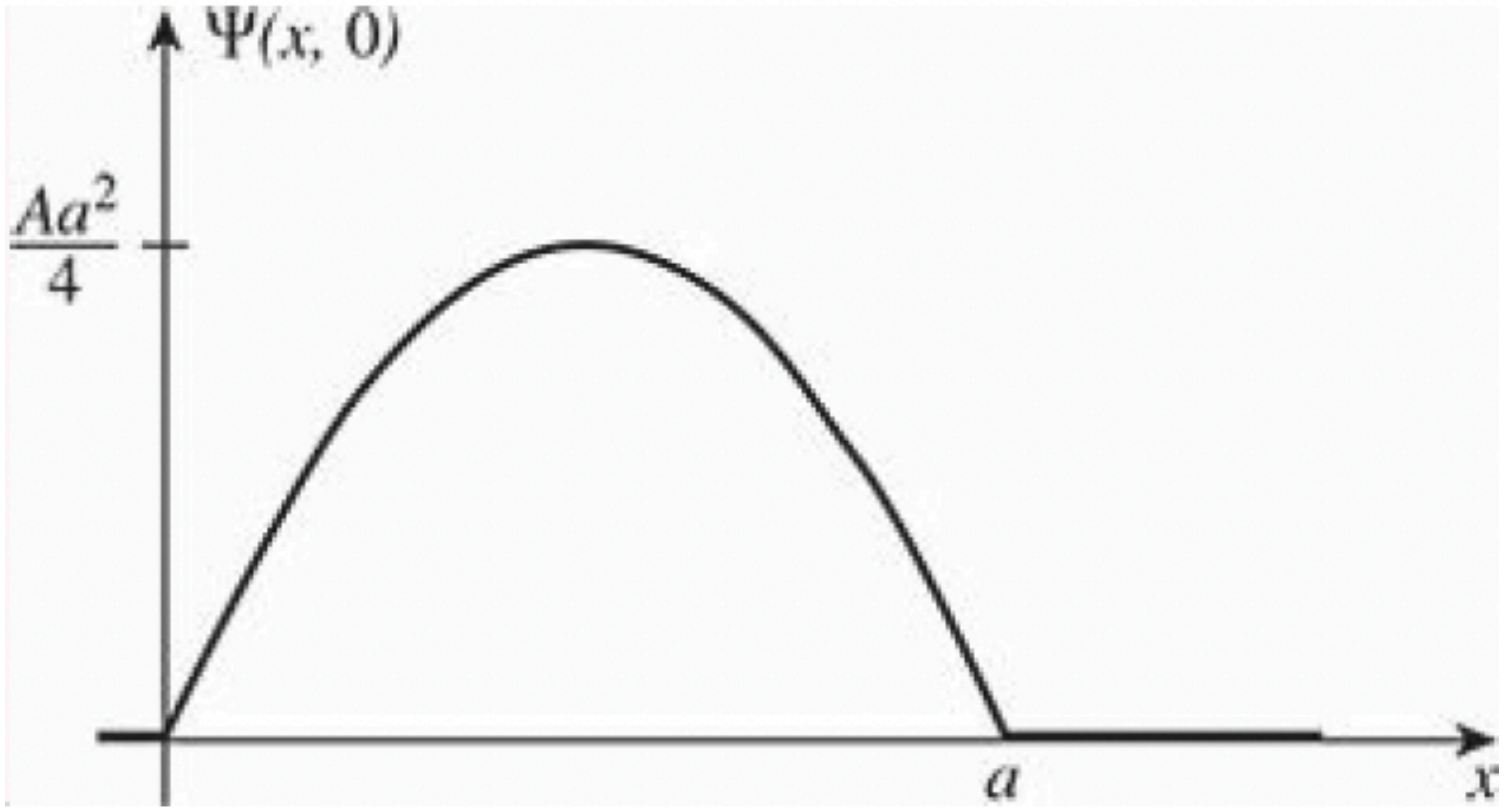
The eigenfunctions are *complete*. Any other functions can be expressed as a linear combination of them.

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

Example. A particle in the infinite square well has the initial wave function

$$\Psi(x,0) = Ax(a-x)$$

For some constant A. Outside the well, of course, $\Psi = 0$. Find $\Psi(x,t)$



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