Chapter 10 Part 4

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Orthogonality

- Recall that the following is true for a normalized wavefunction with quantum number n.

$$\int_{-\infty}^{+\infty} \Psi_n^* \Psi_n d\tau = 1$$

- However, if two wavefunctions with different quantum numbers are used, orthogonality requires the value of the integral to be exactly zero.

$$\int_{-\infty}^{+\infty} \Psi_m^* \Psi_n d\tau = 0 \qquad \Psi_{\mathrm{m}} \neq \Psi_{\mathrm{n}}$$

Orthonormality

- Combining these, we get the idea of orthonormality, which applies to wavefunctions within the same system.

$$\int_{-\infty}^{+\infty} \Psi_m^* \Psi_n d\tau = \begin{Bmatrix} 0 \text{ if } m \neq n \\ 1 \text{ if } m = n \end{Bmatrix}$$

- Note that the orthonormality condition requires that no operator be present inside the integral.

Orthogonality

Demonstrate explicitly that for the 1-D particle-in-a-box, Ψ_1, is orthogonal to Ψ_2.

Orthogonality

$$\int_0^a \left(\sqrt{\frac{2}{a}}\sin\frac{1\pi x}{a}\right)\left(\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}\right)dx = \frac{2}{a}\int_0^a \sin\frac{1\pi x}{a}\sin\frac{2\pi x}{a}$$

$$\frac{2}{a}\cdot\left[\frac{\sin\left(\left(\frac{1\pi}{a}-\frac{2\pi}{a}\right)x\right)}{2\left(\frac{1\pi}{a}-\frac{2\pi}{a}\right)} - \frac{\sin\left(\left(\frac{1\pi}{a}+\frac{2\pi}{a}\right)x\right)}{2\left(\frac{1\pi}{a}+\frac{2\pi}{a}\right)}\Big|_0^a\right]$$

$$= \frac{2}{a}\cdot\left[\frac{\sin\left(\left(\frac{-1\pi}{a}\right)x\right)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\left(\frac{3\pi}{a}\right)x\right)}{\left(\frac{6\pi}{a}\right)}\Big|_0^a\right]$$

$$= \frac{2}{a}\left[\frac{\sin\left(\left(\frac{-1\pi}{a}\right)a\right)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\left(\frac{3\pi}{a}\right)a\right)}{\left(\frac{6\pi}{a}\right)}\right] - \frac{2}{a}\left[\frac{\sin\left(\left(\frac{-1\pi}{a}\right)0\right)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\left(\frac{3\pi}{a}\right)0\right)}{\left(\frac{6\pi}{a}\right)}\right]$$

Orthogonality

$$= \frac{2}{a}\left[\frac{\sin\left(\left(\frac{-1\pi}{a}\right)a\right)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\left(\frac{3\pi}{a}\right)a\right)}{\left(\frac{6\pi}{a}\right)}\right] - \frac{2}{a}\left[\frac{\sin\left(\left(\frac{-1\pi}{a}\right)0\right)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin\left(\left(\frac{3\pi}{a}\right)0\right)}{\left(\frac{6\pi}{a}\right)}\right]$$

$$= \frac{2}{a}\left[\frac{\sin(-\pi)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin(3\pi)}{\left(\frac{6\pi}{a}\right)}\right] - \frac{2}{a}\left[\frac{\sin(0)}{\left(-\frac{2\pi}{a}\right)} - \frac{\sin(0)}{\left(\frac{6\pi}{a}\right)}\right]$$

$$= \frac{2}{a}[0 - 0] - \frac{2}{a}[0 - 0] = 0$$

Nonzero Potential Energies

Verify that Ψ_{111} of the 3D particle-in-a-box is indeed an eigenfunction of the 3D Schrodinger equation and determine the energy eigenvalue. Use 0.75 as the constant potential energy.

Nonzero Potential Energies

$$\Psi_{111}(x,y,z) = \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\cdot\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\cdot\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}$$

$$\frac{-\hbar^2}{2m}\left(YZ\frac{\partial^2}{\partial x^2}X + XZ\frac{\partial^2}{\partial y^2}Y + XY\frac{\partial^2}{\partial z^2}Z\right) = E\Psi(x,y,z)$$

$$\left[\frac{-\hbar^2}{2m}\left(\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\cdot\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}\left(-\frac{\pi^2}{a^2}\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\right) + \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\right.\right.$$
$$\left.\left.\cdot\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}\left(-\frac{\pi^2}{b^2}\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\right) + \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\cdot\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\left(-\frac{\pi^2}{c^2}\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}\right)\right) + 0.75\right]$$
$$= E\Psi(x,y,z)$$

Nonzero Potential Energies

$$\left[\frac{-\hbar^2}{2m}\left(-\frac{\pi^2}{a^2}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\cdot\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\cdot\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}\right)\right.\right.$$

$$-\frac{\pi^2}{b^2}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\cdot\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\cdot\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}\right)$$

$$\left.\left.-\frac{\pi^2}{c^2}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\cdot\sqrt{\frac{2}{b}}\sin\frac{\pi y}{b}\cdot\sqrt{\frac{2}{c}}\sin\frac{\pi z}{c}\right)\right)+0.75\right]=E\Psi(x,y,z)$$

$$\left[\frac{-\hbar^2}{2m}\left(-\frac{\pi^2}{a^2}\Psi(x,y,z)-\frac{\pi^2}{b^2}\Psi(x,y,z)-\frac{\pi^2}{c^2}\Psi(x,y,z)\right)+0.75\right]=E\Psi(x,y,z)$$

$$\left[\frac{\pi^2\hbar^2}{2m}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)+0.75\right]\Psi(x,y,z)=E\Psi(x,y,z)$$

$$E=\left[\frac{\pi^2\hbar^2}{2m}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)+0.75\right]$$