# Exercise 9.4.5

An atomic (quantum mechanical) particle is confined inside a rectangular box of sides $a$, $b$, and $c$. The particle is described by a wave function $\psi$ that satisfies the Schrödinger wave equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi.$$

The wave function is required to vanish at each surface of the box (but not to be identically zero). This condition imposes constraints on the separation constants and therefore on the energy $E$. What is the smallest value of $E$ for which such a solution can be obtained?

$$ANS. \quad E = \frac{\pi^2\hbar^2}{2m}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right).$$

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**Solution**

Since the box is rectangular, the Laplacian operator will be expanded in Cartesian coordinates.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) = E\psi, \qquad \begin{array}{l} 0 < x < a \\ 0 < y < b \\ 0 < z < c \end{array}$$

The boundary conditions associated with the Schrödinger equation are as follows.

$$\begin{array}{lll} \psi(0,y,z)=0 & \psi(x,0,z)=0 & \psi(x,y,0)=0 \\ \psi(a,y,z)=0 & \psi(x,b,z)=0 & \psi(x,y,c)=0 \end{array}$$

Because the PDE and the boundary conditions are linear and homogeneous, the method of separation of variables may be applied. Assume a product solution of the form $\psi(x,y,z) = X(x)Y(y)Z(z)$ and substitute it into the PDE

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}[X(x)Y(y)Z(z)]+\frac{\partial^2}{\partial y^2}[X(x)Y(y)Z(z)]+\frac{\partial^2}{\partial z^2}[X(x)Y(y)Z(z)]\right] = E[X(x)Y(y)Z(z)]$$

and the boundary conditions.

$$\begin{array}{lllll} \psi(0,y,z)=0 & \to & X(0)Y(y)Z(z)=0 & \to & X(0)=0 \\ \psi(a,y,z)=0 & \to & X(a)Y(y)Z(z)=0 & \to & X(a)=0 \\ \psi(x,0,z)=0 & \to & X(x)Y(0)Z(z)=0 & \to & Y(0)=0 \\ \psi(x,b,z)=0 & \to & X(x)Y(b)Z(z)=0 & \to & Y(b)=0 \\ \psi(x,y,0)=0 & \to & X(x)Y(y)Z(0)=0 & \to & Z(0)=0 \\ \psi(x,y,c)=0 & \to & X(x)Y(y)Z(c)=0 & \to & Z(c)=0 \end{array}$$

Proceed to separate variables in the PDE.

$$-\frac{\hbar^2}{2m}\left[X''(x)Y(y)Z(z)+X(x)Y''(y)Z(z)+X(x)Y(y)Z''(z)\right] = E[X(x)Y(y)Z(z)]$$

Multiply both sides by $-2m/\hbar^2$.

$$X''(x)Y(y)Z(z)+X(x)Y''(y)Z(z)+X(x)Y(y)Z''(z) = -\frac{2mE}{\hbar^2}X(x)Y(y)Z(z)$$

Divide both sides by $X(x)Y(y)Z(z)$.

$$\frac{X''}{X}+\frac{Y''}{Y}+\frac{Z''}{Z}=-\frac{2mE}{\hbar^2}$$

Bring the second and third terms to the right side.

$$\underbrace{\frac{X''}{X}}_{\text{function of } x}=\underbrace{-\frac{2mE}{\hbar^2}-\frac{Y''}{Y}-\frac{Z''}{Z}}_{\text{function of } y \text{ and } z}$$

The only way for a function of $x$ to be equal to a function of $y$ and $z$ is if both are equal to a constant $\lambda$.

$$\frac{X''}{X}=-\frac{2mE}{\hbar^2}-\frac{Y''}{Y}-\frac{Z''}{Z}=\lambda$$

The second of these equations is

$$-\frac{2mE}{\hbar^2}-\frac{Y''}{Y}-\frac{Z''}{Z}=\lambda.$$

Bring the second term to the right side and bring $\lambda$ to the left side.

$$\underbrace{-\frac{2mE}{\hbar^2}-\lambda-\frac{Z''}{Z}}_{\text{function of } z}=\underbrace{\frac{Y''}{Y}}_{\text{function of } y}$$

The only way for a function of $z$ to be equal to a function of $y$ is if both are equal to another constant $\mu$.

$$-\frac{2mE}{\hbar^2}-\lambda-\frac{Z''}{Z}=\frac{Y''}{Y}=\mu$$

In summary, by using the method of separation of variables, the PDE has reduced to three ODEs—one in $x$, one in $y$, and one in $z$.

$$\left.\begin{aligned}\frac{X''}{X}&=\lambda\\ \frac{Y''}{Y}&=\mu\\ -\frac{2mE}{\hbar^2}-\lambda-\frac{Z''}{Z}&=\mu\end{aligned}\right\}$$

Values of $\lambda$ and $\mu$ that result in nontrivial solutions to the ODEs are called the eigenvalues, and the nontrivial solutions themselves are called the eigenfunctions. The ODE for $X$ will now be solved. Suppose first that $\lambda$ is positive: $\lambda=\alpha^2$.

$$X''=\alpha^2X$$

The general solution is written in terms of hyperbolic sine and hyperbolic cosine.

$$X(x)=C_1\cosh\alpha x+C_2\sinh\alpha x$$

Apply the boundary conditions to determine $C_1$ and $C_2$.

$$\begin{aligned}X(0)&=C_1=0\\ X(a)&=C_1\cosh\alpha a+C_2\sinh\alpha a=0\end{aligned}$$

The second equation reduces to $C_2 \sinh \alpha a = 0$. Since hyperbolic sine is not oscillatory, $C_2$ must be zero. The trivial solution $X(x) = 0$ results, which means there are no positive eigenvalues. Suppose secondly that $\lambda$ is zero: $\lambda = 0$.

$$X'' = 0$$

The general solution is obtained by integrating both sides with respect to $x$ twice.

$$X(x) = C_3 x + C_4$$

Apply the boundary conditions to determine $C_3$ and $C_4$.

$$\begin{aligned} X(0) &= C_4 = 0 \\ X(a) &= C_3 a + C_4 = 0 \end{aligned}$$

The second equation reduces to $C_3 = 0$. The trivial solution $X(x) = 0$ is obtained, which means zero is not an eigenvalue. Suppose thirdly that $\lambda$ is negative: $\lambda = -\beta^2$.

$$X'' = -\beta^2 X$$

The general solution is written in terms of sine and cosine.

$$X(x) = C_5 \cos \beta x + C_6 \sin \beta x$$

Apply the boundary conditions to determine $C_5$ and $C_6$.

$$\begin{aligned} X(0) &= C_5 = 0 \\ X(a) &= C_5 \cos \beta a + C_6 \sin \beta a = 0 \end{aligned}$$

The second equation reduces to $C_6 \sin \beta a = 0$. To avoid getting the trivial solution, we insist that $C_6 \neq 0$. Then

$$\begin{aligned} \sin \beta a &= 0 \\ \beta a &= k\pi, \quad k = 1, 2, \ldots \\ \beta_k &= \frac{k\pi}{a}, \quad k = 1, 2, \ldots. \end{aligned}$$

Note that negative values of $k$ are excluded because they lead to redundant values of $\lambda$. The negative eigenvalues are $\lambda = -k^2\pi^2/a^2$, and the eigenfunctions associated with them are

$$\begin{aligned} X(x) &= C_5 \cos \beta x + C_6 \sin \beta x \\ &= C_6 \sin \beta x \quad \to \quad X_k(x) = \sin \frac{k\pi x}{a}. \end{aligned}$$

The ODE for $Y$ is the same as the one for $X$, and its boundary conditions are similar. Thus, there are negative eigenvalues $\mu = -l^2\pi^2/b^2$ for $l = 1, 2, \ldots$, and the eigenfunctions associated with them are

$$Y_l(x) = \sin \frac{l\pi y}{b}.$$

The ODE for $Z$ will now be solved.

$$-\frac{2mE}{\hbar^2} - \lambda - \frac{Z''}{Z} = \mu, \qquad Z(0) = 0, \; Z(c) = 0$$

Substitute the values for $\lambda$ and $\mu$.

$$-\frac{2mE}{\hbar^2} + \frac{k^2\pi^2}{a^2} - \frac{Z''}{Z} = -\frac{l^2\pi^2}{b^2}$$

$$Z'' = -\left(\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}\right) Z$$

If the value in parentheses is negative, then $Z$ will be in terms of hyperbolic sine and hyperbolic cosine. This will lead to the trivial solution as before. The same is true if the value in parentheses is zero. We will assume then that it is positive.

$$Z(z) = C_7 \cos\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}z + C_8 \sin\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}z$$

Apply the boundary conditions to determine $C_7$ and $C_8$.

$$Z(0) = C_7 = 0$$

$$Z(c) = C_7 \cos\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}c + C_8 \sin\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}c = 0$$

The second equation reduces to

$$C_8 \sin\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}c = 0.$$

To avoid getting the trivial solution, we insist that $C_8 \neq 0$. Then

$$\sin\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}c = 0$$

$$\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}c = n\pi, \quad n = 1, 2, \ldots$$

$$\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}} = \frac{n\pi}{c}.$$

Square both sides and solve for the energy $E$.

$$\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2} = \frac{n^2\pi^2}{c^2}$$

$$\frac{2mE}{\hbar^2} = \frac{k^2\pi^2}{a^2} + \frac{l^2\pi^2}{b^2} + \frac{n^2\pi^2}{c^2}$$

$$= \pi^2\left(\frac{k^2}{a^2} + \frac{l^2}{b^2} + \frac{n^2}{c^2}\right)$$

Multiply both sides by $\hbar^2/(2m)$.

$$E = \frac{\pi^2\hbar^2}{2m}\left(\frac{k^2}{a^2} + \frac{l^2}{b^2} + \frac{n^2}{c^2}\right)$$

The eigenfunctions associated with $E$ are

$$\begin{aligned} Z(z) &= C_7 \cos\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}z + C_8 \sin\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}z \\ &= C_8 \sin\sqrt{\frac{2mE}{\hbar^2} - \frac{k^2\pi^2}{a^2} - \frac{l^2\pi^2}{b^2}}z \quad \rightarrow \quad Z_n(z) = \sin\frac{n\pi z}{c}. \end{aligned}$$

The smallest energy occurs for the smallest values of $k$, $l$, and $n$, namely $k = 1$, $l = 1$, and $n = 1$. Therefore,

$$E_{\text{minimum}} = \frac{\pi^2\hbar^2}{2m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right).$$

According to the principle of superposition, the general solution for the wave function is a linear combination of the eigenfunctions over all values of $k$, $l$, and $n$.

$$\psi(x, y, z) = \sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\sum_{n=1}^{\infty} B_{kln} \sin\frac{k\pi x}{a} \sin\frac{l\pi y}{b} \sin\frac{n\pi z}{c}$$