(3.4.) Show that \((\cos ax)(\cos by)(\cos cz)\) is an eigenfunction of the operator,

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]

which is called the Laplacian operator.

\[
\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \cos (a x) \cos (b y) \cos (c z)
\]

\[
= \left[-a^2 \cos (a x)\right] \cos (b y) \cos (c z)
\]

\[
+ \cos (a x) \left[-b^2 \cos (b y)\right] \cos (c z)
\]

\[
+ \cos (a x) \cos (b y) \left[-c^2 \cos (c z)\right]
\]

\[
= (-a^2 - b^2 - c^2) \cos (a x) \cos (b y) \cos (c z)
\]

\(\text{QED}\)

it is an eigenfunction of the Laplacian, with eigenvalue

\[-(a^2 + b^2 + c^2)\]
In Section 3–5, we applied the equations for a particle in a box to the π electrons in butadiene. This simple model is called the free-electron model. Using the same argument, show that the length of hexatriene can be estimated to be 867 pm. Show that the first electronic transition is predicted to occur at $2.8 \times 10^4 \text{ cm}^{-1}$. (Remember that hexatriene has six π electrons.)

$$E_n = \frac{\hbar^2 n^2}{8m_e a^2}, n = 1, 2, \ldots$$

$$\lambda \sim \frac{\pi}{k} = \frac{\pi}{2\pi} \times 0.77 \AA + 3 \times 1.35 \AA + 2 \times 1.54 \AA = 8.25 \AA$$

The six π-electrons fill levels 1, 2, 3.

The lowest transition is therefore from $n = 3$ to $n = 4$.

$$\Delta E = \left( \frac{4^2 - 3^2}{2} \right) \hbar^2 = \frac{(6 - 9)(6.626 \times 10^{-34} \text{ g cm}^2 \text{ s}^{-1})^2}{8 \times 9.109 \times 10^{-31} \text{ g} \times (8.25 \times 10^{-12} \text{ cm})}$$

$$\Delta E = 6.196 \times 10^{-12} \text{ erg}$$

$$\frac{\Delta E}{\hbar c} = \frac{6.196 \times 10^{-12} \text{ g cm}^2 \text{ s}^{-2}}{6.626 \times 10^{-34} \text{ g cm}^2 \text{ s}^{-1} \times 2.9979 \times 10^{10} \text{ cm} \text{s}^{-1}} = 3.12 \times 10^4 \text{ cm}^{-1}$$

hexatriene

$$l = 2 \times 0.77 \AA + 3 \times 1.35 \AA + 2 \times 1.54 \AA = 8.67 \AA$$

$$\Delta E = \frac{(4^2 - 3^2) \hbar^2}{8m_e a^2} > \frac{(6-9)(6.626 \times 10^{-34} \text{ g cm}^2 \text{ s}^{-1})^2}{8 \times 9.109 \times 10^{-31} \text{ g} \times (8.67 \times 10^{-10} \text{ cm})^2}$$

$$\Delta E = 5.61 \times 10^{-12} \text{ erg}$$

$$\frac{\Delta E}{\hbar c} = \frac{5.61 \times 10^{-12} \text{ erg}}{6.626 \times 10^{-34} \text{ g cm}^2 \text{ s}^{-1} \times 3 \times 10^{10} \text{ cm} \text{s}^{-1}} = 2.82 \times 10^4 \text{ cm}^{-1}$$
3.7. Prove that if \( \psi(x) \) is a solution to the Schrödinger equation, then any constant times \( \psi(x) \) is also a solution.

\[
\psi \equiv E \psi \\
H(\psi) = a \ H \psi = a \ E \psi = E(a \ \psi) \quad \text{QED}
\]

3.9. What are the units, if any, for the wave function of a particle in a one-dimensional box?

\[
\int_0^a \psi^2(x) \, dx = 1 \quad \text{normalization condition}
\]

Thus \( \psi^2(x) \) must have units of \( \text{distance}^{-1/2} \)

and thus \( \psi(x) \) has units of \( \text{distance}^{-1/2} \)

3.11. Show that

\[
(x) = \frac{a}{2}
\]

for all the states of a particle in a box. Is this result physically reasonable?

\[
\psi_n(x) = \left( \frac{2}{a} \right)^{\frac{1}{2}} \sin \left( \frac{n \pi x}{a} \right) \quad 0 \leq x \leq a \quad n = 1, 2, 3, \ldots
\]

\[
\langle n | x | n \rangle = \int_0^a \psi_n^*(x) \psi_n(x) \, dx = \frac{2}{a} \int_0^a x \sin^2 \left( \frac{n \pi x}{a} \right) \, dx
\]

Standard integral

\[
\int_0^a x \sin^2 b x \, dx = \frac{x^2}{4} - \frac{x \sin(2bx)}{4b} - \frac{\cos(2bx)}{8b^2}
\]

\[
\langle n | x | n \rangle = \frac{2}{a} \left[ \frac{a^2}{4} - \frac{a \sin(2b a)}{4 b} - \frac{\cos(2b a)}{8 b^2} \right] + \frac{1}{8 b^2}
\]

\[
\langle n | x | n \rangle = \frac{2}{a} \left[ \frac{a^2}{4} - 0 - \frac{1}{8 (\pi n)^2} \right] = \frac{a^2}{4} - \frac{1}{8 (\pi n)^2} = \frac{a^2}{4}
\]
(3-17) Prove that the set of functions

\[ \psi_n(x) = (2a)^{-1/2}e^{in\pi x/a} \quad n = 0, \pm 1, \pm 2, \ldots \]

is orthonormal (cf. Problem 3-16) over the interval \(-a \leq x \leq a\). A compact way to express orthonormality in the \(\psi_n\) is to write

\[ \int_{-a}^{a} \psi_n^*(x)\psi_m dx = \delta_{mn} \]

The symbol \(\delta_{mn}\) is called a Kronecker delta and is defined by

\[ \delta_{mn} = 1 \quad \text{if} \quad m = n \]

\[ \delta_{mn} = 0 \quad \text{if} \quad m \neq n \]

\[ \int_{-a}^{a} \psi_n^*(x)\psi_m(x) dx \]

\[ = \frac{1}{2a} \int_{-a}^{a} e^{i\pi n x/a} e^{i\pi m x/a} dx \]

\[ I = \frac{1}{2a} \int_{-a}^{a} e^{i\pi (m-n) x/a} dx = \frac{1}{2a} \left. \frac{a}{i\pi (m-n)} e^{i\pi (m-n) x/a} \right|_{-a}^{a} \]

\[ = \frac{1}{2a} \frac{a}{i\pi (m-n)} \left[ e^{i\pi (m-n) a} - e^{-i\pi (m-n)} \right] \]

Since

\[ e^{i\phi} = \cos \phi + i\sin \phi \]

\[ e^{-i\phi} = \cos \phi - i\sin \phi \]

\[ \frac{1}{i\pi} (e^{i\phi} - e^{-i\phi}) = \sin \phi \]

\[ I = \frac{1}{\pi (m-n)} \sin \pi (m-n) \]

Since \( m \neq n \) and \( m-n \) is an integer, \( \sin \pi (m-n) = 0 \)

\[ I = 0 \quad m \neq n \]

For \( m = n \)

\[ I = \frac{1}{2a} \int_{-a}^{a} e^{0} dx = \frac{1}{2a} \int_{-a}^{a} dx = \frac{a - (-a)}{2a} = 1 \]
3-32. The quantized energies of a particle in a box result from the boundary conditions, or from the fact that the particle is restricted to a finite region. In this problem, we investigate the quantum-mechanical problem of a free particle, one that is not restricted to a finite region. The potential energy \( V(x) \) is equal to zero and the Schrödinger equation is

\[
\frac{d^2 \psi}{dx^2} + \frac{2mE}{\hbar^2} \psi(x) = 0 \quad -\infty < x < \infty
\]

Note that the particle can lie anywhere along the \( x \)-axis in this problem. Show that the two solutions of this Schrödinger equation are

\[
\psi_1(x) = A_1 e^{(\frac{2mE}{\hbar^2})^{1/2}x/\hbar} = A_1 e^{ikx}
\]

and

\[
\psi_2(x) = A_2 e^{-\left(\frac{2mE}{\hbar^2}\right)^{1/2}x/\hbar} = A_2 e^{-ikx}
\]

where

\[
k = \frac{(2mE)^{1/2}}{\hbar}
\]

Show that if \( E \) is allowed to take on negative values, then the wave functions become unbounded for large \( x \). Therefore, we will require that the energy, \( E \), be a positive quantity. We saw in our discussion of the Bohr atom that negative energies correspond to bound states and positive energies correspond to unbound states, and so our requirement that \( E \) be positive is consistent with the picture of a free particle.

\[
\text{IF } E < 0 \text{ then } k \text{ is imaginary say } k = i\kappa \text{ with } \kappa \text{ real and positive}
\]

\[
\psi = A e^{\pm i\kappa x} = A e^{\pm i(k) x} = A e^{\pm i\kappa x}
\]

For \( \psi_1 = A_1 e^{-\kappa x} \) this blows up for \( x \to -\infty \)

For \( \psi_2 = A_2 e^{\kappa x} \) this blows up for \( x \to +\infty \)
To get a physical interpretation of the states that $\psi_1(x)$ and $\psi_2(x)$ describe, operate on $\psi_1(x)$ and $\psi_2(x)$ with the momentum operator $\hat{p}$ (Equation 3.11), and show that

$$\hat{p}\psi_1 = -i\hbar \frac{d\psi_1}{dx} = \hbar k \psi_1$$

and

$$\hat{p}\psi_2 = -i\hbar \frac{d\psi_2}{dx} = -\hbar k \psi_2$$

Notice that these are eigenvalue equations. Our interpretation of these two equations is that $\psi_1$ describes a free particle with fixed momentum $\hbar k$ and that $\psi_2$ describes a particle with fixed momentum $-\hbar k$. Thus, $\psi_1$ describes a particle moving to the right and $\psi_2$ describes a particle moving to the left, both with a fixed momentum. Notice also that there are no restrictions on $k$, and so the particle can have any value of momentum. Now show that

$$E = \frac{\hbar^2 k^2}{2m}$$

Notice that the energy is not quantized; the energy of the particle can have any positive value in this case because no boundaries are associated with this problem.

$$E = \frac{p^2}{2m} = \frac{(\pm i\hbar k)^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

Last, show that $\psi_1^* \psi_1(x) = A_1^* A_1 = |A_1|^2$ = constant and that $\psi_2^* \psi_2(x) = A_2^* A_2 = |A_2|^2$ = constant. Discuss this result in terms of the probabilistic interpretation of $\psi^* \psi$. Also discuss the application of the Uncertainty Principle to this problem. What are $\sigma_x$ and $\sigma_p$?

$$\psi_1^* \psi_1(x) = (A_1 e^{i\hbar k})^* A_1 e^{i\hbar k} = A_1^* A_1 e^{-i\hbar k} e^{i\hbar k} = A_1^* A_1$$

$$\psi_2^* \psi_2(x) = (A_2 e^{-i\hbar k})^* (A_2 e^{-i\hbar k}) = A_2^* A_2 e^{i\hbar k} e^{-i\hbar k} = A_2^* A_2$$

$\psi$ has equal probability everywhere $\Delta x = \infty$, $\sigma_x = \infty$ $\Delta p = 0$ (by Uncertainty Principle)
3.33. Derive the equation for the allowed energies of a particle in a one-dimensional box by assuming that the particle is described by standing de Broglie waves within the box.

In order for the de Broglie waves to be standing waves in the box, \( \frac{n \pi}{2} \), \( \frac{3n \pi}{2} \), \( \frac{5n \pi}{2} \) ... \( \frac{na}{2} \)

or half-waves must be equal to the length of the box,

\[
\frac{n \pi}{2} = a
\]

\[
a \lambda = \frac{2a}{n} \quad \text{for } n = 1, 2, ... \\
\Rightarrow \quad \frac{p}{h} = \frac{h}{2a/n} = \frac{nh}{2a}
\]

\[
E = \frac{p^2}{2m} \quad \text{(all energy is kinetic, within the box)}
\]

\[
E_n = \frac{(nh/2a)^2}{2m} = \frac{n^2 h^2 / 4a^2}{2m} = \frac{n^2 h^2}{8ma^2} \quad \text{for } n = 1, 2, 3, ...
\]
2. assigned 9/12/02

In class we presented the classical one-dimensional time-independent wave equation

\[
\frac{d^2 \psi(x)}{dx^2} = \left(\frac{2\pi}{\lambda}\right)^2 \psi(x)
\]

(1)

Show that the classical one-dimensional time-dependent wave equation

\[
\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2}
\]

(2)

reduces to eq(1) if you assume that

\[
\Psi(x,t) = \psi(x)e^{i\omega t}
\]

(3)

Where \( \omega \) is the radial frequency and \( v \) in eq(2) is the velocity of the wave.

\[
\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2}
\]

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi(x)}{\partial t^2}
\]

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{1}{v^2} \psi(x) \frac{\partial^2 \psi(x)}{\partial t^2}
\]

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{1}{v^2} \psi(x) (i\omega)^2 e^{i\omega t}
\]

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{\omega^2}{v^2} \psi(x)
\]

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{\omega^2}{v^2} \frac{\psi(x)}{v^2 \lambda^2}
\]

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi(x)
\]

\( \Box \)