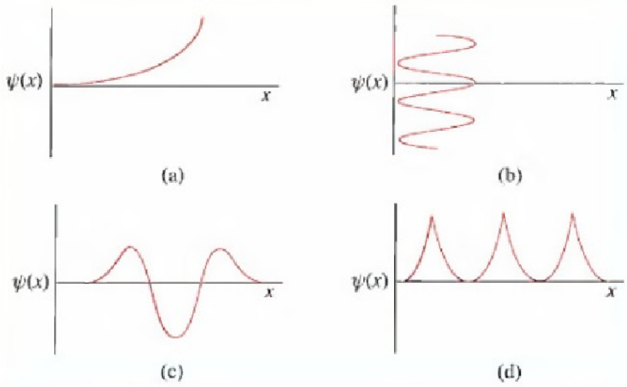
1. Which of the wavefunctions shown in the figure are well behaved? Give reasons for your answer.



2. The wavefunction of a particle confined to the x axis is $\psi = e^{-x}$ for $x > 0$ and $\psi = e^{+x}$ for $x < 0$. Normalize this wavefunction and calculate the probability of finding the particle between $x = -1$ and $x = 1$.

3. State, giving your reasons, which of the following functions would make satisfactory wavefunctions for all values of the variable x: (i) Ne^{ax^2}; (ii) Ne^{-ax^2}; (iii) $Ne^{-ax^2}/(3 - x)$; and (iv) Ne^{-ax}, where N and a are constants.

4. Calculate the wavelength of the radiation that will be absorbed in promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in butadiene.

5. Calculate the energy separation between the $n = 1$ and $n = 2$ levels of a nitrogen molecule, confined in a one-dimensional box of length 1 cm. Find the value of n that corresponds to the average thermal energy of a nitrogen molecule at a temperature of 300 K. The average thermal energy = $\frac{1}{2}k_B T$ for movement in one dimension, where k_B is the Boltzmann constant. Comment on the value for n obtained.

6. For a one-dimensional gallium arsenide quantum well of width 21 nm, calculate the difference in energies between the $n = 2$ and $n = 3$ states for travel of conduction electrons across the width of the well. Compare your answer with the experimentally determined value of approximately 0.05 eV.

7. For a particle moving freely along the x-axis, show that the Heisenberg uncertainty principle can be written in the alternative form:

$$\Delta\lambda\Delta x \geq \frac{\lambda^2}{4\pi}$$

where Δx is the uncertainty in position of the particle and $\Delta\lambda$ is the simultaneous uncertainty in the de Broglie wavelength.

8. Consider a particle whose normalized wave function is

$$\psi(x) = 2\alpha\sqrt{\alpha}xe^{-\alpha x} \qquad x > 0$$
$$= 0 \qquad x < 0$$

(a) For what value of x does $P(x) = |\psi(x)|^2$ peak?
(b) Calculate $\langle x \rangle$ and $\langle x^2 \rangle$.
(c) What is the probability that the particle is found between $x = 0$ and $x = 1/\alpha$?

9. The wavefunction of a particle moving in the x-dimension is

$$\psi(x) = \begin{cases} Nx(L-x) & 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

(a) Normalize the wavefunction.
(b) Calculate $\langle x \rangle$, $\langle x^2 \rangle$, Δx.
(c) Calculate $\langle p_x \rangle$, $\langle p_x^2 \rangle$, Δp_x.

10. If the normalized wave function of a particle in a box is given by

$$\psi(x) = \begin{cases} \sqrt{\frac{30}{L^5}}x(L-x) & 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

what is the probability of obtaining the energy of the ground state, E_1, if a measurement of the energy is carried out?

11. Show that the function

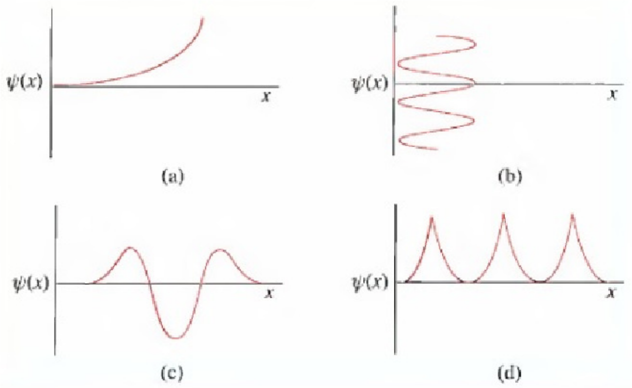
$$\Psi(x,t) = \frac{e^{-iE_1 t}}{\hbar}\psi_1(x) + \frac{e^{-iE_2 t}}{\hbar}\psi_2(x)$$

is normalized. Calculate $\langle E \rangle$ and ΔE for this state.

12. Determine $\langle E \rangle$ for a particle in a box with wave function

$$\psi(x) = \begin{cases} \sqrt{\frac{30}{L^5}}x(L-x) & 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

1. Which of the wavefunctions shown in the figure are well behaved? Give reasons for your answer.



Answer: Only the wavefunction shown in (c) is well behaved. The one shown in (a) tends towards infinity, and therefore violates the rule that the integral of $\psi^*\psi$ over all space must be equal to one because the particle is certain to be somewhere. This requires that the wavefunction is finite. The one shown in (b) has multiple values of for a given value of x, and the one shown in (d) has discontinuities in the gradient, so that dy/fdx cannot be defined at certain points.

2. The wavefunction of a particle confined to the x axis is $\psi = \mathrm{e}^{-x}$ for $x > 0$ and $\psi = \mathrm{e}^{+x}$ for $x < 0$. Normalize this wavefunction and calculate the probability of finding the particle between $x = -1$ and $x = 1$.

Answer: Normalization refers to the requirement that

$$\int_{-infty}^{\infty} \psi^*\psi \, \mathrm{d}x = 1.$$

If ψ does not satisfy this property, because it is a solution to the Schrödinger equation (SE), which is a linear equation, $N\psi$, where N is a constant, is also a solution to the SE.

Ignoring the acceptability of the given function to be a wavefunction, we proceed to normalize the function. We look for a N, such that $\int N\psi^* N\psi \, \mathrm{d}x = 1$. That is

$$N^2 \left(\int_0^{\infty} \mathrm{e}^{-x}\mathrm{e}^{-x} \, \mathrm{d}x + \int_0^{-\infty} \mathrm{e}^{x}\mathrm{e}^{x} \, \mathrm{d}x \right) = 1$$

Each of the integrals is a $\frac{1}{2}$ so $N^2 = 1$ or the wavefunction is normalized.

The probability of finding the particle between $x = -1$ and $x = 1$ is obtained by integrating $\psi^*\psi$ over this domain.

$$P = \frac{\int_{-1}^{1} \psi^*\psi \, \mathrm{d}x}{\int_{-\infty}^{\infty} \psi^*\psi \, \mathrm{d}x}$$

In this instance, the denominator in the above expression is unity. The probability of finding the particle in the desired region is

$$P = \left(\int_0^{1} \mathrm{e}^{-x}\mathrm{e}^{-x} \, \mathrm{d}x + \int_0^{-1} \mathrm{e}^{x}\mathrm{e}^{x} \, \mathrm{d}x \right) = \frac{1}{2} \left(\mathrm{e}^{2} - \mathrm{e}^{-2} \right)$$

3. State, giving your reasons, which of the following functions would make satisfactory wavefunctions for all values of the variable x: (i) Ne^{ax^2}; (ii) Ne^{-ax^2}; (iii) $Ne^{-ax^2}/(3-x)$; and (iv) Ne^{-ax}, where N and a are constants.

   Answer: (i) Not satisfactory; function not finite as $x \to \infty$.
   (ii) Satisfactory.
   (iii) Not satisfactory; function not finite at $x = 3$.
   (iv) Not satisfactory; function not finite as $x \to -\infty$.

4. Calculate the wavelength of the radiation that will be absorbed in promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in butadiene.

   Answer: First, an estimate has to be made of the length of the potential well, L, in which the π-electrons move. It seems reasonable to take the mean C-C distance to be equal to the average of the carbon-carbon single and double bond lengths found in a variety of non-conjugated compounds - this is a different approach from that adopted in HW4. With $d(\mathrm{C{-}C})$= 154 pm and $d(\mathrm{C{=}C})$ = 135 pm, this leads to a value of 144.5 pm. The total length of the box is then taken to be equal to four carbon-carbon bond lengths, giving $L = 578\,\mathrm{pm}$.

   The highest occupied n electron state has $n = 2$, and the lowest unoccupied state has $n = 3$. The energy required to promote an electron from one state to the other is given by the equation:

$$E_3 - E_2 = \frac{\left(3^2 - 2^2\right) h^2}{8mL^2} = \frac{5 \times \left(6.626 \times 10^{-34}\,\mathrm{J\,s^{-1}}\right)^2}{8 \times 9.109 \times 10^{-31}\,\mathrm{kg} \times (578 \times 10^{-12}\,\mathrm{m})^2}$$

5. Calculate the energy separation between the $n = 1$ and $n = 2$ levels of a nitrogen molecule, confined in a one-dimensional box of length 1 cm. Find the value of n that corresponds to the average thermal energy of a nitrogen molecule at a temperature of 300 K. The average thermal energy = $\frac{1}{2}k_B T$ for movement in one dimension, where k_B is the Boltzmann constant. Comment on the value for n obtained.

   Answer: The energy separation between the first and second state of nitrogen molecule ($m_{\mathrm{N_2}} = 28 \times 1.661 \times 10^{-27}\,\mathrm{kg}$ in a box of length 1 cm is

$$E_2 - E_1 = \frac{\left(2^2 - 1^2\right) h^2}{8m_{\mathrm{N_2}}L^2} = \frac{3 \times \left(6.626 \times 10^{-34}\,\mathrm{J\,s^{-1}}\right)^2}{8 \times 4.651 \times 10^{-26}\,\mathrm{kg} \times (1.0 \times 10^{-2}\,\mathrm{m})^2}$$

$$\Delta E = 3.54 \times 10^{-38}\,\mathrm{J}$$

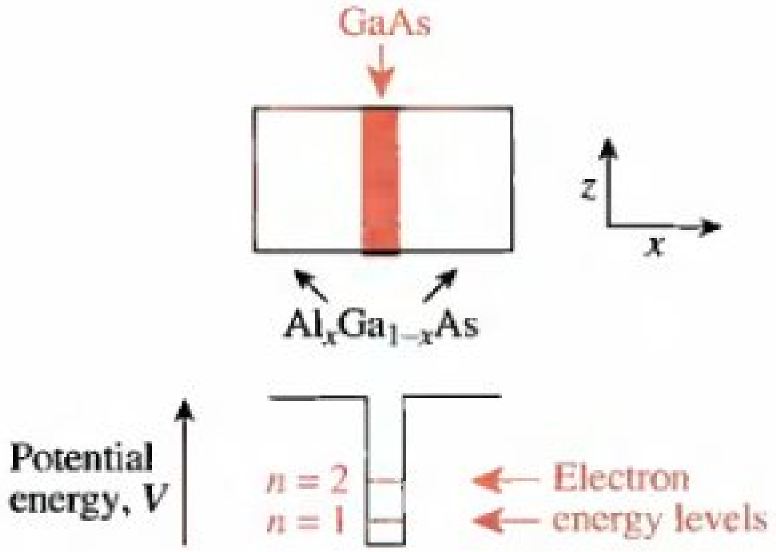
   The value of n that corresponds to the thermal energy at 300 K is

$$\begin{aligned} n &= \sqrt{\frac{k_B T}{2}\frac{8m_{\mathrm{N_2}}L^2}{h^2}} \\ &= \sqrt{\frac{(1.381 \times 10^{-23}\,\mathrm{m^2\,kg\,s^{-2}\,K^{-1}}300\,\mathrm{K})8(4.651 \times 10^{-26}\,\mathrm{kg})(1.0 \times 10^{-2}\,\mathrm{m})^2}{2(6.626 \times 10^{-34}\,\mathrm{J\,s^{-1}})^2}} \\ &= 4.19 \times 10^8 \end{aligned}$$

   The n corresponding to thermal energy is so high that quantum effects are unlikely to be observed.

6. For a one-dimensional gallium arsenide quantum well of width 21 nm, calculate the difference in energies between the $n = 2$ and $n = 3$ states for travel of conduction electrons across the width of the well. Compare your answer with the experimentally determined value of approximately 0.05 eV.

Answer: Semiconductor quantum wells are sandwich structures made from semiconducting materials. They have numerous applications in modern electronic devices. An example is illustrated in the figure below. The base material is the III/V semi-



conductor gallium arsenide (GaAs). A thin layer of pure GaAs was been created between two layers of aluminium gallium arsenide, a material in which some of the gallium has been replaced with aluminium to give the formula $Al_xGa_{1-x}As$. Nearly free electrons, known as conduction electrons, can exist in these semiconductors, and they have a much higher potential energy in $Al_xGa_{1-x}As$ than they do in pure GaAs. Thus, conduction electrons in the pure GaAs become trapped between two potential walls and behave like particles in a one-dimensional box when moving in the x-direction, although they have complete freedom of movement in the y and z directions. Unlike the idealized particle in an infinite potential well, this one has finite walls. This affects the wavefunctions and energies to a small extent, but the equations derived earlier will still give reasonably accurate values for the energies. The existence of discrete energy levels is confirmed by the observation of selective absorption of laser light at certain frequencies which correspond to the transition of an electron from one energy level to another. The GaAs/$Al_xGa_{1-x}As$ combination mentioned above forms the basis of the semiconductor laser used in compact disc players. The energies are the same as that of a particle in a box, except that the conduction electrons behave as though they have a much smaller mass than ordinary electrons. This mass is known as the effective mass, m^*; for gallium arsenide, $m^* = 0.067m_e$.

$$E_3 - E_2 = \frac{\left(3^2 - 2^2\right) h^2}{8m^* L^2} = \frac{5 \times \left(6.626 \times 10^{-34}\,\mathrm{J\,s^{-1}}\right)^2}{8 \times (0.067 \times 9.109 \times 10^{-31}\,\mathrm{kg}) \times (21 \times 10^{-9}\,\mathrm{m})^2}$$

In eV this is 0.064 eV.

7. For a particle moving freely along the x-axis, show that the Heisenberg uncertainty

principle can be written in the alternative form:

$$\Delta\lambda \Delta x \geq \frac{\lambda^2}{4\pi}$$

where Δx is the uncertainty in position of the particle and $\Delta\lambda$ is the simultaneous uncertainty in the de Broglie wavelength.

Answer: Differentiation of the de Broglie relation, $p = h/\lambda$, gives $\frac{\mathrm{d}p}{\mathrm{d}\lambda} = -h/\lambda^2$. The uncertainty in momentum, Δp_x, can be equated with dp and the uncertainty in wavelength, $\Delta\lambda$, with $-\,\mathrm{d}\lambda$ (the uncertainties are positive). Thus:

$$\frac{\Delta p_x}{\Delta\lambda} = \frac{h}{\lambda^2} \qquad \text{and} \qquad \Delta\lambda\Delta x = \frac{\lambda^2}{h}\Delta p_x \Delta x$$

Plugging in the Heisenberg uncertainty relation yields the desired result.

8. Consider a particle whose normalized wave function is

$$\begin{aligned} \psi(x) &= 2\alpha\sqrt{\alpha}x\mathrm{e}^{-\alpha x} & x > 0 \\ &= 0 & x < 0 \end{aligned}$$

(a) For what value of x does $P(x) = |\psi(x)|^2$ peak?
(b) Calculate $\langle x \rangle$ and $\langle x^2 \rangle$.
(c) What is the probability that the particle is found between $x = 0$ and $x = 1/\alpha$?

Answer: (a) The peak in $P(x)$ occurs when $\frac{\mathrm{d}P(x}{\mathrm{d}x} = 0$ that is, when

$$\frac{\mathrm{d}\left(x^2\mathrm{e}^{-2\alpha x}\right)}{\mathrm{d}x} = 2x(1-\alpha x)\mathrm{e}^{-2\alpha x} = 0$$

which is at $x = 1/\alpha$.

(b)

$$\langle x \rangle = \int_0^{1/\alpha} \mathrm{d}x \left(4\alpha^3\right) x^3 \mathrm{e}^{-2\alpha x} = \frac{1}{4\alpha}\int_0^2 dyy^3\mathrm{e}^{-y} = \frac{3!}{4\alpha} = \frac{3}{2\alpha}$$

$$\langle x^2 \rangle = \int_0^{1/\alpha} \mathrm{d}x \left(4\alpha^3\right) x^4 \mathrm{e}^{-2\alpha x} = \frac{4!}{8\alpha^3} = \frac{3}{\alpha^2}$$

(c) The desired probability is

$$P = \int_0^{1/\alpha} \mathrm{d}x \left(4\alpha^3\right) x^2 \mathrm{e}^{-2\alpha x} = \frac{1}{2}\int_0^2 dyy^2\mathrm{e}^{-y} = 0.32$$

9. The wavefunction of a particle moving in the x-dimension is

$$\psi(x) = \begin{cases} Nx(L-x) & 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

(a) Normalize the wavefunction.
(b) Calculate $\langle x \rangle$, $\langle x^2 \rangle$, Δx.
(c) Calculate $\langle p_x \rangle$, $\langle p_x^2 \rangle$, Δp_x.

Answer: (a)

$$N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} \psi^* x \psi \,\mathrm{d}x}} = \frac{1}{\sqrt{\int_0^L x^2 (L-x)^2 \,\mathrm{d}x}}$$

$$N = \frac{1}{\sqrt{\int_0^L (x^2L^2 - 2Lx^3 + x^4)\,\mathrm{d}x}} = \frac{1}{\sqrt{\frac{L^5}{30}}}$$

(b)

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} x|\psi|^2 \,\mathrm{d}x = \int_0^L x\frac{30}{L^5}x^2(L-x)^2\,\mathrm{d}x \\ &= \frac{30}{L^5}\int_0^L (L^2x^3 - 2Lx^4 + x^5)\,\mathrm{d}x = 30L\left(\frac{1}{4} - \frac{2}{5} + \frac{1}{6}\right) = \frac{L}{2}\end{aligned}$$

$$\begin{aligned}\langle x^2 \rangle &= \int_{-\infty}^{\infty} x^2|\psi|^2 \,\mathrm{d}x = \int_0^L x^2\frac{30}{L^5}x^2(L-x)^2\,\mathrm{d}x \\ &= \frac{30}{L^5}\int_0^L (L^2x^4 - 2Lx^5 + x^6)\,\mathrm{d}x = 30L^2\left(\frac{1}{5} - \frac{2}{6} + \frac{1}{7}\right) = \frac{2L^2}{7}\end{aligned}$$

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x \rangle} = L\sqrt{\frac{2}{7} - \frac{1}{4}}$$

(c)

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* \left(-i\hbar\frac{\partial \psi}{\partial x}\right)\mathrm{d}x = \int_0^L \frac{30}{L^5}x(L-x)(-i\hbar(L-2x))\,\mathrm{d}x = 0$$

$$\begin{aligned}\langle p_x^2 \rangle &= \int_{-\infty}^{\infty} \psi^* \left(-\hbar^2\frac{\partial \psi}{\partial x}\right)\mathrm{d}x \\ &= -\frac{30\hbar^2}{L^5}\int_0^L x(L-x)(-2)\,\mathrm{d}x = \frac{10\hbar^2}{L^2}\end{aligned}$$

$$\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x \rangle} = \sqrt{10}\frac{\hbar}{L}$$

10. If the normalized wave function of a particle in a box is given by

$$\psi(x) = \begin{cases} \sqrt{\frac{30}{L^5}}x(L-x) & 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

what is the probability of obtaining the energy of the ground state, E_1, if a measurement of the energy is carried out?

Answer: To determine the probability, evaluate c_1:

$$c_1 = \int_{-\infty}^{\infty} \psi_1^*(x)\psi(x)\,\mathrm{d}x = \int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\sqrt{\frac{30}{L^5}}x(L-x)\,\mathrm{d}x$$

This integration is easiest performed by making a change of variables $\pi x/L = y$, which yields

$$c_1 = \frac{\sqrt{60}}{\pi^2}\int_0^{\pi} \sin y \left(y - \frac{y^2}{\pi}\right)\mathrm{d}y = \frac{4\sqrt{60}}{\pi^3}$$

11. Show that the function

$$\Psi(x,t) = \frac{e^{-iE_1 t}}{\hbar}\psi_1(x) + \frac{e^{-iE_2 t}}{\hbar}\psi_2(x)$$

is normalized. Calculate $\langle E \rangle$ and ΔE for this state.

Answer: A measurement of the energy yields E_1, the energy of state 1, with probability

$$P_1 = |c_1|^2 = \left| \frac{e^{-iE_1 t/\hbar}}{\sqrt{2}} \right|^2 = \frac{1}{2}$$

or E_2 with probability

$$P_2 = |c_2|^2 = \left| \frac{e^{-iE_2 t/\hbar}}{\sqrt{2}} \right|^2 = \frac{1}{2}$$

Because $\sum_{n=1}^{\infty} |c_n|^2 = 1$, $\Psi(x,t)$ is properly normalized. The expectation value of the energy in the state $\Psi(x,t)$ is

$$\langle E \rangle = \sum_{n=1}^{\infty} P_n E_n = \frac{1}{2}E_1 + \frac{1}{2}E_2$$

Similarly,

$$\langle E^2 \rangle = \sum_{n=1}^{\infty} P_n E_n^2 = \frac{1}{2}E_1^2 + \frac{1}{2}E_2^2.$$

As a result,

$$\Delta E = \sqrt{\langle E^2 \rangle - (\langle E \rangle)^2} = \frac{1}{2}(E_2 - E_1)$$

12. Determine $\langle E \rangle$ for a particle in a box with wave function

$$\psi(x) = \begin{cases} \sqrt{\frac{30}{L^5}}x(L-x) & 0 < x < L \\ 0 & \text{elsewhere} \end{cases}$$

Answer:

$$\begin{aligned}
\langle E \rangle &= \int_{-\infty}^{\infty} \psi^* \hat{\mathfrak{H}} \psi \, dx \\
&= \int_{-\infty}^{\infty} \psi^* \left(\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \right) dx = \frac{30}{L^5} \frac{-\hbar^2}{2m} \int_0^L x(L-x) \frac{\partial^2}{\partial x^2}(x(L-x)) \, dx \\
&= \frac{30}{L^5} \frac{\hbar^2}{m} \int_0^L x(L-x) \, dx = \frac{30}{L^5} \frac{\hbar^2}{m} L^3 \left(\frac{1}{2} - \frac{1}{3} \right) = \frac{5\hbar^2}{mL^2}
\end{aligned}$$