Fundamental 2

The Particle-on-a-Line Model

What can we learn from a simple quantum model?

Pre-Activity Questions

1. Consider an atom moving in a vacuum. Provide an appropriate expression for kinetic energy according to:

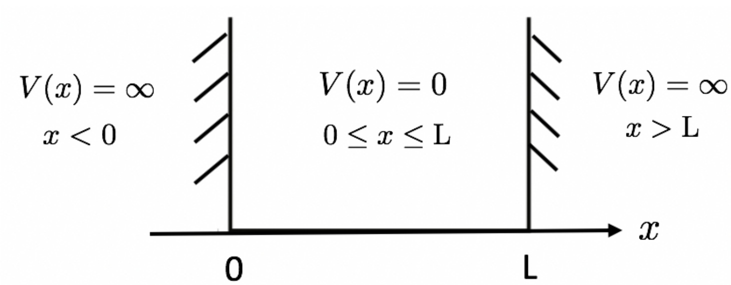
a) classical mechanics

b) quantum mechanics

2. Consider the relationship between force and potential energy. On a single graph, propose two example plots of potential energy as a function of position, one corresponding to a weak force and the second a strong force that would restrict the motion of an object to a 1D region of space. Explain your reasoning

Model 1 1D Model

Consider a particle (*e.g.* an atom, molecule, electron...) with mass, m, restricted to motion in a one-dimensional (1D) region of space of length, L. The potential energy, $V(x)$, is infinite for all values of $x < 0$ and $x >$ L. Between $x = 0$ and $x =$ L the potential energy is zero.



Critical Thinking Questions

1. What is the magnitude of the force for positions $x = 0$ and $x =$ L? (Recall: $F = -\frac{dV}{dx}$)

2. In view of your answer above, describe the space, *i.e.*, possible positions, a particle can be located as defined by this simple model. Explain.

3. Is there energy associated with the moving particle in the region $0 \leq x \leq L$? If so, what type of energy? Present your team's justification.

4. Assume Classical Mechanics is used to characterize Model 1:

a) What is the smallest energy possible for this particle confined to a line? Record your team's justification for this answer.

b) Within a physical range of particle velocities, are there any restrictions to the amount of energy associated with this particle confined to a line? Explain.

5. Assume Quantum Mechanics is used to characterize Model 1

a) Within the region $0 \leq x \leq L$, write the functional form of the Hamiltonian operator, $\hat{\mathcal{H}}$?

b) Use the functional form of the Hamiltonian to write an expression for the corresponding Schrödinger equation for the particle-on-a-line model.

Model 2 1D Solution

The following is a general solution to the particle-on-a-line model Schrödinger equation,

$$\psi(x) = \mathrm{A}\sin(kx) + \mathrm{B}\cos(kx) \tag{F2.1}$$

with

$$E = \frac{k^2\hbar^2}{2m} \tag{F2.2}$$

Critical Thinking Questions

6. Apply the Hamiltonian operator your team proposed in CTQ 5a to the eigenfunction solution, Eq. F2.1, and confirm Eq. F2.2 is the corresponding eigenvalue.

7. Although F2.1 is a solution to the Schrödinger equation, it must also satisfy all of the other rules of "well-behaved" wavefunctions described in F.1 Postulate 1.

   a) In view of CTQ 2, there is no probability of finding the particle at $x < 0$ or $x > L$. What must the value of $\psi(x)$ be in these regions?

   b) Since the wavefunction must be continuous at all x values, what must $\psi(0)$ and $\psi(L)$ be equal to?

   c) The equations $\psi(0) = 0$ and $\psi(L) = 0$ are referred to as **boundary conditions**. What must be true of the values of A and B to ensure that the boundary condition $\psi(0) = 0$ is satisfied?

   d) In summary, write an expression for the particle-on-a-line wavefunction that satisfies the boundary condition, $\psi(0) = 0$.

8. Next, ensure that the function $\psi(x)$ also satisfies the boundary condition, $\psi(L) = 0$.

   a) Identify at least three values of α such that $\sin \alpha = 0$.

   b) Propose a general expression for α that assumes n is any positive integer and identify **all** values that make $\sin \alpha = 0$ a true statement.

   c) In view of your team's answers above, propose a general expression for k (as a function of n) such that $\sin kL = 0$.

9. Rewrite the general particle-on-a-line solution defined in Model 2 consistent with the boundary conditions $\psi(0) = 0$ and $\psi(L) = 0$:

   a) wavefunction, $\psi(x)$

   b) energy, E

10. Consider the particle-on-a-line *wavefunction* identified in CTQ 9.

    a) What new variable was introduced in order to satisfy the boundary conditions? __________

    b) Is $n = 0$ a possible solution? Explain why or why not.

    c) Identify all possible values and range of the **quantum number**, n. (Recall CTQ 8)

    d) How many unique states (wavefunctions) can be defined for a single particle confined to a line?

    e) How is each unique state identified?

11. Consider the particle-on-a-line *energy* identified in CTQ 9.

a) The quantum state with the overall smallest value of energy is called the **ground state**. Identify the value of the quantum number for the particle-on-a-line ground state.

b) The value of the ground state energy is called the **zero point energy**. Is the zero point energy for the particle-on-a-line model equal to zero? Justify this answer.

c) Are there any restrictions to the amount of energy associated with this particle confined to a line? Provide your team's justification for this answer.

12. What happens to the energy, E_n, of the particles as n increases?

13. What happens to the difference in energy between two sequential states, *i.e.*, E_n and E_{n+1}, as n increases?

14. Sketch and label an approximate energy level diagram, $E(n)$, representing the first four energy states (each represented by a horizontal line) corresponding a particle-on-a-line.

15. An electron in a π-system, such as 1,3 butadiene, is spread out (delocalized) over a large region of space in comparison to an electron bound only to a single atom or an electron confined to two atoms in a normal covalent bond.

a) Based on the particle-on-a-line model, would you predict the electrons in a π-system to be at a lower or higher energy than in a normal bond? Provide justification for your team's answer.

b) In view of the assumptions inherent in Model 1, describe why it is remarkable that the particle-on-a-line model is able to predict the length of 1,3 butadiene close to the experimental value.

16. For 1D confined motion (kinetic energy only) between two boundaries, summarize the unique features of the quantum description of energy that differ from a classical description of this system.

Exercises

1. For $n = 1 \ldots 4$, provide an expression for E_n as function of m and L.

2. Develop expressions for the difference in energy between E_1 & E_2, E_2 & E_3, and E_3 & E_4 in terms of m of L. How does the difference in energy between two sequential states change as the mass of the particle increases? Describe the relationship between the difference in energy between two sequential states and the length of the line.

3. Derive an expression for the difference in energy between two sequential states, $\Delta E_{n \to n+1} = E_{n+1} - E_n$. How does this difference in energy change as n increases?

4. Using expressions from Exercise 3, compare the difference in energy between two sequential states for an argon atom confined to a line of length:

a) 300 pm (the diameter of a C_{70} molecule).

b) 1 cm (the diameter of a test tube)

5. Compare the calculated zero-point energies according to Quantum Mechanics and Classical Mechanics for a xenon atom confined to a 10 nm line.

6. Electronic transitions of the molecule butadiene, $CH_2{=}CH{-}CH{=}CH_2$, can be approximated using the particle-on-a-line model, if one assumes an electron in butadiene can span the entire four-carbon chain.

a) If a butadiene molecule absorbs a photon with a wavelength 2170 Å and an electron transitions from the $n = 2$ to the $n = 3$ state, what is the approximate length of the C_4H_6 molecule?

b) Describe why it is quite remarkable that the predicted length of butadiene based on the particle-on-a-line model is close to the experimental value of 4.8 Å.

7. Instead of the boundary conditions defined from $x = 0$ to L, assume that the limits for $x = -L/2$ to $+L/2$. Derive acceptable wave functions for this particle-on-a-line. What are the quantized energies for the particle?