CHM 305 Problem Set 2

Distributed: Tuesday, September 15, 2026
Due: Monday, September 21, 2026 @ 11:59 PM ET

Problem Set Submission: Please submit assignment by uploading your files to Canvas. You may upload scanned handwritten work or digital documents as .pdf files.

Collaboration: Students are encouraged to interact with one another and to collaborate in learning and understanding the course material and homework problems. However, each student's assignments are expected to be their own work, reflecting their own understanding of the course material.

1 1D Particle in a Box

(a) We learned that the 1D particle in a box wavefunctions take the form

$$\psi_n(x) = c_n \sin\left(\frac{n\pi x}{a}\right)$$

where the particle is confined along the x axis between 0 and a, and $n = 1, 2, \ldots$

Normalize $\psi_n(x)$. To do so, you will need to find the normalization constant c_n such that:

$$\int_0^a \psi_n^*(x)\psi_n(x)dx = 1$$

where $\psi_n^*(x)$ is the complex conjugate of $\psi_n(x)$. An integral that might be useful to you is:

$$\int \sin^2(\alpha x)\, dx = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha}$$

(b) Show that the particle-in-a-box wavefunctions are orthogonal, e.g. that

$$\int_0^a \psi_n^*(x)\psi_m(x)dx = 0 \text{ for } m \neq n$$

You may want to use the trigonometric identity

$$\sin(\alpha)\sin(\beta) = \frac{1}{2}\cos(\alpha - \beta) - \frac{1}{2}\cos(\alpha + \beta)$$

2 Particles in Boxes of Higher Dimension

A particle in a 3D box with side lengths of a, b, and c has the following eigenfunctions:

$$\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

with quantum numbers n_x, n_y, and n_z which describe each eigenfunction's structure along the x, y, and z axes respectively.

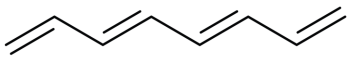
(a) Show that these eigenfunctions are normalized over the 3D region contained by the box, for $x = [0, a]$, $y = [0, b]$, $z = [0, c]$. You may use the trigonometric identities given in Problem 1.

(b) Show that these eigenfunctions are indeed a solution to the 3D *time-independent* Schrödinger equation

$$\hat{H}\psi(x,y,z) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z)$$

and derive an expression for the energy of the system E in terms of the three quantum numbers.

3 Real-World 1D Particle in a Box



Let's consider the energy levels of the π electron network in 1,3,5,7-octatetraene, C_8H_{10} using the 1D particle in a box model.

(a) Sketch out an energy level diagram for the occupied and lowest unoccupied molecular π orbitals of this molecule. Label each energy level with appropriate quantum number n.

(b) Notate how your energy levels are populated with the available π electrons, two electrons per level. What are the values of the quantum number n for the highest occupied (HOMO) and lowest unoccupied (LUMO) energy levels?

(c) What is the length of the 1D "box" that we can use to describe this molecule? To calculate the box length, you may assume that the molecule is linear and take C=C bonds to be 135 pm long, C–C bonds to be 154 pm long, and the radius of a carbon atom to be 77 pm.

(d) What is the frequency of the HOMO to LUMO transition (in Hertz)? What is the equivalent wavelength of light (in nanometers) required to induce this transition?

(e) What is the wavelength of the transition that excites an electron from the next-lowest energy state (HOMO-1) to the LUMO?

(f) Name at least three reasons that a real molecule like 1,3,5,7-octatetraene may not behave exactly like an ideal particle in a box.

4 The Time-Dependent Schrödinger Equation

(a) We learned that if $\psi_n(x)$ is a stationary state (e.g. a solution to the time-*independent* Schrödinger equation) with energy E_n then its full time-dependent form can be written:

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$$

Show that if $\psi_m(x)$ and $\psi_n(x)$ are both stationary states, then the state

$$\Phi(x,t) = c_m\psi_m(x)e^{-iE_mt/\hbar} + c_n\psi_n(x)e^{-iE_nt/\hbar}$$

satisfies the time-dependent Schrödinger equation. E.g., show that

$$\hat{H}\Phi(x,t) = i\hbar\frac{\partial}{\partial t}\Phi(x,t)$$

You may use the fact that $\hat{H}\psi_m(x) = E_m\psi_m(x)$ and $\hat{H}\psi_n(x) = E_n\psi_n(x)$.

(b) Does $\Phi(x,t)$ given in part (a) satisfy the time-*independent* Schrödinger equation, $\hat{H}\Phi(x,t) = E\Phi(x,t)$? Why or why not?

(c) Find the normalization constant C for

$$\Phi(x,t) = C\sum_{n=1}^{N}\psi_n(x)e^{-iE_nt/\hbar}$$

if each $\psi_n(x)$ is normalized.

5 Operators

(a) If two operators act on a wavefunction, as indicated by $\hat{A}\hat{B}f(x)$, it is important to carry out the operations in succession, with the first operation being that nearest to the function. Evaluate the successive operations $\hat{A}\hat{B}f(x)$ for the following values of $\hat{A}$, $\hat{B}$, and $f(x)$:

(i) $\hat{A} = \dfrac{d}{dx}$, $\hat{B} = x^2$, $f(x) = e^{-ikx}$

(ii) $\hat{A} = x^2$, $\hat{B} = \dfrac{d}{dx}$, $f(x) = e^{-ikx}$

Are your answers to parts (i) and (ii) different or identical? We will learn later on that operators that do not commute (e.g. those that give different answers when their order is swapped) will form the basis of Heisenberg's uncertainty principle.

(b) In ordinary algebra, $(P+Q)(P-Q) = P^2 - Q^2$. Expand $(\hat{P}+\hat{Q})(\hat{P}-\hat{Q})$ using what we've learned about how operators behave. Under what conditions do we find the same result as the case of ordinary algebra?

6 Eigenvalue Problems

(a) Operators can be expressed as matrices, and wave functions as column vectors. The operator matrix

$$\hat{O} = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}$$

acts on the wavefunction $\psi = \begin{pmatrix} a \\ b \end{pmatrix}$ according to the rule

$$\hat{O}\psi = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \alpha a + \beta b \\ \gamma a + \delta b \end{pmatrix}$$

The 2×2 operator acting on the 2×1 column vector wavefunction generates another 2×1 wavefunction. If the wavefunction generated by $\hat{O}\psi$ is the original wavefunction ψ multiplied by a constant c, then ψ is an eigenvector of $\hat{O}$, and x is the corresponding eigenvalue. What is the effect of the operator

$$\hat{O} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

on the column vectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$, and $\begin{pmatrix} -1 \\ 1 \end{pmatrix}$? Which of these are eigenfunctions of $\hat{O}$, and what are their eigenvalues?

(b) For each of the following, show that $f(x)$ is an eigenvector of $\hat{A}$ and find the eigenvalue.

(i) $\hat{A} = \frac{d^2}{dx^2}$, $f(x) = \cos(kx)$

(ii) $\hat{A} = \frac{d}{dt}$, $f(x) = e^{i\omega t}$

(iii) $\hat{A} = \frac{d^2}{dx^2} + 2\frac{d}{dx} + 3$, $f(x) = e^{\alpha x}$

(iv) $\hat{A} = \frac{\partial}{\partial y}$, $f(x, y) = x^2 e^{6y}$