Problem Set 2
CHM 305, Fall 2023

Distributed: Thursday, September 14, 2023
Due: Thursday, September 21, 2023 @ 5 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 $n = 1, 2, \dots$

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 Particle in a Box
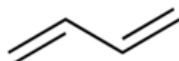
Calculate the energy levels of the π network in butadiene, C_4H_6, using the 1D particle in a box model. To calculate the box length assume that the molecule is linear and use the values 135 and 154 pm for C=C and C–C bonds.

(a) Fill the resulting energy levels with the available π electrons, two electrons per level. What are the values of n for the highest occupied and lowest unoccupied levels?

(b) What is the lowest-energy wavelength of light required to induce a transition from the highest occupied level to the first empty level? How does this compare with the experimentally observed value of $290\,\text{nm}$?

(c) Name at least three reasons that the particle-in-a-box may not be a perfect model for a real molecule like butadiene.

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:

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

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

$$\Psi(x,t) = c_m\psi_m(x)e^{-iE_m t/\hbar} + c_n\psi_n(x)e^{-iE_n t/\hbar}$$

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

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

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

(c) Find the normalization constant C for

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

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