

Problem Set 5

CHM 305, Fall 2023

Distributed: Thursday, October 12, 2023

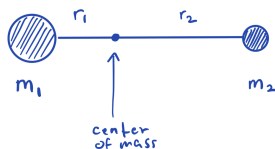
Due: Thursday, October 26, 2023 @ 5 PM ET

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 The Rigid Rotor

- (a) Consider the moment of inertia for a rigid rotor composed of two masses m_1 and m_2 , which lie at distances r_1 and r_2 from the center of mass, respectively:



Show that the moment of inertia $I = m_1 r_1^2 + m_2 r_2^2$ can be written equivalently as $I = \mu r^2$ where $r = r_1 + r_2$ and μ is the reduced mass. **Hint:** Recall that by definition of the center of mass, $m_1 r_1 = m_2 r_2$.

- (b) Consider the three rigid rotor eigenfunctions with $J = 1$:

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$
$$Y_1^1(\theta, \phi) = -\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta \cdot e^{i\phi}$$
$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$$

Show that each of these three functions is a solution to the rigid rotor Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

and find the corresponding energy eigenvalue.

2 The Hydrogen Atom

The ground state wavefunction of an electron bound in a hydrogen atom is expressed in spherical coordinates as:

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

where r is the distance of the electron from the nucleus, and $a \equiv \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$ is the Bohr radius.

- (a) $\psi_{100}(r, \theta, \phi)$ is a radially decaying function with no angular nodes. Sketch this wavefunction. What is this state better known as? e.g. how would you have referred to this state in general chemistry?

- (b) Find the expected value of the electron-nucleus distance, $\langle r \rangle$ in the $\psi_{100}(r, \theta, \phi)$ state.

Note 1: To calculate expectation values here, you will need to perform an integral over all 3D space in spherical coordinates according to:

$$\begin{aligned}\langle \hat{A} \rangle &= \int \int \int dV \psi^*(r, \theta, \phi) \cdot \hat{A} \cdot \psi(r, \theta, \phi) \\ &= \int_0^\infty dr \cdot r^2 \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \psi^*(r, \theta, \phi) \cdot \hat{A} \cdot \psi(r, \theta, \phi)\end{aligned}$$

Note 2: You may use Wolfram Alpha to evaluate any sticky integrals. The following integral identity may also come in handy:

$$\int x^n e^{cx} dx = e^{cx} \sum_{j=0}^n (-1)^{n-j} \cdot \frac{n!}{j! c^{n-j+1}} \cdot x^j$$

- (c) What is the expected value of the electron's position along the Cartesian x axis, $\langle x \rangle$, for the $\psi_{100}(r, \theta, \phi)$ state?

Hint: You should not need to perform any integral here; you can instead make an argument based on the symmetry of the wavefunction.

- (d) What is the **most probable** value of the electron's distance from the nucleus, r_0 , for the $\psi_{100}(r, \theta, \phi)$ state?

Hint: r_0 can be found by finding the value of r which *maximizes the particle's radial probability distribution* $p(r)$, given by

$$p(r)dr = |\psi_{100}(r, \theta, \phi)|^2 \cdot 4\pi r^2 \cdot dr$$

where $4\pi r^2 \cdot dr$ is the differential volume of a shell of radius r , akin to the differential distance dr in a 1D system.

3 A Particle on a Ring

The π -orbitals of an aromatic system like benzene, C_6H_6 , may be crudely modeled using the wavefunctions and energies of a “particle on a ring.” Here, we will treat the particle on a ring problem, then extend it to describe the electronic structure of benzene.

Suppose that a particle of mass m is constrained to move on a circle of radius r in the x, y plane. Assume that the particle’s potential energy is a constant independent of its position with $V(x, y) = 0$.

- (a) Write down the time-independent Schrödinger equation in Cartesian coordinates (x, y) for this system.
- (b) We will now transform our system from Cartesian coordinates (x, y) into *cylindrical* coordinates (r, θ) , with

$$\begin{aligned}x &= r \cdot \cos \theta \\y &= r \cdot \sin \theta\end{aligned}$$

Write down the time-independent Schrödinger equation in cylindrical coordinates for this system. You will want to use the fact that:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$$

Additionally, recall that we can treat r as a constant, since the particle is constrained to move at a fixed radius.

- (c) Find the general form of the solutions to this Schrödinger equation, $\psi(\theta)$.
- (d) The boundary condition for this system is that the wavefunction must “wrap around,” so we have $\psi(\theta) = \psi(\theta + 2\pi)$ for all values of θ .
Apply this boundary condition to your general $\psi(\theta)$ solution from part (c) and solve for the discrete energy eigenvalues that result.
Hint: You should find that $E_n = \frac{n^2 \hbar^2}{2mr^2}$, $n = 0, \pm 1, \pm 2, \dots$
- (e) Draw an energy diagram representing the first three energy levels of this system. Make sure to note the degeneracy of each level correctly.
- (f) Consider the six π electrons of a benzene molecule as particles moving on a ring of radius r . Populate your energy diagram from part (e) with these electrons, making sure to obey the Pauli principle (two electrons of opposite spin per orbital). Write down an expression for the energy it would take to excite an electron from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO).

4 Microwave Spectroscopy with Rigid Rotors

- (a) In the far infrared spectrum of H^{79}Br , there is a series of lines spaced by 16.72 cm^{-1} . Calculate the values of the moment of inertia and the internuclear separation in H^{79}Br .
- (b) The bond length of a $^{12}\text{C}^{16}\text{O}$ carbon monoxide molecule is 113 pm . What is the frequency of its $J = 0$ to $J = 1$ rotational transition in Hz ?

5 Infrared Spectroscopy with Harmonic Oscillators

- (a) The force constant for a $^1\text{H}^{19}\text{F}$ molecule is 966 N/m . Calculate the frequency of light needed to excite this molecule from the ground state ($n = 0$) to the first excited state ($n = 1$) in Hertz. Calculate the zero point vibrational energy for this molecule in Joules.
- (b) In the infrared spectrum of H^{79}Br , there is an intense line at 2559 cm^{-1} . Calculate the force constant of H^{79}Br and the period of vibration of H^{79}Br .

6 Rovibrational Spectroscopy

- (a) Consider a diatomic molecule with vibrational frequency ν and rotational constant B . Use the rigid rotor-harmonic oscillator approximation to draw an energy-level diagram for the first four rotational levels in the $v = 0$ and $v = 1$ vibrational states. Label the quantum numbers and energy of each state. Indicate any allowed rovibrational transitions between the states shown that would appear in a rotationally-resolved infrared absorption experiment. Label whether each transition falls in the R or P branch.
- (b) Given that $B = 56\,000\text{ MHz}$ and $\tilde{\nu} = 2143\text{ cm}^{-1}$ for the CO molecule, calculate the transition frequencies **in wavenumbers** (cm^{-1}) of the first two lines of each of the R and P branches in the rovibrational spectrum of CO .

Note: Recall that units given in wavenumbers $\tilde{\nu} \equiv 1/\lambda$ can be converted to frequency (ν) and angular frequency (ω) according to:

$$\nu = \frac{\omega}{2\pi} = \frac{c}{\lambda} = c \cdot \tilde{\nu}$$