

Homework 5

Due: March 2 at 11:59 PM. Submit on Canvas.

- 25 **Problem 1:** Consider the spin states of a spin- $\frac{3}{2}$ particle.
1. In the basis where angular momentum J_z is diagonal, write down the matrices for J_x , J_y and J_z .
 2. Calculate explicitly the eigenvalues for J_x .¹ Looking at the answer, explain why you could have predicted what you find without doing the explicit calculation.
- 25 **Problem 2 (Flux quantization):** Consider a particle of charge $q = -2e$ and mass M , trapped to move along a conducting ring of radius R , which is placed in a magnetic field of uniform strength B . The Hamiltonian describing the single particle motion is

$$H = \frac{1}{2M} \left(-i\frac{\hbar}{R} \frac{\partial}{\partial \phi} - \frac{qBR}{2} \right)^2. \quad (1)$$

Here ϕ denotes the angular coordinate of the particle on the ring – we neglect its motion in the radial (or vertical) direction for convenience.

1. Show that $[H, L_z] = 0$.
2. Deduce the eigenfunctions of H .
3. Since ϕ is an angular coordinate, we must identify the points ϕ and $\phi + 2\pi$. In particular, all wave functions $\psi(\phi) = \psi(\phi + 2\pi)$. If you did not yet account for this fact, do so, and find the (discrete) energy spectrum of H .
4. If the ring is made out of superconducting material, it turns out that current will begin to flow in such a way that the effective magnetic field through the center of the ring, B , is chosen in a way that H has a zero energy ground state. Show that this requires (here $h = 2\pi\hbar$)

$$\Phi_B = B \times \pi R^2 = n \frac{h}{q}. \quad (2)$$

We find that the magnetic flux Φ_B must be quantized in terms of fundamental constants!

5. In a condensed matter laboratory, it is not too challenging to prepare a magnetic field of 1 T in strength. In zinc, the effective mass is very close to the bare electron mass $M \approx 10^{-30}$ kg. If we have a zinc ring of radius $R = 10^{-6}$ m, will we be able to see a finite magnetic flux penetrating the ring in our experiment (assuming we can make it cold enough to make zinc into a superconductor)?

¹You can use e.g. **Mathematica** to carry out the actual computation, so long as you can explain in words how you would set it up to do by hand as well.

Problem 3 (Covalent bond): Consider the hydrogen molecule ion: H_2^+ . We place the two protons of charge $+e$ at the locations $(x, y, z) = (0, 0, \pm a)$. The Hamiltonian describing the motion of a single electron shared between them is

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{\sqrt{s^2 + (z - a)^2}} + \frac{1}{\sqrt{s^2 + (z + a)^2}} \right] \quad (3)$$

where $s^2 = x^2 + y^2$ is the “radial” coordinate in cylindrical coordinates.

5 **A:** Give an intuitive argument (no math needed) that $[H, L_z] = 0$, but $[H, L_x] = [H, L_y] \neq 0$.

5 **B:** One can show as a consequence that the eigenfunctions of H take the form of

$$\psi_{\alpha m}(s, \phi, z) = \psi_{\alpha m}(s, z) e^{im\phi}, \quad (4)$$

for integer $m \in \mathbb{Z}$. This state is an eigenfunction of L_z , with eigenvalue $L_z = m\hbar$. The label “ α ” denotes any additional information associated with the state, and will include its energy level.

Does the symmetry group generated by L_z imply any degeneracy in the spectrum of H ? Why or why not?

10 **C:** The full symmetry group of H can be shown to include elements of the form $e^{i\alpha L_z/\hbar}$ for any angle α , and the three spatial parity symmetries $P_{x,y,z}$, which are defined (in rectangular coordinates) as, e.g.,

$$P_x \psi(x, y, z) = \psi(-x, y, z). \quad (5)$$

Multiplication of any such group elements are also allowed.

C1. Explain why $[H, P_x] = [H, P_y] = [H, P_z] = 0$.

C2. Using that $L_z = xp_y - yp_x$, show that

$$L_z P_y = -P_y L_z. \quad (6)$$

Conclude that the symmetry group of H is non-Abelian.

10 **D:** In this example, we can try to explicitly see how the higher dimensional irreducible representations of the symmetry group arise (and in turn, understand the symmetry-enforced degeneracy of H).

D1. Explain why (a picture is fine, if you don’t want to explicitly calculate!)

$$P_y \psi_m(s, z) e^{im\phi} = \psi_m(s, z) e^{-im\phi}. \quad (7)$$

D2. Conclude that $\psi_m(s, z)[\alpha \cos(m\phi) + \beta \sin(m\phi)]$ is an eigenfunction of H for any α, β . Conclude that H must have (at least) two-dimensional irreducible representations.

In quantum chemistry, the $|m| = 0, 1, \dots$ irreps are labeled with σ, π, \dots . When one talks about σ -bonds and π -bonds in organic molecules, e.g., they are referring to the molecular orbitals above, which are (approximately) classified by the symmetry group we have found in this problem.²

²In a complicated molecule, the local environment has even less symmetry, but one still often approximately thinks of the wave functions forming each covalent bond as classified by an approximate rotational symmetry around the axis of the bond.

Problem 4 (Geometry of rotations): In this problem, we will explore the “global” properties of rotations in quantum mechanics (as opposed to the “local” commutators between $J_{x,y,z}$).

- 10 **A:** Let us begin by thinking about what angle we need to rotate by, to return to the identity. Namely, for what angle α is $e^{i\alpha J_z/\hbar} = 1$? Let’s consider a spin- $\frac{1}{2}$ particle, where we have seen that

$$J_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2} \sigma_z. \quad (8)$$

A1. Show that³

$$e^{i\alpha J_z/\hbar} = 1 \cdot \cos \frac{\alpha}{2} + \sigma_z \cdot i \sin \frac{\alpha}{2} \quad (9)$$

A2. One rather surprising answer is that only when $\alpha = 4\pi$, do we find $e^{i\alpha J_z/\hbar} = 1$! Argue, however, that there is no quantum experiment that can be done that distinguishes the state $|\psi\rangle$ from the state $e^{2\pi i J_z/\hbar} |\psi\rangle$ (rotation by 2π). In this sense, rotation by 2π indeed gives us the “same physics”.

- 10 **B:** The rotation group generated by J_x , J_y and J_z (for spin- $\frac{1}{2}$) is called $SU(2)$. It turns out (you don’t need to show this) that the most general possible rotation is of the form

$$U = \begin{pmatrix} a_0 + ia_3 & ia_1 - a_2 \\ ia_1 + a_2 & a_0 - ia_3 \end{pmatrix}, \quad (10)$$

subject to the constraint $\det(U) = 1$. Note that (9) corresponds to a particular choice of this U where only $a_0, a_3 \neq 0$.

B1. Evaluate the constraint $\det(U) = 1$ to find a constraint on the $a_{0,1,2,3}$ coefficients. Conclude that the space of possible rotations, $SU(2)$, is identical to the surface of a ball in 4-dimensional space. (This is called the 3-dimensional sphere S^3 , since locally on the sphere, you can move in 3 different directions.)

B2. As in A2, we might consider that not all rotations correspond to distinct quantum states, so long as there is no physical way to tell the states apart. Argue that we can instead think of the set of *physically distinct* rotations as the set of all lines in four-dimensional space passing through the origin. This space is called \mathbb{RP}^3 , and the group of rotations subject to these constraints is $SO(3)$.

$SO(3)$ and $SU(2)$ turn out to be two continuous (Lie) groups generated by the angular momentum algebra, but with a distinct global structure. When quantum mechanics was first created, it realized a very concrete application of the (previously) esoteric mathematics of continuous groups.

Problem 5 (Molecular spectroscopy): A simple molecule such as ammonia (NH_3) has rotational dynamics described by the Hamiltonian

$$H = \frac{L_x^2 + L_y^2}{2I_0} + \frac{L_z^2}{2I_z}. \quad (11)$$

where \mathbf{L} denotes the orbital angular momentum.

- 10 **A:** Show that the energy levels of the Hamiltonian are given by

$$E_{lm} = \frac{\hbar^2}{2I_0} l(l+1) + \left[\frac{\hbar^2}{2I_z} - \frac{\hbar^2}{2I_0} \right] m^2, \quad (l = 0, 1, 2, \dots, m = 0, \pm 1, \dots, \pm l). \quad (12)$$

³Hint: Use the Taylor series for exponentiation, sines and cosines, and identities from Lecture 13.

- 15 **B:** For reasons we will derive later in this course, when a photon is absorbed or emitted by this molecule, the value of l and m can only change by 0 or ± 1 in the most prominent transitions.⁴ A physical chemist finds that the lowest frequencies of light which are absorbed or emitted by a molecule whose rotational degrees of freedom are described by (11) are:

$$\nu \approx 22.4, 57.0, 67.3, 79.4, 91.5, 112, 126, 136, 159 \text{ GHz.} \quad (13)$$

Using only this data, along with the values of fundamental constants, estimate I_0 and I_z .

⁴Actually, the so-called “selection rules” are even more complicated for these molecules, however we will pretend they are simple for convenience. Note that the “experimental data” presented here is also fake, because we are oversimplifying the allowed transitions. Still, this problem should give you the spirit for how a physical chemist would interpret their data.