

Homework 6

Due: 11:59 PM, Tuesday, October 13. Submit your homework via Canvas.

10 points **Problem 1 (Vector operators):** A reasonable definition of a vector operator (V_x, V_y, V_z) in three dimensions is that it (component wise) obeys the commutation relations

$$[V_i, L_j] = i\hbar \sum_k \epsilon_{ijk} V_k, \quad (1)$$

where

$$\epsilon_{ijk} = \begin{cases} 1 & ijk = xyz, yzx, zxy \\ -1 & ijk = xzy, zyx, yxz \\ 0 & \text{otherwise} \end{cases}. \quad (2)$$

Using the definition

$$L_i = \sum_{j,k} \epsilon_{ijk} x_j p_k \quad (3)$$

where $x_i = (x, y, z)$ and $p_i = (p_x, p_y, p_z)$ denote the position and momentum operators, show that x_i and p_i transform as vector operators in quantum mechanics: i.e., they obey (1).¹ Of course, since (1) also holds with $V_i = L_i$, the angular momentum operators are also “vector operators”.

Problem 2 (Rotational spectroscopy): A simple molecule such as ammonia (NH_3) has rotational dynamics described by the Hamiltonian

$$H = \frac{L_x^2 + L_y^2}{2I_0} + \frac{L_z^2}{2I_z}. \quad (4)$$

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

5 points (a) Show that the energy levels of the Hamiltonian are given by²

$$E_{lm} = \frac{\hbar^2}{2I_0} l(l+1) + \left[\frac{\hbar^2}{2I_z} - \frac{\hbar^2}{2I_0} \right] m^2, \quad (l = 0, 1, 2, \dots, m = 0, \pm 1, \dots, \pm l). \quad (5)$$

5 points BONUS (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.³ 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 (4) are:

$$\nu \approx 22.4, 57.0, 67.3, 79.4, 91.5, 112, 126, 136, 159 \text{ GHz}. \quad (6)$$

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

¹Hint: Keep things in terms of indices! You’ll waste a lot of time doing this for each component. Also use the identity $[A, BC] = [A, B]C + B[A, C]$. ϵ_{ijk} , the Levi-Civita tensor, has useful identities: $\epsilon_{ijk} = \epsilon_{jki} = \epsilon_{kij} = -\epsilon_{kji}$.

²Hint: $[\mathbf{L}^2, L_z] = 0$. What is $L_x^2 + L_y^2$?

³Actually, 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.

5 points **Problem 3:** Consider a spin- $\frac{3}{2}$ system. Write down the angular momentum matrices J_x , J_y and J_z , in the standard basis where J_z is diagonal.⁴

Problem 4 (Measuring nuclear spin via spectroscopy): A diatomic molecule A_2 consists of two identical nuclei (A) of unknown spin J .

5 points (a) When are the nuclei bosons, and when are they fermions?

(b) If the nuclei have spin J , how many spin states $|s_{z1}\rangle$ are allowed for a single nuclear spin, on its own? How many allowed spin states $|s_{z1}s_{z2}\rangle$ are there for two spin J nuclei? Show that the number of symmetric spin wave functions is $(J+1)(2J+1)$, and the number of antisymmetric spin wave functions is $J(2J+1)$.

The full nuclear wave function of the A_2 molecule is of the form $\psi(\mathbf{r}_1, s_{z1}, \mathbf{r}_2, s_{z2})$ – it includes both the nucleus position and spin. Defining the relative spherical coordinates

$$x_1 - x_2 = r \sin \theta \cos \phi, \quad (7a)$$

$$y_1 - y_2 = r \sin \theta \sin \phi, \quad (7b)$$

$$z_1 - z_2 = r \cos \theta. \quad (7c)$$

It is often reasonable to look for wave functions of the form

$$\psi(\mathbf{x}_1, s_{z1}, \mathbf{x}_2, s_{z2}) = \psi_{\text{com}}\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}\right) \psi_{\text{radial}}(r) \times Y_{lm}(\theta, \phi)|s_{z1}s_{z2}\rangle. \quad (8)$$

In fact, in this problem, we can ignore the center of mass (com) motion along with the radial relative motion of the nuclei. We thus approximate the wave function by $\psi \approx Y_{lm}(\theta, \phi)|s_{z1}s_{z2}\rangle$.

5 points (c) Argue that if we exchange the positions of the two nuclei, then that is equivalent to taking the angular coordinates $(\theta, \phi) \rightarrow (\pi - \theta, \pi + \phi)$. What happens to the spherical harmonic Y_{lm} under this exchange?

(d) Explain why if we have bosonic nuclei, the allowed wave functions have even l and symmetric spin, or odd l and antisymmetric spin wave function. What happens for fermionic nuclei?

5 points (e) The Hamiltonian for the angular and spin dynamics is well approximated by a “rigid rotor” Hamiltonian which describes the *relative* angular coordinates of the two molecules:

$$H = \frac{\mathbf{L}^2}{2I} \quad (9)$$

where I is the molecule’s moment of inertia and \mathbf{L}^2 is the net *rotational* angular momentum. Describe the eigenstates and eigenvalues of H .

(f) What is the degeneracy of each energy level? Remember to include spin!⁵

5 points (g) When an A_2 molecule emits or absorbs a photon, the spin component of the wave function will not change, while the angular momentum changes by $l \rightarrow l \pm 2$. (Note that such a diatomic gas is relatively weakly interacting with radiation – we will return to this in a later homework!) Show that when $l \gg 1$ is large, the frequency of radiation associated with the $l \rightarrow l - 2$ transition will be

$$\omega_l \approx Bl. \quad (10)$$

Give an expression for the constant prefactor B in terms of I and fundamental constants.

⁴Hint: One can be done by eye. For the other two, use the angular momentum raising and lowering operators.

⁵Interestingly, the answer to this question changes depending on whether we include the rotational degrees of freedom coming from the center of mass dynamics. *Do not* account for this subtlety in this problem!

- (h) At high energy ($l \gg 1$) it is reasonable to approximate that the intensity of the emitted/absorbed radiation is proportional to the number of allowable spin states. Conclude that the intensity of lines of emitted/absorbed radiation will alternate between a smaller value I_- and a larger value I_+ , at evenly spaced frequencies, with ratio

$$\frac{I_-}{I_+} = \frac{J}{J+1}. \quad (11)$$

- (i) Determine the spin J of ^3He , using the experimental data in Figure 1.

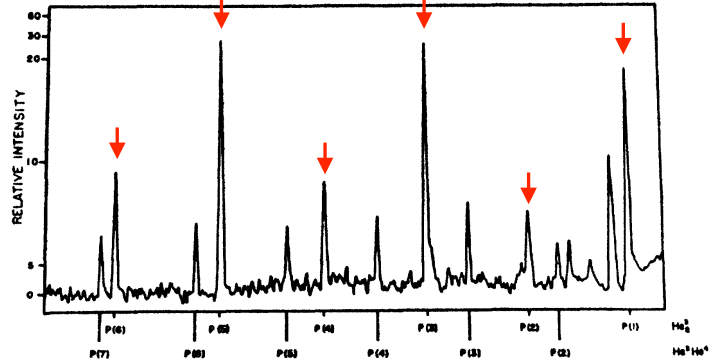


Figure 1: Spectroscopy of helium gas greatly enriched with ^3He (the natural isotope is ^4He). Data from $(^3\text{He})_2$ is emphasized with red arrows. Figure taken from [1].

[1] A. E. Douglas and G. Hertzberg. “The nuclear spin of He^3 ”, *Physical Review* **76** 1529 (1949).