

Homework 4

► **Due:** 11:59 PM, February 15. Submit electronically on Canvas.

► **Prove/show** means to provide a mathematically rigorous proof. **Argue/describe/explain why** means a non-rigorous (but convincing) argument is acceptable.

30 **Problem 1 (Emergent symmetry):** Consider magnetism in a two-dimensional crystal with D_{12} symmetry. The magnetization vector (M_x, M_y) is in an ordinary vector representation, with r corresponding to 60° rotation and s corresponding to reflection in x .

Let's find possible expressions for a D_{12} invariant free energy $F(M_x, M_y)$. One clever way we can do this is to start with a “guess” function

$$f(M_x, M_y) = aM_x^2 + bM_x^4 + cM_x^6, \tag{1}$$

and to find our phenomenological free energy function as

$$F(M_x, M_y) = \frac{1}{12} \sum_{g \in D_{12}} f(g \cdot (M_x, M_y)). \tag{2}$$

- i. Show that $F(M_x, M_y)$ must be D_{12} -invariant.
- ii. For the choice of f in (1), evaluate $F(M_x, M_y)$ explicitly. **Mathematica** may help you do some symbolic algebra.
- iii. Assume $b, c > 0$. What happens to the location of the minimum of F if we decrease a from positive to negative? A few words will suffice.
- iv. Suppose $|a| \ll b, c$. Argue that near the minimum, it is reasonable to approximate that $F(M_x, M_y)$ is a quartic polynomial (i.e. you can approximate $c \approx 0$).
- v. What is the symmetry group of the quartic $F(M_x, M_y)$? Show that it is *larger* than D_{12} .

The idea that emergent symmetry groups can arise in special regions of parameter space is a common theme in much of modern theoretical physics.

Problem 2 (Dihedral symmetry in quantum mechanics): Consider a quantum mechanical non-relativistic particle of mass m in two spatial dimensions, in a potential obeying $V(x, y) = V(\pm x, \pm y) = V(y, x)$.

- 20 (a) This Hamiltonian is invariant under D_8 symmetry, acting in the standard way on the coordinates (x, y) , which was described in Lectures 5 and 6.
 - i. Use the group action of D_8 on the coordinates (x, y) to find $g \cdot f(x, y)$ for any $g \in D_8$, and any function f .
 - ii. Use the projection algorithm of Lecture 7 to show how to project any f onto any of the 5 irreps of D_8 . An explicit formula will help you for later parts!

20 (b) Consider a particle in a box, where

$$V(x, y) = \begin{cases} 0 & |x|, |y| \leq \frac{1}{2}L, \\ \infty & \text{otherwise} \end{cases}. \quad (3)$$

- i. Find the eigenvalues and eigenfunctions of H .
- ii. For each eigenfunction, determine which irrep of D_8 it belongs to.
- iii. Does D_8 representation theory explain all degeneracy in the Hamiltonian?

15 (c) Suppose we modify

$$V(x, y) = \begin{cases} 0 & |x| \leq \frac{1}{2}L_x, |y| \leq \frac{1}{2}L_y, \\ \infty & \text{otherwise} \end{cases}. \quad (4)$$

Assume $L_x \neq L_y$.

- i. Find the eigenvalues and eigenfunctions of H .
- ii. Explain why the symmetry group is now $\mathbb{Z}_2 \times \mathbb{Z}_2$.
- iii. Classify all of the eigenfunctions of H according to irreps of $\mathbb{Z}_2 \times \mathbb{Z}_2$.
- iv. Discuss how the degeneracies of part (b) are broken. Confirm that the way that the irreps of D_8 broke into irreps of $\mathbb{Z}_2 \times \mathbb{Z}_2$ is consistent with what we found in Lecture 8.

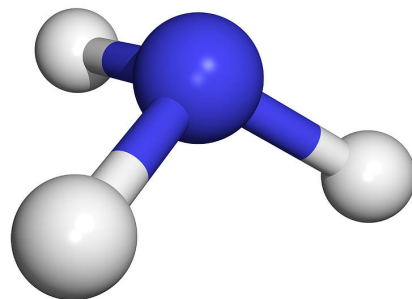


Figure 1: The ammonia molecule. Note that the 3 hydrogen atoms (in white) form an equilateral triangle.

Problem 3 (Vibrational spectroscopy of ammonia): Consider the ammonia molecule NH_3 , shown in Figure 1. The symmetry group of this molecule is D_6 – like in the example of BH_3 in Lecture 1. The character table for $D_6 = S_3$ can be found in Zee II.3, or online!

- 15 (a) Let the displacement coordinates (away from the equilibrium shown in the figure) of the 3 H atoms be $\mathbf{x}_1 = (x_1, y_1, z_1)$, \mathbf{x}_2 and \mathbf{x}_3 ; the N atom's are \mathbf{x}_4 . It will be useful to organize these coordinates into vectors of the form (in bra-ket notation) $x_1 \rightarrow |x1\rangle$. This notation is useful because it will be valuable, in this problem, to think of the vector space as a tensor product of a spatial part ($|x\rangle, |y\rangle, |z\rangle$) with an atom number space ($|1\rangle, |2\rangle, |3\rangle, |4\rangle$).
- i. How do the rotations/reflections which exchange atoms act on coordinates (x, y, z) ? Call these matrices $P(g)$. If the Hs lie in the xy -plane, you could choose

$$P(r) = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad P(s) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (5)$$

- ii. How does D_6 act on atom numbers (namely, how are the atoms exchanged under symmetry transformations)? Call these matrices $M(g)$, and give explicit formulas for $M(r)$ and $M(s)$.
- iii. Let R denote the 12-dimensional reducible representation of D_6 acting on the vector space spanned by $|x1\rangle, \dots, |z4\rangle$. Explain why we can interpret the 12×12 matrix $R(g)$, for $g \in D_6$, as

$$R(g) = P(g) \otimes M(g). \quad (6)$$

10 (b) Abstractly, the low energy dynamics of the molecule is captured by the Hamiltonian

$$H = \frac{1}{2} \left[p_i M_{ij}^{-1} p_j + q_i K_{ij} q_j \right], \quad (7)$$

with M_{ij} a (diagonal) atomic mass matrix, and K_{ij} some complicated matrix corresponding to the couplings between the atomic displacements (collected as the 12-component vector q_j , with conjugate momenta p_j). If we knew M_{ij} and K_{ij} , we could numerically determine the 12 normal mode oscillation frequencies of our molecule. Remarkably, we can use group theory to learn quite a lot about the possible frequencies, without knowing any further microscopic details! We'll start by thinking about the global, equilibrium-adjusting symmetries that we ignored before – translation and rotation.

- i. Consider the vector (x, y, z) of spatial coordinates. In one or two sentences, argue that this vector is in the reducible representation $P = \mathbf{1} \oplus \mathbf{2}$. Don't worry about deriving this rigorously.
- ii. Now consider the vector of angular momenta, (J_x, J_y, J_z) . In one or two sentences, argue that this breaks into $\bar{\mathbf{1}} \oplus \mathbf{2}$.¹
- iii. Explain why global translation/rotation symmetry leads to 6 normal modes of the molecule having zero vibrational frequency. To which representations will these zero modes belong?

20 (c) We're now ready to determine the qualitative structure of the non-zero normal modes.

- i. Show that $\chi^{(R)}(\mathbf{1}) = 12$, $\chi^{(R)}(r) = 0$, and $\chi^{(R)}(s) = 2$.²
- ii. Deduce how many copies of each irrep are contained within R .
- iii. Predict the number of distinct non-zero vibrational frequencies of NH_3 , along with any symmetry-enforced degeneracies.
- iv. Compare your predictions to the (experimentally) known vibrational spectrum of NH_3 , which you should be able to find online. While we haven't discussed the jargon behind the chemistry/solid-state group theory notation you may encounter, you should be able to at least confirm your predictions about the number of distinct modes.

If you are stuck on this problem, reading through Zee III.2 is a good place to start. Watch out though; his treatment of the calculation analogous to part (a) is a bit sloppy and seems to fail for this realistic molecule.

¹Hint: What happens to J_z under reflection?

²Hint: $\text{tr}(A \otimes B) = \text{tr}(A)\text{tr}(B)$.