Q1

For ammonia: identify its point group with corresponding symmetries. How many different irreducible representations are in the point group for ammonia?

Q2

Without looking at the character table, how do you expect the \( p_{2x} \) atomic orbital on the central nitrogen atom to behave (i.e., symmetry or antisymmetric or none) to each of the symmetry elements of the molecule. Write the mathematical representation for this operation (i.e, in \( C_{2v} \)) we would write \( \hat{C}_2 p_{2z} = (+1) p_{2z} \) for a symmetric symmetry; do this for all operations). There is a special term for irreducible representation of this orbital; what is it and why is it call that?

Q3

Without looking at the character table, how do you expect the \( p_{2y} \) atomic orbital on the central nitrogen atom to behave (i.e., symmetry or antisymmetric or none) to each of the symmetry elements of the point group (write the mathematical equation for each operation). What is the irreducible representation of this orbital and how does it differ with the irreducible representation found for \( p_{2z} \) above?

Q4

The term SALC stands for a "Symmetry Adapted Linear Combination" and refers to different "predigested" mixing of atomic orbital typically on periphery of the molecules (like with ligands in inorganic molecules or hydogens in ammonia.)
It is similar to the “predigestion” of generating hybrid orbitals by mixing atomic orbitals together before making molecule orbitals (mathematically, it is the same as addressing all atomic orbitals directly). For ammonia, we can make several and they have the symmetries of the point group. Consider the totally symmetric SALC on each of the hydrogen atoms (labels A, B, C):

\[ | \psi_1 \rangle = N \left[ | 1s_A \rangle + | 1s_B \rangle + | 1s_C \rangle \right] \]

How does \(| \psi_1 \rangle \) behave to each of the symmetry operations of the relevant point group (describe it both in words and the relevant mathematical equation like above)? What is the irreducible representation of \(| \psi_1 \rangle \)?

Q5

For each of the symmetry operations outlined above for the \(| \psi_1 \rangle \) how do these integrals change:

- \(| \langle \psi | \psi_1 \rangle \rangle \)
- \(| \langle \psi \rangle p_{z=2} (N) | p_z (N) \rangle \rangle \)
- \(| \langle \psi \rangle p_{y=2} (N) | p_{y=2} (N) \rangle \rangle \)

Explain these trends in words.

Q6

The direct product of two irreducible representations is obtained by multiplying the respective characters of the representations. The result is again an irreducible representation of the same group. For example, in the \(| C_{(2V)} \rangle \) point group the direct product of \(| A_1 \rangle \) and \(| B_2 \rangle \) (\(| A_1 \rangle \otimes | B_2 \rangle \)):

\[
\begin{array}{c|c|c|c|c}
| A_1 \rangle \otimes | B_2 \rangle & | A_1 \rangle & | A_2 \rangle & | B_1 \rangle & | B_2 \rangle \\
\hline
| A_1 \rangle & 1 & 1 & -1 & -1 \\
| A_2 \rangle & 1 & -1 & -1 & 1 \\
| B_1 \rangle & \langle 1 \times 1 = 1 \rangle & | 1 \times -1 = -1 \rangle & | -1 \times -1 = 1 \rangle & | -1 \times 1 = 1 \rangle \\
| B_2 \rangle & | A_1 \rangle & | A_2 \rangle & | B_1 \rangle & | B_2 \rangle \\
\end{array}
\]

From inspection of the irreducible representations of the \(| C_{(2V)} \rangle \) point group, we can see that the irreducible representation for this piecewise multiplication procedure ("Direct Product") is

\[ | A_1 \rangle \otimes | B_2 = B_1 \rangle \]

Doing this for all possible multiplications for the \(| C_{(2V)} \rangle \) point group results in a Direct Product Table:
Complete the Direct Product table above for \( \Gamma(C_{2v}) \) point group.

Q7

Construct the Direct Product table for the point group associated with ammonia.

Q8

It was argued in class that for a general integral to be non-zero, the integrand must contain (or be) the totally symmetric irreducible representation. This is basically saying that no symmetry operation on the integral (or specifically all the functions in the integrand) will result in a -1 character (i.e., antisymmetric or "odd"). Using the direct product table above evaluate the irreducible representation of the following functions for ammonia:

• \( \langle p_{2z} | p_{2y} \rangle \)
• \( \langle p_{2y} | p_{2z} \rangle \)
• \( \langle p_{2z} | \psi_1 \rangle \)
• \( \langle p_{2z} | \psi_2 \rangle \) (where \( \langle \psi_2 \rangle \) has \( E \) symmetry)

Q9

Evaluate if the following integrals are zero or non-zero based on symmetry

• \( \langle p_{2z} | p_{2y} \rangle \)
• \( \langle p_{2y} | p_{2z} \rangle \)
• \( \langle p_{2z} | \psi_1 \rangle \)
• \( \langle p_{2z} | \psi_1 \rangle \)
Using the direct product table above evaluate the irreducible representation of the following functions for ammonia where $\langle \hat{H} \rangle$ is the Hamiltonian and have the totally symmetric representation:

- $\langle \hat{H} | p_{2z} \rangle | p_{2y} \rangle$
- $\langle \hat{H} | p_{2y} \rangle | p_{2z} \rangle$
- $\langle \hat{H} | p_{2z} \rangle | \psi_1 \rangle$
- $\langle \hat{H} | p_{2z} \rangle | \psi_2 \rangle$ (where $| \psi_2 \rangle$ is a SALC with $E$ symmetry)

Using the direct product table above evaluate the irreducible representation of the following functions for ammonia where $\langle \hat{O} \rangle$ is an operator with $(A_2)$ symmetry:

- $\langle \hat{O} | p_{2z} \rangle | p_{2y} \rangle$
- $\langle \hat{O} | p_{2y} \rangle | p_{2z} \rangle$
- $\langle \hat{O} | p_{2z} \rangle | \psi_1 \rangle$
- $\langle \hat{O} | p_{2z} \rangle | \psi_2 \rangle$ (where $| \psi_2 \rangle$ is a SALC with $E$ symmetry)

Evaluate if the following integrals are zero or non-zero based on symmetry

- $\langle \hat{O} | p_{2z} \rangle | p_{2y} \rangle$
- $\langle \hat{O} | p_{2y} \rangle | p_{2z} \rangle$
- $\langle \hat{O} | p_{2z} \rangle | \psi_1 \rangle$
- $\langle \hat{O} | p_{2z} \rangle | \psi_2 \rangle$ (where $| \psi_2 \rangle$ is a SALC with $E$ symmetry)
\langle p_{2z} | \hat{O} | \psi_2 \rangle (where \| \psi_2 \rangle is a SALC with \|E\) symmetry)