

Week 3

Applications of Representation Theory

3.1 Reducible Representations and Direct Products

10/10:

- PSet is due at the beginning of next class. Email or submit in paper. Show your work!
- Since molecules have more than one point, we need to work with the characters of reducible representations. In particular, when applying group theory to chemical problems, we need to find the IRRs whose sum is the reducible representation.
- **Reduction formula:** The formula which takes a Γ_{red} and decomposes it into a sum of Γ_{IRRS} . *Given by*

$$n(\Gamma_A) = \frac{1}{h} \sum_i g(R) \chi_{\text{IRR}}(R) \chi_{\text{RR}}(R)$$

- $n(\Gamma_A)$ is the number of times the IRR A occurs in Γ_{red} .
- h is the order of the group.
- $g(R)$ is the order of the class under the symmetry operation R .
- $\chi_{\text{IRR}}(R)$ is the character of the IRR under the symmetry operation R .
- $\chi_{\text{RR}}(R)$ is the character of the reducible representation under the symmetry operation R .
- Recall $\Gamma_{\text{red}} = (3, 0, 1)$ in C_{3v} from Lecture 2.2.
 - The number of times each IRR appears is, according to the reduction formula:

$$n(A_1) = \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot 1 \cdot 1) = 1$$

$$n(A_2) = \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot -1 \cdot 1) = 0$$

$$n(E) = \frac{1}{6}(1 \cdot 2 \cdot 3 + 2 \cdot -1 \cdot 0 + 3 \cdot 0 \cdot 1) = 1$$

- Simple cases (like this and the next one) we can often do by inspection.
- Example: $\Gamma_{\text{RR}} = (6, 0, 0)$.
 - Decompose it into $A_1 + A_2 + 2E$.
- **Direct product** (of two representations): The (reducible or irreducible) representation obtained by multiplying the characters of the two representations which correspond under each operation. *Denoted by $M \times N$, where M, N are Mulliken symbols.*

- Examples:
 - $A_1 \times E = E$.
 - $A_2 \times E = E$.
 - $E \times E = A_1 + A_2 + E$.
 - $A_2 \times A_2 = A_1$.
- We now dive into how to use the symmetry properties of a collection of orbitals to determine the states that arise by populating them with electrons. To do this for a given basis set of valence atomic orbitals, we need to ask what set of IRRs they fall into.
- Procedure.
 1. Generate the characters of this representation by examining the trace of the relevant transform matrices.
 - +1 on the diagonal if a particular basis function is left unchanged during the symmetry operation.
 - 0 on the diagonal if the basis function is transformed to another function.
 - -1 on the diagonal if the function is converted into minus itself.
 - Indeed, only basis set elements that do not move contribute to the trace (i.e., character) of the representation.
 2. Check that the dimension is greater than the largest dimension permissible in the point group. If so, we need to reduce to IRRs. This is an important step to construct SALCs.
- Example: Consider the set of H_{1s} orbitals of NH_3 as the representation.
 - $\Gamma_{3H_{1s}} = (3, 0, 1)$ since all 3 orbitals stay under E , all orbitals move under $2C_3$, and 1 orbital stays under $3\sigma_v$.
 - Decompose into $A_1 + E$.
 - Therefore, the $1s$ orbital of H within C_{3v} of NH_3 transforms in $a_1 + e$ symmetry.
 - Note that we use lowercase Mulliken symbols for atomic/molecular orbitals and vibrational modes and uppercase Mulliken symbols for electronic states.
 - This $a_1 + e$ symmetry for the H_{1s} group orbitals implies that there are 3 SALC orbitals: 1 of a_1 symmetry and 2 of e symmetry.
- Example: H_2O .
 - $\Gamma = (2, 0, 0, 2) = A_1 + B_2$.

3.2 Projection Operations and SALCs

10/12:

- PSet 2 is posted and due 10/21.
 - Go over questions on the HW in the review classes prior to exams.
- **Symmetry-Adapted Linear Combination:** An orthonormal linear combination of one or more sets of orthonormal functions (which are either atomic orbitals or internal coordinates of a molecule) taken in such a way that the combinations form bases for irreducible representations of the symmetry group of the molecule. *Also known as SALC.*
- Last time, we investigated the SALCs of NH_3 . We found them by decomposing a reducible representation of the H_{1s} basis set to its irreducible representations and naming them via the character table.

- Goal: What do the SALCs of NH_3 look like?
 - We know that we need 3 SALCs, 1 of a_1 symmetry and 2 of e symmetry.
 - To achieve the goal, we apply the **projection operator** to each irreducible representation.
- **Projection operator** (on an IRR): The operator defined as follows, which acts on IRRs. *Denoted by \hat{P} . Given by*

$$\hat{P}(\Gamma_i) = \frac{\ell_i}{h} \sum_R \chi_i(R) \hat{R}$$

- ℓ_i is the dimension(ality) of the IRR.
- Γ_i is the IRR.
- \hat{R} is the symmetry operation to be applied to the basis.
- $\chi_i(R)$ is the character of the given symmetry operation for Γ_i .
- In other words, we need to evaluate what happens to the H_{1s} orbitals under each symmetry operation.
- It follows that we need the character table to evaluate what happens to the H_{1s} orbitals for each symmetry operation.
 - Note that for the projection operator, we do *not* do this by class (i.e., we do need to apply *every single* symmetry operation)^[1].
 - Focus on one orbital in particular, and see to which orbital each symmetry operation takes it.
- NH_3 example.

- We have

$$E : x_1 \mapsto x_1 \quad C_3 : x_1 \mapsto x_2 \quad C_3^2 : x_1 \mapsto x_3 \quad \sigma_v : x_1 \mapsto x_1 \quad \sigma'_v : x_1 \mapsto x_3 \quad \sigma''_v : x_1 \mapsto x_2$$

- We can do the same for where x_2, x_3 go.
- It follows that

$$\hat{P}(A_1)_{x_1} = 1x_1 + 1x_2 + 1x_3 + 1x_1 + 1x_3 + 1x_2 = 2(x_1 + x_2 + x_3) \approx x_1 + x_2 + x_3$$

- This implies that under the totally symmetric representation, all orbitals are the same, as we might expect. Note that the constant factor of 2 does not affect the functional form and therefore does not affect the symmetry properties.
- We don't carry through ℓ_i/h because it's a constant??
- Note that

$$\hat{P}(A_1)_{x_2} = \hat{P}(A_1)_{x_3} = \hat{P}(A_1)_{x_1}$$

- As another example,

$$\hat{P}(E)_{x_1} = 2x_1 - x_2 - x_3 + 0x_1 + 0x_3 + 0x_2 = 2x_1 - x_2 - x_3$$

- Similarly,

$$\hat{P}(E)_{x_2} = 2x_2 - x_3 - x_1$$

$$\hat{P}(E)_{x_3} = 2x_3 - x_1 - x_2$$

- Note that all of these functions must be orthonormal.
 - We have three functions, but we only need 2 in e ! Thus, we employ the orthonormal rule to figure it out.

¹Notice that the order of the class is not present in the projection operator!

- We have that the first and second, and first and third are not orthogonal:

$$(\Psi_{E,x_1}, \Psi_{E,x_2}) = (2)(-1) + (2)(-1) + (-1)(-1) = 3 \neq 0$$

$$(\Psi_{E,x_1}, \Psi_{E,x_3}) = (2)(-1) + (-1)(-1) + (-1)(2) = 3 \neq 0$$

- What we can do is take a linear combination of 2 and 3 so that it's orthogonal to 1.

- Let's try

$$\Psi_{E,\text{new}} = \Psi_{E,x_2} - \Psi_{E,x_3} = 3x_2 - 3x_3 \approx x_2 - x_3$$

- Indeed,

$$(\Psi_{E,x_1}, \Psi_{E,\text{new}}) = (2)(0) + (-1)(1) + (-1)(-1) = 0$$

as desired.

- Note that adding does not get us something orthogonal.

– Normalize the SALCs.

- At this point, we have that

$$\Psi_{A_1 \text{ SALC}} = x_1 + x_2 + x_3 \quad \Psi_{E \text{ SALC}} = 2x_1 - x_2 - x_3 \quad \Psi_{E \text{ SALC}} = x_2 - x_3$$

- Normalization means adjusting the normalization constant N such that

$$\int [N(x_1 + x_2 + x_3)]^2 = 1$$

- More simply, we multiply each of the above by 1 over the square root of the sum of the squares of the extant coefficients. So

$$\begin{aligned} \Psi_{A_1 \text{ SALC}} &= \frac{1}{\sqrt{1^2 + 1^2 + 1^2}}(x_1 + x_2 + x_3) & \Psi_{E \text{ SALC}} &= \frac{1}{\sqrt{2^2 + (-1)^2 + (-1)^2}}(2x_1 - x_2 - x_3) \\ &= \frac{1}{\sqrt{3}}(x_1 + x_2 + x_3) & &= \frac{1}{\sqrt{6}}(2x_1 - x_2 - x_3) \end{aligned}$$

$$\begin{aligned} \Psi_{E \text{ SALC}} &= \frac{1}{\sqrt{0^2 + 1^2 + (-1)^2}}(x_2 - x_3) \\ &= \frac{1}{\sqrt{2}}(x_2 - x_3) \end{aligned}$$

– Lastly, we can draw the orbitals.

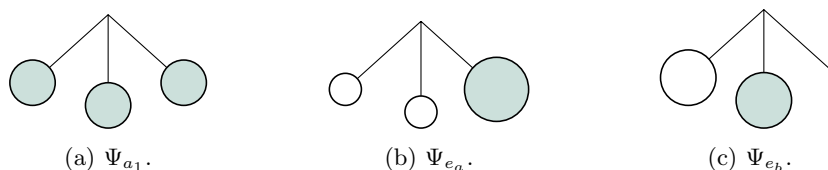


Figure 3.1: NH_3 SALCs.

3.3 Vibrational Modes and Symmetry

10/14:

- Purposes of the basis set \rightarrow RRs \rightarrow IRRs \rightarrow SALCs workflow.

1. Helps us understand the symmetry properties of molecular vibrations (we are going to look at this first).
2. Helps us understand MO diagrams (we will look at this after Exam 1).

- Symmetry properties of molecular vibrations: Any vibrational motion of a molecule can be decomposed in a combination of normal modes, and all normal modes form the basis of an irreducible representation of the point group of the molecule.
- How many normal modes do we have for a given molecule?
 - N atoms.
 - $3N$ degrees of freedom.
 - 3 translations.
 - 3 rotations (2 for linear molecules).
 - $3N - 6$ (resp. $3N - 5$) vibrations (i.e., normal modes).
- How to determine normal modes.
 1. Determine the point group.
 2. Consider the motion of atoms independently.
 3. Use the Cartesian displacement method, reduce $\Gamma_{\text{Cartesian}}$ to IRRs, and compare with the character table to determine which can be accounted for by translation (x, y, z) and rotation (R_x, R_y, R_z) .
 4. Use the stretching and/or bending vectors as basis sets and use \hat{P} to determine what the normal modes look like.
- Example: H_2O .
 1. C_{2v} .
 2. 3 degrees of freedom for each atom (atom i can move in the x_i, y_i, z_i direction for $i = 1, 2, 3$).
 3. Multiple steps:
 - (a) Find $\Gamma_{\text{unmoved}} = (3, 1, 1, 3)$.
 - (b) Find Γ_{xyz} : From the relevant character table, $\Gamma_{xyz} = A_1 + B_1 + B_2 = (3, -1, 1, 1)$.
 - (c) Find $\Gamma_{\text{Cartesian}} = \Gamma_{\text{unmoved}} \times \Gamma_{xyz} = (9, -1, 1, 3)$.
 - (d) Apply the reduction formula: $\Gamma_{\text{Cartesian}} = 3A_1 + A_2 + 2B_1 + 3B_2$.
 - (e) Notice that A_1 corresponds to the z -translation, A_2 corresponds to the z -rotation, B_1 corresponds to the x -translation and y -rotation, and B_2 corresponds to the y -translation and x -rotation. If we want to determine the vibrational modes of symmetry, we need to subtract out the modes corresponding to translations and rotations of the full molecule. Thus,

$$\Gamma_{\text{vibs}} = 3A_1 + A_2 + 2B_1 + 3B_2 - (A_1 + A_2 + 2B_1 + 2B_2) = 2A_1 + B_2$$

4. Multiple steps:
 - (a) Stretching IRR(s): Label the bond vectors r_1, r_2 . Find their representation.

$$\Gamma_1 = (2, 0, 0, 2) = A_1 + B_2$$

- Since Γ_1 decomposes into two IRRs, this basis set accounts for 2/3 of the normal vibrational modes.
- To get the last, we'll need another basis set, but we'll do that later.

- (b) Stretching SALC(s): Apply the projection operator to these normal modes.

$$\hat{P}(A_1)_{r_1} = 2(r_1 + r_2) \approx r_1 + r_2$$

$$\hat{P}(B_2)_{r_1} = 2(r_1 - r_2) \approx r_1 - r_2$$

- (c) Bending IRR(s): Label the bending basis (angle between r_1, r_2) $\Delta\theta$. Find its representation.

$$\Gamma_2 = (1, 1, 1, 1) = A_1$$

- (d) Bending SALC(s): Apply the projection operator to this normal mode.

$$\hat{P}(A_1)_{\Delta\theta} = 4\Delta\theta \approx \Delta\theta$$

- (e) Visualize the normal modes: $r_1 + r_2$ corresponds to a symmetric stretch ν_s , $r_1 - r_2$ corresponds to an asymmetric stretch ν_a , and $\Delta\theta$ corresponds to a bend δ .

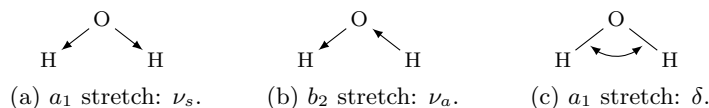


Figure 3.2: H₂O vibrational modes.

- (f) Quantum mechanically calculate the stretching frequencies: For H₂O, $\nu_s = 3657 \text{ cm}^{-1}$, $\nu_a = 3756 \text{ cm}^{-1}$, and $\delta = 1595 \text{ cm}^{-1}$.

- Example: PH₃ stretching modes.

- C_{3v} .
- $\Gamma_\nu = (3, 0, 1) = a_1 + e$.
- Projecting:

$$\hat{P}(A_1)_{r_1} \approx r_1 + r_2 + r_3 \quad \hat{P}(E)_{r_1} \approx 2r_1 - r_2 - r_3 \quad \hat{P}(E)_{r_2-r_3} \approx r_2 - r_3$$

- Drawing:

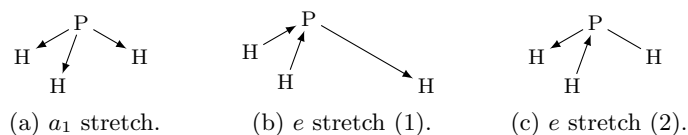


Figure 3.3: PH₃ vibrational modes.

- Note that we don't need Γ_{3N} to derive Γ_ν ! We would only need it for Γ_δ , unless Wuttig gives us a bending basis with which to work.
- Some observation on orthogonal projections.
 - Suppose we want to derive $3r_2 - 3r_3$. Since \hat{P} is a linear operator, we can equally well take the difference $\hat{P}(E)_{r_2} - \hat{P}(E)_{r_3}$ and project out $r_2 - r_3$ via $\hat{P}_{r_2-r_3}$ to start.
 - Moreover, I suspect that the projection operator is unitary (i.e., maps orthogonal vectors to orthogonal vectors). At least in this case, notice that r_1 and $r_2 - r_3$ are very much orthogonal (see Figure 3.4), just like their projections.

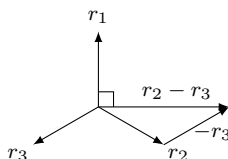


Figure 3.4: Orthogonal stretching basis.