# Example: NH_3 normal modes

For construction of symmetry adapted vibrational modes, it is by far most convenient to work in internal coordinates. We used Cartesian coordinates for the motional analysis to tell us which irreps correspond to normal modes. However, now that we have information we can use bond stretching, angle bending and torsions to construct the symmetry modes. For NH_3 the vibrational modes transform as $2a_1 + 2e$. We need to realize that there are two sets of internal coordinates that are relevant, the stretches and the bends.
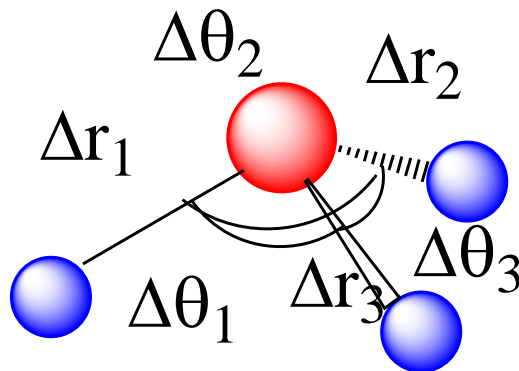
We see that the set of bond stretching coordinates, Δr_i, are related to each other by symmetry. This means that the symmetry operations of the group can transform one Δr_i into another Δr_j. The same is true for the angle bends. However, the angle bends cannot be transformed into the bond stretches and vice versa. Thus, they form two distinct sets (bases).
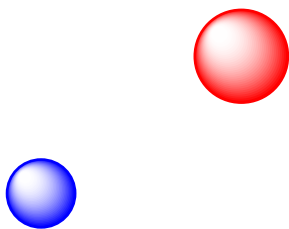
We can construct a table for each showing how each symmetry operation transforms a representative member of the set.

Projections based on the pure rotations

      To apply the projection operator method we choose any one of the members of the set. We then apply each of the symmetry operations of the group. Then we multiply by the character appropriate to the irreducible representation. Using these projections for form linear combinations. The table shows us what these will be using only the pure rotation subgroup (which is usually all that we need).

	E	C_3	C_3^2
	Δr_1	Δr_2	Δr_3
A_1	1	1	1
E	2	-1	-1

The totally symmetric stretching mode

For example, we will apply the a_1 projection operator to the bond stretch, Δr_1.

$$P^{a_1}(\Delta r_1) = P^E(\Delta r_1) + P^{C_3}(\Delta r_1) + P^{C_3^2}(\Delta r_1)$$

$$a_1 = \Delta r_1 + \Delta r_2 + \Delta r_3$$

Note that if we used the full character table we would obtain the same result.

$$P^{a_1}(\Delta r_1) = P^E(\Delta r_1) + P^{C_3}(\Delta r_1) + P^{C_3^2}(\Delta r_1) + P^{\sigma_v}(\Delta r_1) + P^{\sigma_v'}(\Delta r_1) + P^{\sigma_v''}(\Delta r_1)$$

$$a_1 = \Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_1 + \Delta r_3 + \Delta r_2$$

The e symmetry stretching mode

For the e projection operator applied to the bond stretch, Δr_1 the reflections are 0 in any case. Thus, we find:

$$P^e(\Delta r_1) = 2P^E(\Delta r_1) - P^{C_3}(\Delta r_1) - P^{C_3^2}(\Delta r_1)$$

$$e = 2\Delta r_1 - \Delta r_2 - \Delta r_3$$

Note that this is only one linear combination of a doubly degenerate set. The other member can be obtained by orthogonality.

$$e' = \Delta r_2 - \Delta r_3$$

The a_1 and e symmetric bending modes

Using the pure rotation subgroup we can construct The a_1 combination of the bending mode. The total symmetric bending mode is:

$$P^{a_1}(\Delta\theta_1) = P^E(\Delta\theta_1) + P^{C_3}(\Delta\theta_1) + P^{C_3{}^2}(\Delta\theta_1)$$

$$a_1 = \Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3$$

The first e-symmetry bending mode is:

$$P^e(\Delta\theta_1) = 2P^E(\Delta\theta_1) - P^{C_3}(\Delta\theta_1) - P^{C_3{}^2}(\Delta\theta_1)$$

$$e = 2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3$$

And by orthogonality

$$e' = \Delta\theta_2 - \Delta\theta_3$$

These modes are not normalized. Furthermore, we have only found one of the two modes in the doubly degenerate e irrep. The second mode must by found using the condition of orthonormality. First, we can normalize the a_1 modes.

$$N^2|a_1|^2 = N(\Delta r_1 + \Delta r_2 + \Delta r_3)N(\Delta r_1 + \Delta r_2 + \Delta r_3) = 1$$

Assuming that the cross terms are zero and the individual bond extensions are separately normalized, $\Delta r_1{}^2 = 1$, we have:

$$N^2\left(\Delta r_1{}^2 + \Delta r_2{}^2 + \Delta r_3{}^2\right) = 1$$

$$3N^2 = 1$$

$$N = \frac{1}{\sqrt{3}}$$

We note that the procedure is identical for the bending mode. Thus, for the a_1 modes we have a totally symmetric stretching and bending mode:

$$a_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$$

Using a similar procedure for the e mode:

$$N^2|e|^2 = N(2\Delta r_1 - \Delta r_2 - \Delta r_3)N(2\Delta r_1 - \Delta r_2 - \Delta r_3) = 1$$

Making the same assumption of no cross terms, we find:

$$N^2\left(4\Delta r_1{}^2 + \Delta r_2{}^2 + \Delta r_3{}^2\right) = 1$$

$$6N^2 = 1$$

$$N = \frac{1}{\sqrt{6}}$$

$$e = \frac{1}{\sqrt{6}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$$

We can use the same procedure for the angle bending modes:

$$a_1 = \frac{1}{\sqrt{3}}(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3) \qquad e = \frac{1}{\sqrt{6}}(2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3)$$

Summary for applications of projection operators

1. Determine the irreps that describe the linear combinations of atomic orbitals or vibrational modes.

2. Use an appropriate basis to define symmetry related sets of basis functions.

3. Apply a projection operator to one member of the set.

4. Using the irreps that describe the LCAOs or normal modes create symmetry adapted linear combinations.

5. Normalize the linear combinations and obtain an degenerate linear combinations using orthonormality.