Projection operator method

The projection operator method is used to generated symmetry adapted linear combinations in a basis.

One needs to identify a symmetry-related set of objects (i.e. orbitals, bond vectors, bond angles etc.) that have been determined to have a relevant irrep in a decomposition.

Then one needs to choose one representative member of of the symmetry related set. One can construct a table showing how the symmetry operations transform the representative member.

One can then use the coefficients of the irreps as coefficients for the transformed members of the symmetry-related set.

Example: benzene π-orbitals

We can use the benzene orbitals as an example. We can generate a reducible representation of the 6 p-orbitals of benzene. We can decompose that reducible representation into irreps (basis vectors) in the D_{6h} point group. Then we can form symmetry adapted linear combinations using the projections of a representative orbital of the set of 6.

Here we will simply assume the result for the analysis.

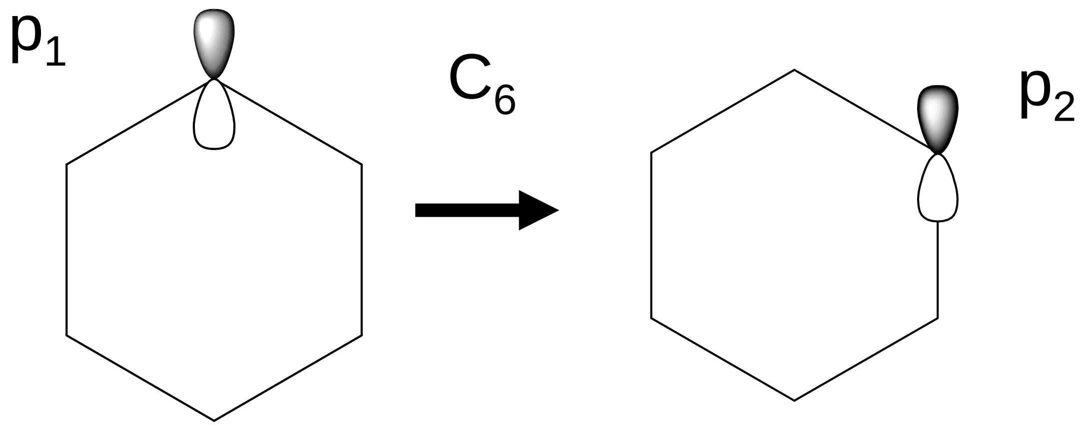
$$\Gamma_{\pi} = b_{2g} + e_{1g} + a_{2u} + e_{2u}$$

We will construct a table. One important point is that we frequently can use the pure rotation subgroup to make our job easier. In D_{6h} this means that we will use only the 6 rotations shown in the next slides. This is all we need to generate the appropriate linear combinations.

Projection operator approach

The operation required to carry the reference p_1 orbital into any of the others.

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
p_1	E	1	1	2	2
p_2	C_6	1	-1	1	-1
P_3	C_3	1	1	-1	-1
p_4	C_2	1	-1	-2	2
p_5	C_3^2	1	1	-1	-1
p_6	C_6^5	1	-1	1	-1



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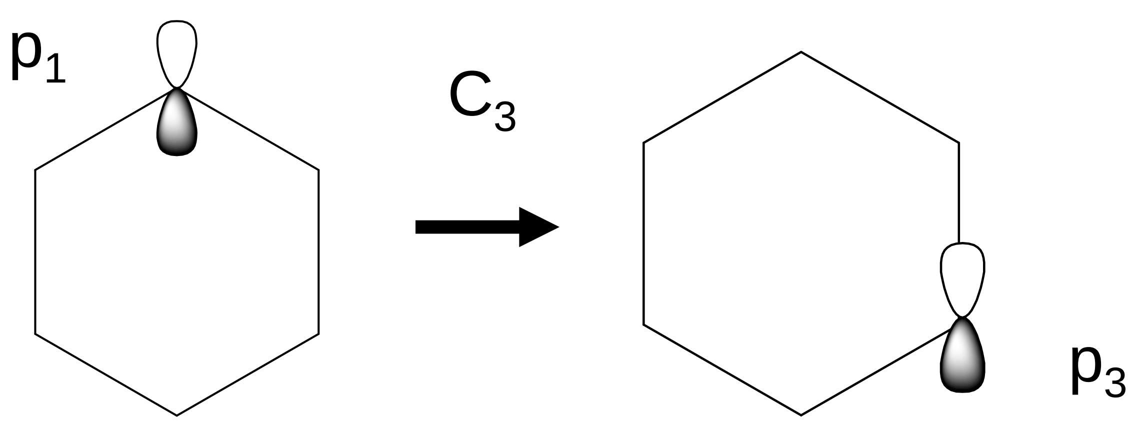
p_5	C_3^2	1	1	-1	-1
p_6	C_6^5	1	-1	1	-1



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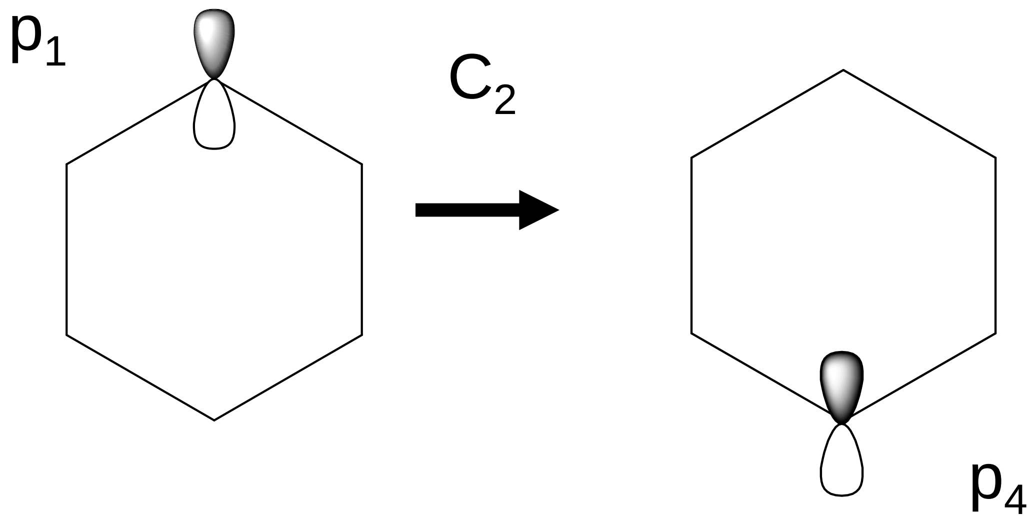

Constructing linear combinations

Once we have the projections we can use information from the character table to form the linear combinations that we call symmetry adapted linear combinations (SALCs).

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
p_1	E	1	1	2	2
p_2	C_6	1	-1	1	-1
P_3	C_3	1	1	-1	-1
p_4	C_2	1	-1	-2	2
p_5	C_3^2	1	1	-1	-1
p_6	C_6^5	1	-1	1	-1

For example, we can see that the a_{2u} irrep has all 1's. The coefficient for each projected orbital is 1. We have The SALC

$$\Psi_{a_{2u}} = \frac{1}{\sqrt{6}}(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)$$

Constructing linear combinations

We continue using a similar approach for b_{2g} using the fact That the coefficients alternate 1 and -1 around the ring.

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
p_1	E	1	1	2	2
p_2	C_6	1	-1	1	-1
P_3	C_3	1	1	-1	-1
p_4	C_2	1	-1	-2	2
p_5	C_3^2	1	1	-1	-1
p_6	C_6^5	1	-1	1	-1

$$\Psi_{b_{2g}} = \frac{1}{\sqrt{6}}(p_1 - p_2 + p_3 - p_4 + p_5 - p_6)$$

$$\Psi_{a_{2u}} = \frac{1}{\sqrt{6}}(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)$$

Constructing linear combinations

For e_{1g} we see that some of the p orbitals have a coefficient of 2. We use that value exactly as given.

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
p_1	E	1	1	2	2
p_2	C_6	1	-1	1	-1
P_3	C_3	1	1	-1	-1
p_4	C_2	1	-1	-2	2
p_5	C_3^2	1	1	-1	-1
p_6	C_6^5	1	-1	1	-1

$$\Psi_{e_{1g}} = \frac{1}{\sqrt{12}}(2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6)$$

Constructing linear combinations

For e_{2u} we have the same situation with some coefficients 1 (or -1) and some as 2.

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
p_1	E	1	1	2	2
p_2	C_6	1	-1	1	-1
P_3	C_3	1	1	-1	-1
p_4	C_2	1	-1	-2	2
p_5	C_3^2	1	1	-1	-1
p_6	C_6^5	1	-1	1	-1

$$\Psi_{e_{1g}} = \frac{1}{\sqrt{12}}(2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6)$$

$$\Psi_{e_{2u}} = \frac{1}{\sqrt{12}}(2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6)$$