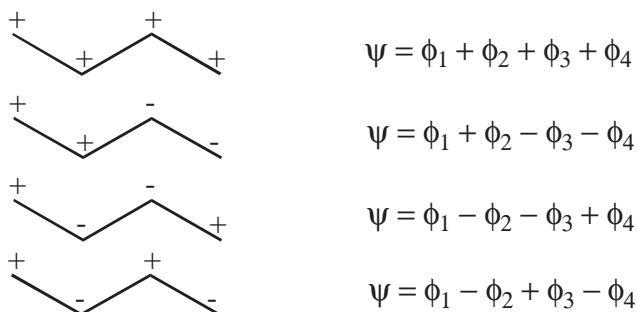


## Chapter 6

### 6.1 Introductory Remarks

In your Physical and Inorganic Chemistry classes you learned about linear combinations of atomic orbitals (LCAOs). In introductory settings, these are frequently constructed in the context of a ring or chain of the same atoms. For example, butadiene may be represented as follows:



We did this by inspection using the knowledge that as the number of nodes increases, so does the energy of the molecule. Still the construction was done in a cursory fashion. Your instructor probably glossed over why the first node went between carbons 2 & 3 above, instead of 1 & 2, for example. The use of symmetry operations explains how they are generated, with the functions called symmetry adapted linear combinations.

### 6.2 Derivation of Projection Operators

A projection operator is a function that maps a vector space onto a subspace. You may find the Wikipedia website ([http://en.wikipedia.org/wiki/Projection\\_\(linear\\_algebra\)](http://en.wikipedia.org/wiki/Projection_(linear_algebra))) on this topic helpful, but a summary appears here. A simple example of a projection involves suspending an object over a sheet of paper, place a light above it, and then tracing the object on the paper. The drawing is a 2-dimensional projection of the 3-dimensional object. (i.e. 2D space is a subset of 3D space). In this example, we take all points (x, y, z) and convert the z component to zero. It is

important to note that, in this example, there are an infinite number of resulting projections because all we have to do is take the object and rotate it about either or both the x- and y-axes to change the projection. The particular example is called an orthonormal projection because it projects 3 dimensions into 2 dimensions.

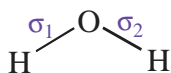
The important equation for us is 6.2-4 on p. 116 and I leave it's derivation to the book. It may be written slightly differently and you may use whichever format is easier for you to remember.

$$\hat{P}^{\Gamma_i}(f_j) = \frac{\ell_i}{h} \sum_{\hat{R}} \chi_{\hat{R}}(\Gamma_i) \hat{R}(f_j)$$

where  $f_j$  is just a function, a wave function in our case.  $\Gamma_i$  is the irreducible representation under consideration,  $\chi$  is the character of the irreducible representation for the element  $\hat{R}$  in the group. This function will only yield a nonzero result if the function is either described by the particular irreducible representation under consideration or contains it as a component of several irreducible representations. As usual, it may be easier to understand the equation by using it.

### 6.3 Using Projection Operators to Construct SALCs

Your book works through ethylene, we'll do water.



Simply by inspection, one can come up with the LCAO/SALC for this molecule. Since there are two MOs going in, there must be two combinations coming out. Since it's a linear combination, only addition and subtraction are permitted so:  $\sigma_1 + \sigma_2$  and  $\sigma_1 - \sigma_2$ . Now let's go through the math to show how to get this combination the using the proper methodology.

We begin by determining the point group of the molecule, then generating a reducible representation. In this situation, if a bond does not move, it is assigned a value of 1, if it does move it is a 0. Another words, we are forming a representation with the two bonding orbitals, called basis functions because they form the basis of the reducible representation. If a basis function translates (moves), it cannot contribute to the reducible representation. The book demonstrates this on the top of p. 121 nicely. Thus, if we assume the xz plane includes the atoms in water, we generate:

$C_{2v}$	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma$	2	0	2	0

We can now extract the irreducible representations from  $\Gamma$  by the standard method:

$$A_1: \frac{1}{4}[(1)(1)(2) + (1)(1)(0) + (1)(1)(2) + (1)(1)(0)] = 1$$

$$A_2: \frac{1}{4}[(1)(1)(2) + (1)(1)(0) + (1)(-1)(2) + (1)(-1)(0)] = 0$$

$$B_1: \frac{1}{4}[(1)(1)(2) + (1)(-1)(0) + (1)(1)(2) + (1)(-1)(0)] = 1$$

$$B_2: \frac{1}{4}[(1)(1)(2) + (1)(-1)(0) + (1)(-1)(2) + (1)(1)(0)] = 0$$

So the reducible representation is comprised of  $A_1 + B_1$ . Now generate the SALC of orbitals that arise from these irreducible representations. This works as follows:

- 1) We know that  $\sigma_1$  and  $\sigma_2$  are energetically the same and are symmetry equivalent.
- 2) The projection operator moves the orbital (in this case  $\sigma_1$ ), through each of the symmetry operations in succession. Thus, applying  $C_2$  to  $\sigma_1$  causes it to occupy the position that  $\sigma_2$  is in initially. It is thus entered as  $\sigma_2$  in the table below.
- 3) The resulting basis function is then multiplied by the character of the irreducible representation of the projection operator being used at the time.

$C_{2v}$	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$	
$\hat{P}^{A_1}(\sigma_1)$	$\sigma_1$	$\sigma_2$	$\sigma_1$	$\sigma_2$	$\rightarrow 2\sigma_1 + 2\sigma_2 \propto \sigma_1 + \sigma_2$
$\hat{P}^{B_1}(\sigma_1)$	$\sigma_1$	$-\sigma_2$	$\sigma_1$	$-\sigma_2$	$\rightarrow 2\sigma_1 - 2\sigma_2 \propto \sigma_1 - \sigma_2$

Note that these are the same two linear combinations we came up with at the beginning without doing any math. Of course, this is the easiest example (i.e. exactly two equivalent bonds).

Things with 3 or more bonds require the math. Attempts to do this “by inspection” as in the example on p. 1 of the notes always assume things in this method.

This does not yield normalized functions (note the proportionality). The normalization factor is  $\frac{1}{\sqrt{\sum i^2}}$  where  $i$  are the coefficients on the functions in the unnormalized answer. In

this case,  $\frac{1}{\sqrt{1^2+1^2}} = \frac{1}{\sqrt{2}}$ . So the SALC functions for water are:

$$\psi_1 = \frac{1}{\sqrt{2}}(\sigma_1 + \sigma_2) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2)$$

Now we will work through the book example  $MH_6$ , on pp. 123 – 124. The molecule is  $O_h$  symmetry so:

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma$	6	0	0	2	2	0	0	0	4	2

To save space, only the nonzero irreducible representations are solve for below.

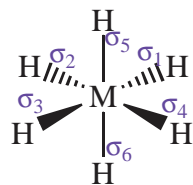
$$A_{1g}: \frac{1}{48} ((1)(1)(6) + (8)(1)(0) + (6)(1)(0) + (6)(1)(2) + (3)(1)(2) + (1)(1)(0) + (6)(1)(0) + (8)(1)(0) + (3)(1)(4) + (6)(1)(2)) = 1$$

$$E_g: \frac{1}{48} ((1)(2)(6) + (8)(-1)(0) + (6)(0)(0) + (6)(0)(2) + (3)(2)(2) + (1)(2)(0) + (6)(0)(0))$$

$$+ (8)(-1)(0) + (3)(2)(4) + (6)(0)(2)] = 1$$

$$T_{1u}: \quad \frac{1}{48} ((1)(3)(6) + (8)(0)(0) + (6)(-1)(0) + (6)(1)(2) + (3)(-1)(2) + (1)(-3)(0) + (6)(-1)(0) \\ + (8)(0)(0) + (3)(1)(4) + (6)(1)(2)] = 1$$

The book tells you about using the  $O$  point group as a short cut, but that's really no help to you in the long run since you don't know when you can do this, so we'll go through it the long way from here on out. So at this point we apply the projection operator to all 3 irreducible representations. For this we'll need a number scheme for the molecule so first that:



Not surprisingly, the solution here is more complicated than for water. For example there are 4  $C_3$  axes in the molecule (one each passing through M and the 1-5-4, 1-2-5, 3-4-5, and 2-3-5 triangles), each of which can turn  $120^\circ$  and  $240^\circ$ . We must ask what happens to  $\sigma_1$  after each of these rotations. This is too cumbersome to put into a table as for water so we'll do this longhand.

$$\hat{P}^{A_{1g}}(\sigma_1) = E(\sigma_1) + (4C_3(\sigma_1) + 4C_3^2(\sigma_1)) + 6C_2(\sigma_1) + (3C_4(\sigma_1) + 3C_4^2(\sigma_1)) + 3C_2(\sigma_1) + i(\sigma_1) + \\ (3S_4(\sigma_1) + 3S_4^3(\sigma_1)) + (4S_6(\sigma_1) + 4S_6^5(\sigma_1)) + 3\sigma_h(\sigma_1) + 6\sigma_d(\sigma_1) \\ = \sigma_1 + [2\sigma_3 + 2\sigma_4 + 2\sigma_5 + 2\sigma_6] + [2\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6] + [2\sigma_1 + \sigma_3 + \sigma_4 + \sigma_5 + \\ \sigma_6] + [\sigma_1 + 2\sigma_2] + \sigma_2 + [2\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6] + [2\sigma_3 + 2\sigma_4 + 2\sigma_5 + 2\sigma_6] \\ + [2\sigma_1 + \sigma_2] + [2\sigma_1 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6] \\ = 8\sigma_1 + 8\sigma_2 + 8\sigma_3 + 8\sigma_4 + 8\sigma_5 + 8\sigma_6 \\ \propto \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$$

$$\psi = \frac{1}{\sqrt{6}} (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$

This is exactly what you'd expect for the total symmetric irreducible representation,  $A_{1g}$ . Your book works through the  $T_{1u}$  state for you. You should try the  $E_g$  on your own.

### A Cyclic $\pi$ -System

The book sets this up and goes through  $A_2''$  fine. Let's look at the  $E''$  irreducible representation, however. We begin by treating  $E''$  just like  $A_2''$  and generating the SALC:

$$\psi = \frac{1}{\sqrt{6}} (2\sigma_1 - \sigma_2 - \sigma_3)$$

But, since this is a two-dimensional irreducible representation, there must be a second, orthonormal companion function to this one that also differs only by a constant  $\pm 1$  multiplier.

The following is an alternative method to getting the same, second function.

We begin by using  $\sigma_2$  and  $\sigma_3$  in place of  $\sigma_1$  when applying the  $E''$  irreducible representation.

In this case, the very similar wave functions

$$\psi' = 2\sigma_2 - \sigma_1 - \sigma_3 \quad \& \quad \psi'' = 2\sigma_3 - \sigma_2 - \sigma_1$$

are generated, respectively. If we add these two functions we find that

$$\psi' + \psi'' = -2\sigma_1 + \sigma_2 + \sigma_3 = -1(2\sigma_1 - \sigma_2 - \sigma_3).$$

This is the original function multiplied by -1, but it's the same thing, not orthonormal. To create the orthonormal version, subtract one function from the other

$$\psi' - \psi'' = (2\sigma_2 - \sigma_1 - \sigma_3) - (2\sigma_3 - \sigma_1 - \sigma_2) = \sigma_2 - \sigma_3$$

This is the partner function to  $\psi$  and when normalized it takes the form:  $\frac{1}{\sqrt{2}} (\sigma_2 - \sigma_3)$ . Thus, we

can generate the equations by a simple LCAO process, in this case subtraction. The only thing

left here is to demonstrate that they are, in fact, normalized.

$$\begin{aligned}(2\sigma_1 - \sigma_2 - \sigma_3)(\sigma_2 - \sigma_3) &= 2\sigma_1\sigma_2 - 2\sigma_1\sigma_3 - \sigma_2^2 + \sigma_2\sigma_3 - \sigma_3\sigma_2 + \sigma_3^2 \\ &= 2\sigma_1\sigma_2 - 2\sigma_1\sigma_3 - \sigma_2^2 + \sigma_3^2\end{aligned}$$

but since  $\sigma_1 = \sigma_2 = \sigma_3$ ,

$$\begin{aligned}&= 2\sigma_1^2 - 2\sigma_1^2 - \sigma_1^2 + \sigma_1^2 \\ &= 0\end{aligned}$$

Thus the functions are indeed orthonormal.