Symmetry and Group Theory

The material we will be covering follows most closely to Tinkham's book "Group Theory and Quantum Mechanics". See also Cotton's book "Chemical Applications of Group Theory" for a introductory treatment with more applications to chemistry.

1 Introduction

What is symmetry?

1. Some operation which leaves the system unchanged.
2. Some operator which commutes with the Hamiltonian.

Why do we care?

1. Simplifies the solution to the problem.
2. Gives insight into the solution.

If we have two observables corresponding to operators $\hat{A}$ and $\hat{B}$

- if $[\hat{A},\hat{B}]=0 \rightarrow$ observables are compatible.
- if $[\hat{A},\hat{B}]\neq 0 \rightarrow$ observables are incompatible.

Compatible observables have the same eigenfunctions. This means that the eigenvalues of operator $\hat{A}$ can be used to label the eigenvalues of operator $\hat{B}$.

Proof
Suppose that $[\hat{A},\hat{B}]=0$. Then we have:

$$\langle a''|[\hat{A},\hat{B}]|a'\rangle = (a''-a')\langle a''|\hat{B}|a'\rangle = 0 \tag{1}$$

Therefore $\langle a''|\hat{B}|a'\rangle$ must vanish unless $a''=a'$. This demonstrates that $\hat{B}$ is diagonal when represented in the basis of $\hat{A}$. If you want to know the eigenvalues of $\hat{B}$, it is clearly very useful if you know the eigenvectors of $\hat{B}$. Typically, the operator $\hat{B}$ will be the Hamiltonian of the interest, and $\hat{A}$ is some operator which is easier to diagonalize than the Hamiltonian. The eigenvalues of $\hat{A}$ are said to be "good quantum numbers" or "constants of motion", motivated by the implications of Heisenberg's equation of motion $\frac{d\hat{A}}{dt}=[\hat{A},\hat{H}]$. Let us take an example from atomic physics:

$$[\hat{L^2},\hat{L^z}]=[\hat{L^2},\hat{H}]=[\hat{L^z},\hat{H}]=0 \tag{2}$$

The orbital quantum number $\ell=0,1,2,\ldots$ and the magnetic quantum number $m=-\ell\ldots\ell$ are good quantum numbers which are used to label the eigenfunctions. Of course, the Hamiltonian that we are concerned with is the Kohn-Sham equation:

$$H_{KS}=-\frac{1}{2}\bigtriangledown^2+V_H(r)+V_{KS}(r)+V_{ext}(r) \tag{3}$$

We are going to need to find all of the symmetry operations which leave the H_{KS} invariant. H_{KS} has four terms, and we will only need to consider the lowest symmetry term. What if we wanted to translate the entire system by some fixed amount, or possibly rotate the coordinate system by some arbitrary angle? By inspecting each term you will see that the only term that will not be invariant is the $V_{ext}(r)$, which is the lowest symmetry term in the Hamiltonian. Therefore, this is the term that we will need to concentrate one, and it is determined by the arrangement of the nuclei. We need to find all the operations that leave $V_{ext}(r)$ invariant. What kind of operations might these be? If we are dealing with a crystal, then we will have all possible translation vectors. We also might have nontranslational symmetry such as rotation axes, mirror planes, points of inversion, etc. In general, we will have some set of symmetry operations $\{R_i\}$ which commute with the Hamiltonian but do *not* necessarily commute with each other.

Ultimately, what are we trying to accomplish?

$\rightarrow$ Block diagonalize the Hamiltonian

Recall that minimizing the Hamiltonian within some basis amounts to diagonalizing the Hamiltonian in that basis. Consider a Hamiltonian which has been expressed in some basis with ten orbitals:

$$\hat{H} = \begin{pmatrix} H_{00} & H_{01} & H_{02} & H_{03} & H_{04} & H_{05} & H_{06} & H_{07} & H_{08} & H_{09} \\ H_{10} & H_{11} & H_{12} & H_{13} & H_{14} & H_{15} & H_{16} & H_{17} & H_{18} & H_{19} \\ H_{20} & H_{21} & H_{22} & H_{23} & H_{24} & H_{25} & H_{26} & H_{27} & H_{28} & H_{29} \\ H_{30} & H_{31} & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} & H_{37} & H_{38} & H_{39} \\ H_{40} & H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} & H_{47} & H_{48} & H_{49} \\ H_{50} & H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} & H_{57} & H_{58} & H_{59} \\ H_{60} & H_{61} & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} & H_{67} & H_{68} & H_{69} \\ H_{70} & H_{71} & H_{72} & H_{73} & H_{74} & H_{75} & H_{76} & H_{77} & H_{78} & H_{79} \\ H_{80} & H_{81} & H_{82} & H_{83} & H_{84} & H_{85} & H_{86} & H_{87} & H_{88} & H_{89} \\ H_{90} & H_{91} & H_{92} & H_{93} & H_{94} & H_{95} & H_{96} & H_{97} & H_{98} & H_{99} \end{pmatrix} \tag{4}$$

Now if there is some symmetry in the system, we will be able to "block diagonalize" the Hamiltonian. Hypothetically, this could look something like this:

$$U^\dagger \hat{H} U = \begin{pmatrix} H_{00} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & H_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{22} & H_{23} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{32} & H_{33} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{44} & H_{45} & H_{46} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{54} & H_{55} & H_{56} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{64} & H_{65} & H_{66} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & H_{77} & H_{78} & H_{79} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & H_{87} & H_{88} & H_{89} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & H_{97} & H_{98} & H_{99} \end{pmatrix} \tag{5}$$

Where U is some matrix that can be constructed using the symmetry of the system. Clearly, the Hamiltonian has been reduced to a series of blocks which do not couple to each other (ie. the matrix elements from one block to another are zero). There are two one-dimensional blocks, one two-dimensional block, and two three-dimensional blocks. Each of these blocks can be treated completely independently, and this is a huge advantage because it is much easier to find the eigenvalues of a few smaller matrices as opposed to one big matrix. More importantly, this gives us physical insight into the problem. So now I have to show you how you actually do this, and this will require the introduction of group theory.

2 Group Theory

We will start by defining what a group is.

A group is a set of elements $A, B, C, \ldots$ which have a "group multiplication" which produces a new element given any pair and satisfy the following rules:

1. The product of any two elements must also be a member of the set.
2. associative law holds $\rightarrow A(BC) = (AB)C$
3. the identity element is present (ie. $EA = AE = E$ where E is the identity and A is any member of the set).
4. there is an inverse for each element in the group (ie $AA^{-1} = A^{-1}A = E$ where A and A^{-1} are members of the set).

If all of these properties hold, then this set qualifies as a group. Let us take some simple and familiar examples.

Example 1 - The set of all positive and negative integers including zero with group multiplication defined as addition. Does this set satisfy all the requirements of a group? What if we instead defined group multiplication as multiplication? This group is called "abelian" because all members of the group commute with one another (ie. $AB = BA$).

Example 2 - The set of all $n \times n$ matrices with a non-vanishing determinant with group multiplication defined as matrix multiplication. Does this set satisfy all the requirements of a group? This group is called "non-abelian" because all members of the group do not commute with one another. As you can imagine, abelian groups are simpler than non-abelian groups.

Example 3 - Now let us consider a more relevant example. Consider all of the symmetry elements in R^2 (ie. in two-dimensional real space) which leave the square invariant.

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad R_{\pi/2} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

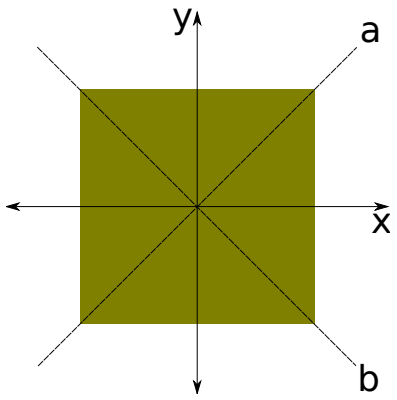

Figure 1: A square.

$$R_\pi = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \qquad R_{3\pi/2} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

$$R_{ma} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad R_{mb} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

$$R_{mx} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad R_{my} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

Now in order to check if these elements form a group, we will need to know the multiplication table.

	E	$R_{\pi/2}$	R_π	$R_{3\pi/2}$	R_{ma}	R_{mb}	R_{mx}	R_{my}
E	E	$R_{\pi/2}$	R_π	$R_{3\pi/2}$	R_{ma}	R_{mb}	R_{mx}	R_{my}
$R_{\pi/2}$	$R_{\pi/2}$	R_π	$R_{3\pi/2}$	E	R_{mx}	R_{my}	R_{mb}	R_{ma}
R_π	R_π	$R_{3\pi/2}$	E	$R_{\pi/2}$	R_{mb}	R_{ma}	R_{my}	R_{mx}
$R_{3\pi/2}$	$R_{3\pi/2}$	E	$R_{\pi/2}$	R_π	R_{my}	R_{mx}	R_{ma}	R_{mb}
R_{ma}	R_{ma}	R_{my}	R_{mb}	R_{mx}	E	R_π	$R_{3\pi/2}$	$R_{\pi/2}$
R_{mb}	R_{mb}	R_{mx}	R_{ma}	R_{my}	R_π	E	$R_{\pi/2}$	$R_{3\pi/2}$
R_{mx}	R_{mx}	R_{ma}	R_{my}	R_{mb}	$R_{\pi/2}$	$R_{3\pi/2}$	E	R_π
R_{my}	R_{my}	R_{mb}	R_{mx}	R_{ma}	$R_{3\pi/2}$	$R_{\pi/2}$	R_π	E

(6)

The multiplication table tells us the products and it also immediately reveals the inverse. A very useful point to note is the *rearrangement theorem*, which states that each element only appears once in each row and each column. Anyway, now one can verify that the above does constitute a group.
We will proceed by introducing a few more definitions that we will need:

1. h is the order of the group, which is the number of elements in the group.

2. Subrgroup - some fraction of the elements of the group which also constitute a group on their own. The order of the subgroup must be an integer divisor of the order of the group.

3. Cyclic group is $X, X^2, X^3, \ldots, X^n = E$

Now that we know a few things about groups, we can generically explore the properties of groups having small orders.

1. There is only one group of order 1, which is: E.

2. There is only one group of order 2, which is: E,A.

	E	A
E	E	A
A	A	E

(7)

3. There are two possible groups of order 4. One is the cyclic group, and the other is:

	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

(8)

   Why could we not have chosen $A^2 = E$? If this were the case then E, A would be a subgroup and this would violate the rearrangement theorem.

4. At order four there is still only two possibilites. We will stop this exercise now. As you can imagine, the number of groups at a particular order will increase as the order increase.

At this point we have discussed how to determine if a set is a group, and we have gone through some abstract and concrete examples. In order to accomplish our goal of block diagonalizing the Hamiltonian we must continue to introduce a few more definitions.

Conjugate - B is conjugate to A if $B = XAX^{-1}$ where X is some member of the group.

One can prove that if B and C are conjugate to A, then they are conjugate to each other.

Given $B = XAX^{-1}$ and $C = YAY^{-1}$, then $A = Y^{-1}CY$ and we have:

$$B = XY^{-1}CYX^{-1} \tag{9}$$
$$(YX^{-1})(XY^{-1}) = 1 \tag{10}$$
$$(XY^{-1})^{-1}(XY^{-1}) = 1 \tag{11}$$
$$\rightarrow YX^{-1} = (XY^{-1})^{-1} \tag{12}$$
$$B = XY^{-1}C(XY^{-1})^{-1} = ZCZ^{-1} \tag{13}$$

Class - Set of elements which are mutually conjugate.

How do we form a class? Pick one element and form all terms $A_1A_iA_1^{-1}, A_2A_iA_2^{-1}, \ldots$. Some elements will appear more than once and that is fine. A few points to note:

1. E is always in a class by itself.

2. For abelian groups, each element is in a class by itself.

Isomorphy - Two groups are said to be isomorphic if there is a one-to-one correspondence between elemtents $A, B, C, \ldots$ of one group and $A', B', C', \ldots$ of the other group such that $AB = C \leftrightarrow A'B' = C'$. This is satisfied if two groups have the same multiplication tables.

Homomorphism - Two groups are said to be homomorphic if there is a correspondence $A \leftrightarrow A'_1A'_2A'_3$ such that if $AB = C$ then any A'_i multiplied by any of the B'_i will give one of the C'_i.

1. this is a one-to-many correspondence.

2. every group is homomorphic to E.

3. isomorphic groups are homomorphic.

Now let us work some examples out to help make these definitions a bit more concrete.

1. Let us consider 2 groups. The first has elements 1 and -1 with scalar multiplication as the group multiplication. The other is the order 2 permutation group, which consists of two elements:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad P = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{14}$$

   Are these groups isomorphic? Of course they are. We showed above that there is only one possible multiplication table for order two groups so they must be.

2. Once again, the first has elements 1 and -1 with scalar multiplication as the group multiplication. The other group is the group corresponding to the operations of the square above. Are these two groups isomorphic? Clearly not as they are not of the some order. Are these two groups homomorphic? Inspect the character table above and see if you can find any trend. Cleary, one can identify the following:

$$1 \leftrightarrow E, R_{\pi/2}, R_{\pi}, R_{3\pi/2} \quad \text{and} \quad -1 \leftrightarrow R_{ma}, R_{mb}, R_{mx}, R_{my} \tag{15}$$

Representation of an abstract group: Any group that is homomorphic to the abstract group is considered a representation of the group.

1. In this course, we will only be concerned with representations that are square matrices with matrix multiplication as the group multiplication. We associate a matrix $\Gamma(A)$ with each element A such that:

2. The number of rows/columns in the matrix Γ is the dimensionality of the representation.

3. Isomorphic representations are said to be 'true' or 'faithful' representations.

$$\Gamma(A)\Gamma(B) = \Gamma(C) \leftrightarrow AB = C \tag{16}$$

Similarity transformation: a transformation whish leaves matrix equations unchanged:

$$\Gamma'(A) = S^{-1}\Gamma(A)S \tag{17}$$
$$\Gamma'(A)\Gamma'(B) = \left[S^{-1}\Gamma(A)S\right]\left[S^{-1}\Gamma(B)S\right] \tag{18}$$
$$= S^{-1}\Gamma(A)\Gamma(B)S \tag{19}$$
$$= \Gamma'(C) \tag{20}$$

If Γ forms a representation of the group then so does Γ'. Representations that are related by a similarity transformation are said to be "equivalent".

It is about time that we take a concrete example for a representation of a group. Let us assume that we are dealing with a square molecule pictured in figure **??**. In this case we know we are dealing with a Hamiltonian with square symmetry that we have already explored above. From the picture, we deduce that we are dealing with a variational wavefunction something like this:

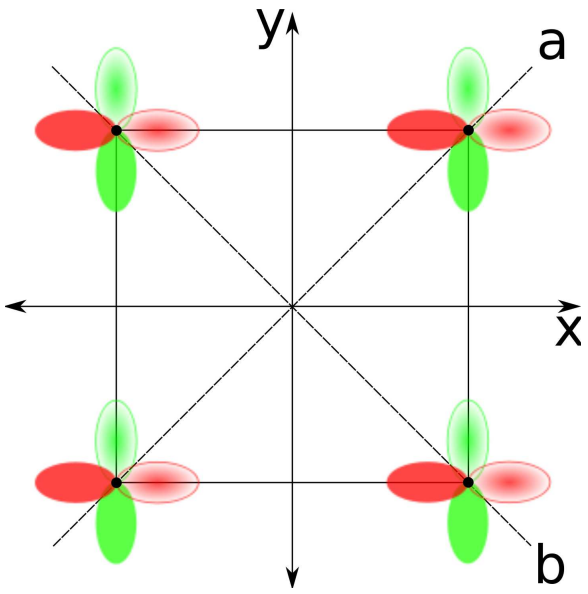

Figure 2: A schematic of a square molecule. The black dots denote the nuclei. The p-like orbitals are the basis functions for this hypothetical problem.

$$\Phi(x,y) = c_1\phi_x(x-a,y-a) + c_2\phi_y(x-a,y-a) + \tag{21}$$
$$c_3\phi_x(x+a,y-a) + c_4\phi_y(x+a,y-a) + \tag{22}$$
$$c_5\phi_x(x-a,y-a) + c_6\phi_y(x-a,y-a) + \tag{23}$$
$$c_7\phi_x(x-a,y+a) + c_8\phi_y(x-a,y+a) \tag{24}$$

$$|\Phi\rangle = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ c_7 \\ c_8 \end{pmatrix} \tag{25}$$

The different shading of the lobes is supposed to indicate positive versus negative values of the function. We already now what our group is, which is that of the square. Now we need to find a representation of the group. What will the dimension of our representation be? It must be 8 because there are 8 basis functions. Therefore we will need one 8×8 matrix which represents each of the eight elements of the square group. Let us try and build those matrices:

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} R_{\pi/2} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$$R_{\pi} = \begin{pmatrix} 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \end{pmatrix} R_{3\pi/2} = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$R_{ma} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} R_{mb} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix}$$

$$R_{mx} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} R_{my} = \begin{pmatrix} 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

Is this indeed a representation of the square group? Well, you can confirm this by cheching the multiplication table. Is there any connection between the order of the group (ie. 8) and the dimension of the representation (ie. 8)? Absolutely not. If we

added more orbitals to our basis, say another s-orbital on each site, then the dimension of the representation would be 12 while the order of the group is of course unchanged.

Reducible and Irreducible representations: One can take two representations and stack them:

$$\Gamma(A) = \begin{pmatrix} \Gamma^1(A) & 0 \\ 0 & \Gamma^2(A) \end{pmatrix} \tag{26}$$

This representation is clearly "reducible" in the sense that it is clearly two seperate representations. However, this would not at all be obvious if we scrambled the matrix with some random similarity transformation. Let us now define reducibility.

Reducibility : The ability to further block diagonalize every element of the group with the same similarity transformation. If a representaion cannot be reduced further, it is said to be irreducible. When we are expressing that a representation may be decomposed, we say mathematically that $\Gamma = \Gamma^1 + \Gamma^2$ or $\Gamma = \sum_i a_i \Gamma^i$ where a_i is the number of times that a represenation appears in the decomposition. Please note that this is NOT matrix addition.

Trace : Because all representations related through a unitary transformation are equivalent, there is arbitrariness. How doe we characterize a given representation? Given that the trace of a matrix is invariant to a unitary transformation, the trace will prove to be the proper mathematical tool to fingerprint a representation.

$$\chi(A) = tr\left(\Gamma(A)\right) = \sum_i \Gamma(A)_{ii} \tag{27}$$

One can prove the invariance of the trace as follows:

$$\Gamma'(A) = U\Gamma(A)U^\dagger \quad \Gamma'(A)_{ij} = \sum_{lm} U_{il}\Gamma(A)_{lm}U^*_{jm} \tag{28}$$

$$\chi'(A) = \sum_{ilm} U_{il}\Gamma(A)_{lm}U^*_{im} = \sum_{lm} \delta_{lm}\Gamma(A)_{lm} = \sum_i \Gamma(A)_{ii} = \chi(A) \tag{29}$$

Elements in same class have same trace : This is due to the fact that all elements in the same class are related by a similarity transformation.

Great Orthogonality Theorem : Any representation by matrices with nonvanishing determinants is equivalent through a similarity transformation to a representation by unitary matrices. If we consider all inequivalent, irreducible, unitary representations of a group, then:

$$\sum_R \Gamma^i(R)^*_{\mu\nu}\Gamma^j(R)_{\alpha\beta} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta} \tag{30}$$

R goes over all the elements in the group, l is the dimension of the representation, h is the order of the group, i/j labele the irreducible representation, and Γ are square matrices. It is possible to make a geometric analogy for this equation. On the left hand side we are summing over all the elements in the group, and therefore you can think of each group element as an "axis" in group element space (ie. each dimension that you would integrate over in cartesian space). Therefore h, the order of the group, is the dimension of the space in this geometric analogy. Now the vectors in this space would be enumerated by the labels i, μ, ν. How many of these orthogonal vectors are there? If we summed over all $i, j, \mu, \nu, \alpha, \beta$, how many times would we count a 1 on the right hand side? This would be $\sum_i l_i^2$. Clearly the number of orthogonal vectors cannot exceed the dimensionality of the space, so one could guess the following important relation:

$$h = \sum_i l_i^2 \tag{31}$$

This is a non-trivial result which relates the dimensions of the irreducible representations to the order of the group! Of course, this can be derived in a rigorous fashion (see Tinkham for details).

Now lets see what else we can learn from the Great Orthogonality Theorem. Let us focus on traces. First set $\mu = \nu$ and $\alpha = \beta$.

$$\sum_R \Gamma^i(R)^*_{\mu\mu} \Gamma^j(R)_{\alpha\alpha} = \frac{h}{l_i} \delta_{ij} \delta_{\mu\alpha} \delta_{\mu\alpha} \tag{32}$$

Now let us sum over μ and α:

$$\sum_R \chi^i(R)^* \chi^j(R) = \frac{h}{l_i} \delta_{ij} \sum_{\alpha\beta} \delta_{\mu\alpha} = h\delta_{ij} \tag{33}$$

Thus we see that the characters have their own orthogonality relation. Given that the characters are identical within a class, it is sensible to collect terms according to classes:

$$\sum_k \chi^i(C_k)^* \chi^j(C_k) N_k = \frac{h}{l_i} \delta_{ij} \sum_{\alpha\beta} \delta_{\mu\alpha} = h\delta_{ij} \tag{34}$$

Now we can make the same sort of "geometric interpretation" that we did before. In this case the 'axes' would be labeled by the class and hence the total dimensionality would be the number of classes. The vector is labeled by the irreducible representation. Therefore, this correctly suggests that:

$\rightarrow$**Number of irreducible representations equals the number of classes.**

Character Table Given the abstract group, one can determine what the possible irreducible representations are and construct an irreducible representation matrix for each element in the group. Of course, one would not want to reinvent the wheel and rederive these every time. It would make sense to tabulate them for every group and

publish them in a book. However, this is rarely done (although Cornwell's book "Group Theory in Physics" has them!). Normally one will find a "character table" which contains less information, but enough to get by without too much work. A character table is a square table of characters (ie. traces) with classes labeling columns and the irreducible representations labeling rows. Let us take for example the character table corresponding to the group of the square (ie. C_{4v}).

	E	R_π	$R_{\pi/2}R_{3\pi/2}$	$R_{mx}R_{my}$	$R_{ma}R_{mb}$
	C_1	C_2	C_3	C_4	C_5
A_1	1	1	1	1	1
B_1	1	1	-1	1	-1
A_2	1	1	1	-1	-1
B_2	1	1	-1	-1	1
E	2	-2	0	0	0

(35)

1. The first row is always the "identity representation".

2. We already proved that the rows are orthogonal and satisfy

$$\sum_k \chi^i(C_k)^* \chi^j(C_k) N_k = \frac{h}{l_i}\delta_{ij} \sum_{\alpha\beta} \delta_{\mu\alpha} = h\delta_{ij} \tag{36}$$

   This is how we justified that it should be square as well.

3. We did not prove that the columns also satisfy an orthogonality relation, but they do:

$$\sum_i \chi^i(C_k)^* \chi^i(C_l) = \frac{h}{N_k}\delta_{kl} \tag{37}$$

Decomposing a representation So lets say that you build a representation for a group kind of like we did in the example above where we made a basis using p-orbitals. So when you start with the representation, you will need to know which irreducible representations are present. You will not know apriori. You will know what can be present, but not what is present. In order to do this, you will form the characters for all the classes of your representation. Then we will make use of the following decompose the representation:

$$\chi(R) = \sum_j a_j \chi^j(R) \tag{38}$$

Where a_j is the number of times that irreducible representation j occurs. The important point is that this decomposition is unique!

Let us consider our representation that we built above and try to decompose it. First let us construct the traces:

E	R_π	$R_{\pi/2}R_{3\pi/2}$	$R_{mx}R_{my}$	$R_{ma}R_{mb}$
C_1	C_2	C_3	C_4	C_5
8	0	0	0	0

(39)

So what does our representation decompose to? $\Gamma = 2E + A_1 + B_1 + A_2 + B_2$. There is no other possibility.

Scalar Fields: We will now introduce a group which operates on scalar fields and is isomorphic to the abstract group. Supose that we have some function $f(x, y, z)$. The element P_R operates on the function resulting in the following:

$$\begin{aligned} P_R f(x,y,z) &= f(R^{-1}[x,y,z]) \\ &= f(R_{11}^{-1}x + R_{12}^{-1}y + R_{13}^{-1}z, R_{21}^{-1}x + R_{22}^{-1}y + R_{23}^{-1}z, R_{31}^{-1}x + R_{32}^{-1}y + R_{33}^{-1}z) \end{aligned}$$

So the arguments of the function are treated like a vector which the symmetry element in R^3 acts upon. You might wonder why P_R requires R^{-1} on the right-hand-side. This is a convention that Wigner chose. I believe you could choose the opposite convention with no consequences, but we will not.

It is istructive to do a few examples. Consider a function of two variables and let us use $R_{pi/2}$ as an example.

$$R_{\pi/2} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad R_{\pi/2}^{-1} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{40}$$

$$f(x,y) = x^2 + y^2 \tag{41}$$

$$P_R f(x,y) = x^2 + y^2 \tag{42}$$

$$f(x,y) = x(x^2 + y^2) \tag{43}$$

$$P_R f(x,y) = -y(x^2 + y^2) \tag{44}$$

Degenerate eigenfunctions as a basis for irreducible represenation: We will now prove that the set of ℓ_n degenerate eigenfunctions $\psi_\nu^{(n)}$ having energy E_n form basis functions for a ℓ_n-dimensional irreducible representation Γ^n of the group of the Schrodinger equation.

$$P_R H \psi_\nu^{(n)} = H P_R \psi_\nu^{(n)} = E P_R \psi_\nu^{(n)} \tag{45}$$

Therefore $P_R\psi_\nu^{(n)}$ must be some linear combination of the ℓ_n degenerate eigenfunctions given that $P_R\psi_\nu^{(n)}$ is itself an eigenfunction. Therefore we can write:

$$P_R \psi_\nu^{(n)} = \sum_{k=1}^{\ell_n} \psi_k^{(n)} \Gamma^{(n)}(R)_{k\nu} \tag{46}$$

Now we can prove that $\Gamma^{(n)}(R)$ form a representation of the group.

$$P_{R_1}P_{R_2}\psi^{(n)}_\nu = P_{R_1}\sum_{k=1}^{\ell_n}\psi^{(n)}_k\Gamma^{(n)}(R_2)_{k\nu} \tag{47}$$

$$= \sum_{k\lambda}^{\ell_n}\psi^{(n)}_\lambda\Gamma^{(n)}(R_1)_{\lambda k}\Gamma^{(n)}(R_2)_{k\nu} \tag{48}$$

$$= \sum_{\lambda}^{\ell_n}\psi^{(n)}_\lambda\left[\Gamma^{(n)}(R_1)\Gamma^{(n)}(R_2)\right]_{\lambda\nu} \tag{49}$$

$$\tag{50}$$

But we also know that:

$$P_{R_1R_2}\psi^{(n)}_\nu = \sum_{\lambda}^{\ell_n}\psi^{(n)}_\lambda\Gamma^{(n)}(R_1R_2)_{\lambda\nu} \tag{51}$$

Therefore we have proven that:

$$\Gamma^{(n)}(R_1R_2) = \Gamma^{(n)}(R_1)\Gamma^{(n)}(R_2) \tag{52}$$

Projection Operator: Above we proved that the eigenvectors of a given eigenvalue form a basis for a representation of the group. However, we would like invert this by finding basis functions that transform as irreducible representations and then we will have either the eigenvectors or a block diagonalized Hamiltonian. In order to do this, we will use the so-called projection operator, which takes a function and projects out any component onto a given irreducible representation:

$$P^{(\alpha)} = \frac{\ell_\alpha}{h}\sum_R \chi(R)R \tag{53}$$

Let us take some examples to see how this works. Let us start with the example of polynomials. First we will need to know how each symmetry element operates on each function. Let us make a table:

$f(x)$	E	R_π	$R_{\pi/2}$	$R_{3\pi/2}$	R_{ma}	R_{mb}	R_{mx}	R_{my}
x	x	$-x$	y	$-y$	y	$-y$	x	$-x$
x^2	x^2	x^2	y^2	y^2	y^2	y^2	x^2	x^2

(54)

Now we can take the projections:

$$P^{(A_1)}x = 0 \tag{55}$$
$$P^{(E_1)}x = x \tag{56}$$
$$P^{(A_1)}x^2 = \frac{1}{2}(x^2 + y^2) \tag{57}$$
$$P^{(E_1)}x^2 = 0 \tag{58}$$
$$\tag{59}$$

Of course, E_1 is a two dimensional representation so there should be two linearly independent vectors which transform as E_1. We will address this below.

Constructing multi-dimensional irreducible representation matrices: Although we can look up the irreducible representation matrices for cases where the dimension is greater than one, there is some insight to be gained by constructing them oneself. Let us stick with the point group for the square C_{4v} and construct the irreducible representation matrices for the irrep E_1. In the previous section we learned about the projection operator. Let us create a basis for E_1. First we need to guess a test function and use the projection operator to see if we have properly guessed something with a component of E_1. Let us start with a guess of the vector $\frac{1}{\sqrt{2}}(\hat{i} + \hat{j})$. Now let us apply the projection operator:

$$P^E \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{4}\left(\frac{2}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} + \frac{2}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}\right) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = |E_1^{(1)}\rangle \tag{60}$$

It looks like we perfectly guessed a function that transforms like E_1, so now we have one of our two E_1 vectors which we denote as $|E_1^{(1)}\rangle$. So now how can we get the other partner function that transforms like E_1? Just operate with members of the group until you get something linearly independent. Let us hit it with $R_{\pi/2}$.

$$R_{\pi/2} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{61}$$

We see that we got a linearly independent vector. In fact, you can already see that it is orthogonal. If it were not, you would need to orthogonalize it yourself. Therefore, we have:

$$|E_1^{(1)}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{62}$$
$$|E_1^{(2)}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{63}$$

Now that we have a proper basis set for E_1, we can construct the irreducible representation matrices by representing the symmetry operations in the new basis.

$$R_i = \begin{pmatrix} \langle E_1^{(1)}|R_i|E_1^{(1)}\rangle & \langle E_1^{(1)}|R_i|E_1^{(2)}\rangle \\ \langle E_1^{(1)}|R_i|E_1^{(2)}\rangle & \langle E_1^{(2)}|R_i|E_1^{(2)}\rangle \end{pmatrix} \tag{64}$$

$$R_E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad R_{\pi/2} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{65}$$

$$R_\pi = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad R_{3\pi/2} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{66}$$

$$R_{ma} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad R_{mb} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \tag{67}$$

$$R_{mx} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad R_{my} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \tag{68}$$

$$\tag{69}$$

First let us check that these have the correct traces. Clearly they do as the identity and R_π have traces of 2 and -2, respectively. If we inspect these, we see that these are the same set of matrices as the rotations in R^2, but different elements correspond to different matrices. Remember, this set of matrices is only unique up to a similarity transformation. What if we would have chose a test vector of $\hat{i}$ instead of $\hat{i}+\hat{j}$? Then if we had followed the same procedure we would have gotten:

$$|E_1^{(1)}\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{70}$$

$$|E_1^{(2)}\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{71}$$

Clearly, in this case we would have just gotten back the original rotation matrices in R^2. We would have gotten a different answer. Therefore, there must be a similarity transformation relating the matrices. Let us check this out with an example of R_{my}, where we obtained:

$$R_{my} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \text{ or } R_{my} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \tag{72}$$

$$\tag{73}$$

You might be able to guess that the similarity transformation is:

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \tag{74}$$

$$U \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} U^\dagger = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \tag{75}$$

One can verify that this unitary transformation relates all of the symmetry elements. To conclude, this generic procedure that we outlined can always be used to construct the irreducible representation matrices.

More on the projection Operator: Now that we have the irrep matrices, we can use a more specific projection operator which projects onto an individual partner function of a multi-dimensional representation.

$$P^{(\alpha_n)} = \frac{\ell_\alpha}{h} \sum_R \Gamma^{(\alpha)}_{nn}(R)^* R \tag{76}$$

Of course, one does not need to use this more specific projection operator. One could simply use the same procedure above where we constructed an orthogonal basis set for the irreducible representation. However, this may be less convenient if performing this procedure with a large basis set.

Orthogonality and block diagonalization: We are now prepared to show the advantage of having functions which transform like the irreducible representations. *First we will demonstrate that functions transforming like different irreducible representations or different rows of the same irreducible representation are orthoganol.* Consider the scalar product $\langle \phi^j_k | \psi^{j'}_{k'} \rangle$, where the subscript labels the irreducible representation and the superscript labels the row of the irreducible representation. The scalar product will be invariant if we operate on both vectors with the same symmetry element. Let us do this with each symmetry element in the group and then divide by the order of the group.

$$\langle \phi^j_k | \psi^{j'}_{k'} \rangle = \frac{1}{h} \sum_R \langle P_R \phi^j_k | P_R \psi^{j'}_{k'} \rangle = \frac{1}{h} \sum_R \sum_{\lambda\lambda'} \Gamma^j(R)^*_{\lambda k} \Gamma^{j'}(R)^*_{\lambda' k'} \langle \phi^j_\lambda | \psi^{j'}_{\lambda'} \rangle \tag{77}$$

$$= \delta_{jj'} \delta_{kk'} \sum_{\lambda=1}^{\ell_j} \frac{1}{\ell_j} \langle \phi^j_\lambda | \psi^j_\lambda \rangle \tag{78}$$

where the second line is obtained using the grand orthogonality theorem.

Now for block diagonalization we want to know the fate of $\langle \phi^j_k | H | \psi^{j'}_{k'} \rangle$. We can do the same trick, and because $[H, P_R] = 0$ we will get:

$$\langle \phi^j_k | H | \psi^{j'}_{k'} \rangle = \frac{1}{h} \sum_R \langle P_R \phi^j_k | P_R H \psi^{j'}_{k'} \rangle = \frac{1}{h} \sum_R \langle P_R \phi^j_k | H | P_R \psi^{j'}_{k'} \rangle \tag{79}$$

$$= \frac{1}{h} \sum_R \sum_{\lambda\lambda'} \Gamma^j(R)^*_{\lambda k} \Gamma^{j'}(R)^*_{\lambda' k'} \langle \phi^j_\lambda | H | \psi^{j'}_{\lambda'} \rangle \tag{80}$$

$$= \delta_{jj'} \delta_{kk'} \sum_{\lambda=1}^{\ell_j} \frac{1}{\ell_j} \langle \phi^j_\lambda | H | \psi^j_\lambda \rangle \tag{81}$$

Therefore, the matrix elements between differen partner functions transforming like different irreducible representations or different rows of the same irreducible representation are zero. This means that the Hamiltonian is block diagonal in the symmetrized basis.

Examples: We are now in a position to put to work everything that we learned. We will study several examples in the context of tight-binding Hamiltonians of molecules. First let us consider the diatomic molecule:

Figure 3:

Let us assume that we have one s-like basis orbital per site and that the are orthogonal. Let us assume that the following matrix elements have been given to us:

$$\langle\phi_1|H|\phi_1\rangle = \langle\phi_2|H|\phi_2\rangle = \epsilon \tag{82}$$
$$\langle\phi_1|H|\phi_2\rangle = \langle\phi_2|H|\phi_1\rangle = t \tag{83}$$
$$\tag{84}$$

Now we can write out the Hamiltonian:

$$H = \epsilon(|\phi_1\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_2|) + t(|\phi_1\rangle\langle\phi_2| + |\phi_1\rangle\langle\phi_2|) = \begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix} \tag{85}$$

What is the group that leaves this Hamiltonian invariant? Clearly there are two operations: the identity and the permutation. One can easily construct the representation matrices for these two operators in this basis.

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad R = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{86}$$

This is a group of order two and so there is only one possible character table and it can easily be deduced.

	E	R
A	1	1
B	1	-1

(87)

Taking the trace of our representation, we see we have $\chi = 1, 0$ and therefore $\Gamma = A+B$. Let us now construct partner functions for A and B using the projection operator:

$$P^A \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \rightarrow \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = |\phi_A\rangle \tag{88}$$

$$P^A \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} - \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \rightarrow \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = |\phi_B\rangle \tag{89}$$

The Hamiltonian will be diagonal if expressed in this basis set, so let us do this:

$$\langle \phi_A | H | \phi_A \rangle = (\langle \phi_1 | + \langle \phi_2 |) H (|\phi_1\rangle + |\phi_2\rangle) \frac{1}{2} \tag{90}$$

$$= (1 \;\; 1) \begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \frac{1}{2} = \epsilon + t \tag{91}$$

$$\langle \phi_B | H | \phi_B \rangle = (\langle \phi_1 | - \langle \phi_2 |) H (|\phi_1\rangle - |\phi_2\rangle) \frac{1}{2} \tag{92}$$

$$= (1 \;\; -1) \begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \frac{1}{2} = \epsilon - t \tag{93}$$

$$\langle \phi_A | H | \phi_B \rangle = (\langle \phi_1 | + \langle \phi_2 |) H (|\phi_1\rangle - |\phi_2\rangle) \frac{1}{2} \tag{94}$$

$$= (1 \;\; 1) \begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \frac{1}{2} = 0 \tag{95}$$

$$\tag{96}$$

We see that $|\phi_A\rangle$ and $|\phi_B\rangle >$ are indeed eigenvectors of the Hamiltonian and we have found the eigenvalues/eigenvalues solely using symmetry. This is exactly what we would have gotten by diagonalizing the Hamiltonian in the original basis set.

Let us now move on to the next example. Let us consider a square molecule which has a potential at the vertices and at the center of the square. What is the group for this molecule? It is C_{4v}, which we have dealt with numerous times now. Once again, let us assume that all sites have a s-like basis function, and we therefore have five orbitals in our basis set. We will need to form a representation for our symmetry operators in this basis. In other words, we need a 5×5 matrix for each symmetry operator. For example, let us construct the matrix for mirror line σ_a.

$$R_{\sigma_a} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{pmatrix} \tag{97}$$

Now we need to do this for every element in the group and then we can take the traces and decompose this representation. However, let us think for a second in order to save ourselves some work. The orbital on atom zero will never mix into the other orbitals,

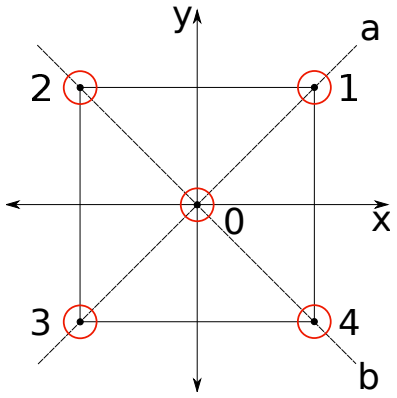

Figure 4:

and in fact it will always be left unchanged by the symmetry operations. Therefore, it is clear that we can form seperate representations for the center orbital and the corner orbitals. Furthermore, we can already deduce that orbital zero transforms like A_1 given that every symmetry element leaves it invariant. Therefore, we just need to construct 4×4 representation matrices for the orbitals at the corners. Let us do this now.

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} R_{\pi/2} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$R_{\pi} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} R_{3\pi/2} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

$$R_{ma} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} R_{mb} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$R_{mx} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} R_{my} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Let us now find the character for the representation of the corner orbitals:

$$\chi = (4, 0, 0, 0, 2) = A_1 + B_2 + E \tag{98}$$

Also recall that the center orbital transforms like A_1, so overall we will have $2A_1 + B_2 + E$. We can easily construct the 5×5 matrices including orbital zero by adding and

additional row and column with 1 as the first entry. If this is confusing simply inspect the two matrices above for R_{σ_a}. Now we need to find the symetrized orbitals using the projection operator. As our test orbital we can use the orbital at site one.

$$P^{A_1}\begin{pmatrix}0\\1\\0\\0\\0\end{pmatrix}=\begin{pmatrix}0\\1\\1\\1\\1\end{pmatrix}\rightarrow|\phi_1^{A_1}\rangle=\frac{1}{2}\begin{pmatrix}0\\1\\1\\1\\1\end{pmatrix} \tag{99}$$

$$P^{B_2}\begin{pmatrix}0\\1\\0\\0\\0\end{pmatrix}=\begin{pmatrix}0\\1\\-1\\1\\-1\end{pmatrix}\rightarrow|\phi^{B_1}\rangle=\frac{1}{2}\begin{pmatrix}0\\1\\-1\\1\\-1\end{pmatrix} \tag{100}$$

$$P^{E}\begin{pmatrix}0\\1\\0\\0\\0\end{pmatrix}=\begin{pmatrix}0\\0\\1\\0\\-1\end{pmatrix}\rightarrow|\phi_1^{E}\rangle=\frac{1}{\sqrt{2}}\begin{pmatrix}0\\0\\1\\0\\-1\end{pmatrix} \tag{101}$$

$$R_{\pi/2}|\phi_1^E\rangle=\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\0\\1\\0\end{pmatrix}\rightarrow|\phi_2^E\rangle=\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\0\\1\\0\end{pmatrix} \tag{102}$$

$$|\phi_0^{A_1}\rangle=\begin{pmatrix}1\\0\\0\\0\\0\end{pmatrix} \tag{103}$$

Let us assume that we have both nearest neighbor and next nearest neighbor hopping. Assume that the nearest neighbor hopping between orbital zero and one is t (ie. $\langle\phi_0|H|\phi_1\rangle=t$). What about the hopping from zero to the other orbitals? These can be generated from symmetry using the identity.

$$\langle\phi_0|H|\phi_1\rangle=\langle\phi_0|HR_{3\pi/2}R_{\pi/2}|\phi_1\rangle=\langle\phi_0|H|\phi_2\rangle \tag{104}$$

$$=\langle\phi_0|HR_{\pi}R_{\pi}|\phi_1\rangle=\langle\phi_0|H|\phi_3\rangle \tag{105}$$

$$=\langle\phi_0|HR_{mx}R_{mx}|\phi_1\rangle=\langle\phi_0|H|\phi_4\rangle \tag{106}$$

We will also include the second neighbor hopping which is between pairs of orbitals at the corners (ie. $\langle\phi_1|H|\phi_2\rangle=t'$). Once again, one can show the hopping between any

two pairs is t' using the procedure above. We can now write the Hamiltonian in the original basis set:

$$H = \begin{pmatrix} \epsilon & t & t & t & t \\ t & \epsilon & t' & 0 & t' \\ t & t' & \epsilon & t' & 0 \\ t & 0 & t' & \epsilon & t' \\ t & t' & 0 & t' & \epsilon \end{pmatrix} \tag{107}$$

You can use your favorite symbolic program (ie. maple, mathematica, etc) to symbollically find the eigenvalues and you will get:

$$\begin{pmatrix} \epsilon - 2t' \\ \epsilon \\ \epsilon \\ \epsilon + t' + \sqrt{t'^2 + 4t^2} \\ \epsilon + t' - \sqrt{t'^2 + 4t^2} \end{pmatrix} \tag{108}$$

Now we can transorm the Hamiltonian to the symmetrized basis where it will be block diagonal. The only block that will not be diagonal is A_1 as their are two partner functions transforming like A_1. Computing all the matrix elements, you should find:

$$H' = \begin{pmatrix} \epsilon & t & 0 & 0 & 0 \\ t & \epsilon + 2t' & 0 & 0 & 0 \\ 0 & 0 & \epsilon - 2t' & 0 & 0 \\ 0 & 0 & 0 & \epsilon & 0 \\ 0 & 0 & 0 & 0 & \epsilon \end{pmatrix} \tag{109}$$

Diagonalizing the A_1 block will give the remaining two eigenvalues.

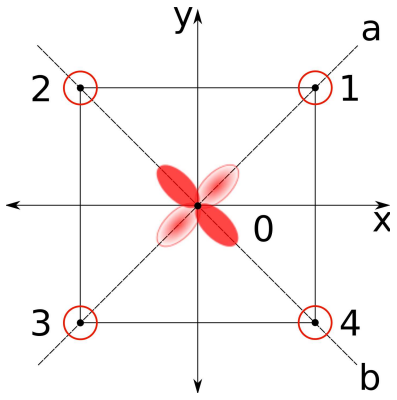

Figure 5:

What if we wanted to change things up and consider the case where we put a xy type orbital at the center instead of an s orbital? In this case one can show that the

xy orbital transforms like B_2, so now we will have $A_1 + 2B_2 + E$. We already have the symmetrized oxygen orbitals so we are all set to go. Let us assume that $\langle\phi_0|H|\phi_1\rangle = t$. One can generate the remaining hoppings by inserting the indentity as above. We would get $\langle\phi_0|H|\phi_2\rangle = \langle\phi_0|H|\phi_4\rangle = -t$ and $\langle\phi_0|H|\phi_1\rangle = \langle\phi_0|H|\phi_3\rangle = t$. In the unsymmetrized basis we have:

$$H = \begin{pmatrix} \epsilon_0 & t & -t & t & -t \\ t & \epsilon & t' & 0 & t' \\ -t & t' & \epsilon & t' & 0 \\ t & 0 & t' & \epsilon & t' \\ -t & t' & 0 & t' & \epsilon \end{pmatrix} \tag{110}$$

If we transform the Hamiltonian to the symmetrized basis, we will get:

$$H' = \begin{pmatrix} \epsilon_0 & 2t & 0 & 0 & 0 \\ 2t & \epsilon - 2t' & 0 & 0 & 0 \\ 0 & 0 & \epsilon + 2t' & 0 & 0 \\ 0 & 0 & 0 & \epsilon & 0 \\ 0 & 0 & 0 & 0 & \epsilon \end{pmatrix} \tag{111}$$

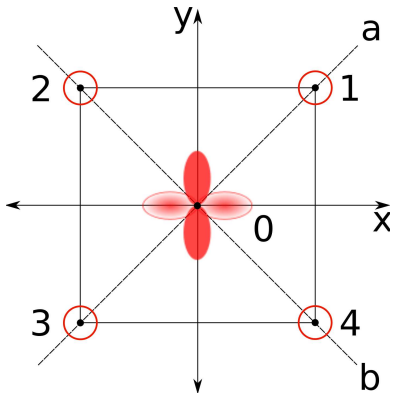

Figure 6:

Let us consider one more complication. What if we put a x^2-y^2 orbital at the center of the molecule? Well, one can show that $x^2 - y^2$ transforms like B_1, so we would have $\Gamma = A_1 + B_1 + B_2 + E$. This would imply that the Hamiltonian is completely diagonal in the symmetrized basis. The center orbital would not mix with ANY of the linear combination of the s orbitals at the corners. One can easily see this by considering the matrix element between the orbital at aero and 1.

$$\langle\phi_0|H|\phi_1\rangle = \langle\phi_0|HR_{ma}R_{ma}|\phi_1\rangle = -\langle\phi_0|H|\phi_1\rangle = 0 \tag{112}$$

One can easily work out the matrix elements for the symmetrized orbitals as in the previous cases.

Translation group: Up until now we have only considered symmetry operations about some point in space. Now let us move on to the translation group. The translation group is abelian, due to the fact that group multiplication is simply the addition of vectors. The translation group in one dimension is cyclic, and the three dimensional translation group may be considered as a direct product of three cyclic groups. Let us start by defining the three dimensional translation group as all possible integer linear combinations of three linearly independent real vectors $\overrightarrow{a_1}, \overrightarrow{a_2}, \overrightarrow{a_3}$. The set of all lattice vectors is given by $\overrightarrow{t_n} = n_1\overrightarrow{a_1} + n_2\overrightarrow{a_2} + n_3\overrightarrow{a_3}$ where $n_1, n_2, n_3 = -\infty \ldots \infty, -\infty \ldots \infty, -\infty \ldots \infty$. This group is of infinite order, and this is highly inconvenient to work with. Intuitively, we know that real crystals are in fact not infinite, so this is physically unnecessary as well. Therefore, we need some means to convert this to a finite group. This can be done with Born-VonKarman (BVK) or cyclic boundary conditions. We will assume that once you reach an edge of the crystal that you loop back to the other side. Considering some real space function which has the symmetry of the crystal, this would mean that:

$$\phi(\overrightarrow{r}) = \phi(\overrightarrow{r} + N_1\overrightarrow{a_1}) = \phi(\overrightarrow{r} + N_2\overrightarrow{a_2}) = \phi(\overrightarrow{r} + N_3\overrightarrow{a_3}) = \phi(\overrightarrow{r} + N_1\overrightarrow{a_1} + N_2\overrightarrow{a_2} + N_3\overrightarrow{a_3}) \tag{113}$$

where N_1, N_2, N_3 are large positive integers. In terms of the representation of the translation operator, this means that:

$$P(N_j\overrightarrow{a_j}) = P(0) \text{ for } j = 1, 2, 3 \tag{114}$$

$$P(\overrightarrow{t_n} + N_j\overrightarrow{a_j}) = P(\overrightarrow{t_n}) \text{ for any } \overrightarrow{t_n} \tag{115}$$

$$\tag{116}$$

Therefore the set of distinct operations is:

$$P(n_1\overrightarrow{a_1} + n_2\overrightarrow{a_2} + n_3\overrightarrow{a_3}) \text{ where } 0 \leq n_j < N_j \text{ and } j = 1, 2, 3 \tag{117}$$

Now we have a finite abelian group of order $N_1N_2N_3$, and therefore each element will be in a class by itself. We would now like to construct the character table. We know there will be $N_1N_2N_3$ one dimensional irreducible representations. Let us derive what these characters will be.

$$\Gamma(\overrightarrow{a_1}) = c_1 \tag{118}$$

$$\Gamma(N_1\overrightarrow{a_1}) = c_1^{N_1} = 1 \tag{119}$$

$$\rightarrow c_1 = e^{\frac{-2\pi i p_1}{N_1}} \text{ where } p_1 = 0, 1, 2, \ldots, N_j - 1 \tag{120}$$

If p_1 become greater than N_1 there is no effect:

$$e^{\frac{-2\pi i(p_1+N_1)}{N_1}} = e^{\frac{-2\pi i p_1}{N_1}} \tag{121}$$

Therefore there are only N_1 distinct values for p_1. We can easily generalize this to get the character of any multiple of a_1:

$$\Gamma(n_1\overrightarrow{a_1}) = e^{\frac{-2\pi i n_1 p_1}{N_1}} \tag{122}$$

This can straightforwardly be generalized to three dimensions:

$$\Gamma(n_1\overrightarrow{a_1}+n_2\overrightarrow{a_2}+n_3\overrightarrow{a_3}) = e^{-2\pi i(\frac{n_1p_1}{N_1}+\frac{n_2p_2}{N_2}+\frac{n_3p_3}{N_3})} \tag{123}$$

These are the characters for all possible translation operators and all possible irreducible representations. The irreducible representation is labeled by a three dimensional point (p_1, p_2, p_3), and it should be clear that there are $N_1N_2N_3$ of these. Now we are in a position to see the emergence of the notion of a reciprocal lattice. One can see that the quantity in paranthesis in the exponential looks like the result of dotting something with the translation vector. We could write therefore create some new type of vector which characterizes the irreducible representation:

$$-2\pi i(\frac{n_1p_1}{N_1}+\frac{n_2p_2}{N_2}+\frac{n_3p_3}{N_3}) = -i(\frac{p_1}{N_1}\overrightarrow{b_1}+\frac{p_2}{N_2}\overrightarrow{b_2}+\frac{p_3}{N_3}\overrightarrow{b_3})\cdot(n_1\overrightarrow{a_1}+n_2\overrightarrow{a_2}+n_3\overrightarrow{a_3})$$

if

$$\overrightarrow{a_j}\cdot\overrightarrow{b_k} = 2\pi\delta_{jk}$$

The condition $\overrightarrow{a_j}\cdot\overrightarrow{b_k} = 2\pi\delta_{jk}$ is sufficient to define this new set of vectors $\overrightarrow{b_1}, \overrightarrow{b_2}, \overrightarrow{b_3}$, and one can show that in three dimensions the following definitions satisfy this condition:

$$\overrightarrow{b_1} = 2\pi\frac{\overrightarrow{a_2}\times\overrightarrow{a_3}}{\overrightarrow{a_1}\cdot(\overrightarrow{a_2}\times\overrightarrow{a_3})} \tag{124}$$

$$\overrightarrow{b_2} = 2\pi\frac{\overrightarrow{a_1}\times\overrightarrow{a_3}}{\overrightarrow{a_1}\cdot(\overrightarrow{a_2}\times\overrightarrow{a_3})} \tag{125}$$

$$\overrightarrow{b_3} = 2\pi\frac{\overrightarrow{a_1}\times\overrightarrow{a_2}}{\overrightarrow{a_1}\cdot(\overrightarrow{a_2}\times\overrightarrow{a_3})} \tag{126}$$

$$\tag{127}$$

Therefore all distinct irreducible representations can be characterized by the k vectors:

$$\overrightarrow{K} = k_1\overrightarrow{b_1}+k_2\overrightarrow{b_2}+k_3\overrightarrow{b_3} = \frac{p_1}{N_1}\overrightarrow{b_1}+\frac{p_2}{N_2}\overrightarrow{b_2}+\frac{p_3}{N_3}\overrightarrow{b_3} \tag{128}$$

and we can write the characters as:

$$\Gamma(\overrightarrow{t_n}) = e^{-i\overrightarrow{K}\cdot\overrightarrow{t_n}} \tag{129}$$

Now we can derive the consequences of this. Let us act on some function which transforms like a given k-point.

$$P(\overrightarrow{t_n})\phi^{\overrightarrow{K}}(r) = \Gamma(\overrightarrow{t_n})\phi^{\overrightarrow{K}}(r) = e^{-i\overrightarrow{K}\cdot\overrightarrow{t_n}}\phi^{\overrightarrow{K}}(r) \tag{130}$$

$$= \phi^{\overrightarrow{K}}(\overrightarrow{t_n}^{-1}r) = \phi^{\overrightarrow{K}}(r-\overrightarrow{t_n}) \tag{131}$$

We have just derived Blochs theorem, which says $\phi^{\overrightarrow{K}}(r-\overrightarrow{t_n}) = e^{-i\overrightarrow{K}\cdot\overrightarrow{t_n}}\phi^{\overrightarrow{K}}(r)$. This is also equivalent to saying that $\phi^{\overrightarrow{K}}(r) = e^{i\overrightarrow{K}\cdot\overrightarrow{r}}u_{\overrightarrow{K}}(r)$ where $u_{\overrightarrow{K}}(r)$ is a function which has

the periodicity of the lattice. We see that Blochs theorem is a purely group theoretical result that naturally falls out of the formalism that we have been developing.

Now let us consider an example. Let us consider a one-dimensional array of protons and a single electron moving in this potential. The Hamiltonian would be:

$$H = \sum_n \frac{1}{r - na} - \frac{1}{2}\nabla^2 \tag{132}$$

where a is the primitive translation vector. Now, our trial function is going to be an s-like orbital on each site.

$$\Psi(r) = c_0\phi(r) + c_1\phi(r-a) + \cdots + c_N\phi(r-Na) \tag{133}$$

We will assume that these set of orbitals are orthogonal. Without the use of translational symmetry, we would have to diagonalize a $N \times N$ matrix where N is a large integer. However, we will not have to do this given that we will symmetrize our basis. Normally, we would need to build $N \times N$ represenetation matrices for each symmetry element and then take the trace to find out which irreducible representations are present. In the case of an abelian group this is not necessary. One can show that each irreducible representation will appear as many times as there are orbitals within the primitive unit cell. In this case, each irreducible representation will only appear once. Now let us employ the projection operator to symmetrize the basis functions:

$$P^k\phi(r) = \sum_n \chi_n P(na)\phi(r) = \sum_n e^{-ikna} P(na)\phi(r) = \sum_n e^{-ikna}\phi(r-na) \tag{134}$$

$$\rightarrow \psi_k(r) = \frac{1}{\sqrt{N}} \sum_n e^{-ikna}\phi(r-na) \tag{135}$$

Now we only need to consider matrix elements between basis states transforming like the same irrep.

$$\langle\psi_k|H|\psi_k\rangle = \frac{1}{N}\sum_{nm} e^{ika(n-m)} \int \phi(r-na)^* H\phi(r-ma)dr \tag{136}$$

$$= \sum_n e^{-ikna} \int \phi(r)^* H\phi(r-na)dr \tag{137}$$

Now let us assume the "tight-binding" approximation where there is only hopping between nearest neighbor orbitals, where $t = \int \phi(r)^* H\phi(r-a)dr = \int \phi(r)^* H\phi(r+a)dr$.

$$\langle\psi_k|H|\psi_k\rangle = t(e^{ika} - e^{-ika}) = 2t\cos(ka) \tag{138}$$

We see that the eigenvalues form a cosine band.