CHAPTER 1

Symmetry

1.1 Symmetry Groups

In this section we will discuss applications of symmetry to electronic structure computations. Symmetry is not only useful to classify solutions of the Schrödinger equation, it also plays an important role in reducing the computational cost of computations.

Let us start by considering symmetry in a very simple context, that of functions of one variable, $f(x)$. Consider the transformation $\hat{I}$ that replaces x with $-x$, that is $\hat{I}x = -x$. This operator plus the identity operator $\hat{E}$ (defined as $\hat{E}x = x$) form a group because any sequence of operations chosen from $\{\hat{E}, \hat{I}\}$ either acts as $\hat{E}$ or $\hat{I}$. In other words, a group is closed under the multiplication operation. We can see this if we apply $\hat{I}$ twice to x:

$$\hat{I}^2 x = \hat{I}(\hat{I}x) = \hat{I}(-x) = -\hat{I}x = x = \hat{E}x, \tag{1.1}$$

which shows that $\hat{I}^2 = \hat{E}$. Similarly one can show that $\hat{I}\hat{E} = \hat{E}\hat{I} = \hat{I}$, and $\hat{E}^2 = \hat{E}$. We can summarize this information with a group multiplication table

$$\begin{array}{c|cc} \times & \hat{E} & \hat{I} \\ \hline \hat{E} & \hat{E} & \hat{I} \\ \hat{I} & \hat{I} & \hat{E} \end{array} \tag{1.2}$$

Groups can be used to classify the symmetry properties of functions. When functions "behave" like groups, we say that they represent a group. For example, among all possible functions $f(x)$ we can identify two special type of functions that are transformed by the group $\{\hat{E}, \hat{I}\}$

1. Symmetric functions (f_+) that satisfy

$$\begin{aligned} \hat{E} f_+(x) &= f_+(x) \\ \hat{I} f_+(x) &= f_+(-x) = f_+(x) \end{aligned} \tag{1.3}$$

   Examples of symmetric functions are $\exp(-x^2)$, $\cos(x)$, x^4, etc.

2. Antisymmetric functions (f_-) that satisfy

$$\begin{aligned} \hat{E} f_-(x) &= f_-(x) \\ \hat{I} f_-(x) &= f_-(-x) = -f_-(x) \end{aligned} \tag{1.4}$$

   Examples of antisymmetric functions are $x\exp(-x^2)$, $\sin(x)$, x^3, etc

Under the operations of the group, these two functions remain the same up to a phase factor ($\pm$). These function are a representation of the group in the sense that the functions f_+ and f_- satisfy the same product operations of the group elements $\hat{E}$ and $\hat{I}$, respectively. For example, the product of two symmetric functions $f_+(x)$ and $g_+(x)$ is a symmetric function

$$f_+(x)g_+(x) = h_+(x), \tag{1.5}$$

and this relationship reflects the group property $\hat{E}\hat{E} = \hat{E}$. To verify that Eq. (1.5) is a symmetric function we just apply $\hat{I}$ to the left hand side of this expression[1]

$$\hat{I}\left[f_+(x)g_+(x)\right] = \hat{I}f_+(x)\hat{I}g_+(x) = f_+(x)g_+(x). \tag{1.6}$$

[1] Note that when we apply a transformation like $\hat{I}$ to a product of functions $f(x)g(x)$ the result is the product of the original functions all transformed by $\hat{I}$, that is, $[\hat{I}f(x)][\hat{I}g(x)]$.

Since $\hat{I}$ acting on $f_+(x)g_+(x)$ gives us back $f_+(x)g_+(x)$, this product is a symmetric function $h_+(x)$. Similarly we can verify that the product of a symmetric function $f_+(x)$ and an antisymmetric function $g_-(x)$ is an antisymmetric function

$$f_+(x)g_-(x) = h_-(x), \tag{1.7}$$

again by testing what happens when we apply the inversion operator to this product

$$\hat{I}\left[f_+(x)g_-(x)\right] = \hat{I}f_+(x)\hat{I}g_-(x) = -f_+(x)g_-(x). \tag{1.8}$$

The final result is multiplied by a minus sign and so $f_+(x)g_-(x)$ is an antisymmetric function.

Representations of group operations (like f_+ and f_-) can be classified according to their **character**, that is, the way they transform under equivalent classes of symmetry operations. The following table shows the character table for the inversion group, which classifies all the **irreducible representations** (irreps) of the inversion group

	$\hat{E}$	$\hat{I}$	linear functions	quadratic functions
$\mathrm{A_g}$	$+1$	$+1$	$-$	x^2
$\mathrm{A_u}$	$+1$	-1	x	$-$

(1.9)

The symbols $\mathrm{A_g}$ and $\mathrm{A_u}$ indicate the two irreps of the inversion group. The first representation ($\mathrm{A_g}$) is symmetric (to which f_+ belongs) and it is labeled with a "g" after the German word *gerade* (even). The second representation is antisymmetric (to which f_- belongs) and it is labeled with a "u" after the German word *ungerade* (odd). The numbers under each symmetry operation shows how functions that belong to these two representations transform. In addition, the last two columns classify the linear and quadratic functions in x according to the irreps of this group.

1.2 Point groups

When dealing with molecular problems, we are concerned with so-called **point groups**. These are transformations that leave at least one point unchanged (typically chosen to be the origin of a Cartesian coordinate system). If all the elements of a group **commute**, that is, given two elements A and B

1.3 Examples of point groups

1.3.1 $\mathrm{C_s}$ — Plane symmetry

The $\mathrm{C_s}$ point group contains two elements: the identity and a plane of reflection ($sigma_\mathrm{h}$). This group is Abelian and has only two irreducible representations. Its character table is very similar to the one of the inversion group

irrep	E	σ_h	linear, rotations	quadratic
A'	$+1$	$+1$	x, y, R_z	x^2, y^2, z^2, xy
A''	$+1$	-1	$z, R_x, R_y,$	yz, xz

(1.10)

The product table for the $\mathrm{C_s}$ group is

$$\begin{array}{c|cc} \times & \mathrm{A}' & \mathrm{A}'' \\ \hline \mathrm{A}' & \mathrm{A}' & \mathrm{A}'' \\ A'' & \mathrm{A}'' & \mathrm{A}' \end{array} \tag{1.11}$$

This group is isomorphic to the inversion group, the $\mathrm{C_i}$ group, and the $\mathrm{C_2}$ group.

1.3.2 The $\mathrm{C_{2v}}$ group

The $\mathrm{C_{2v}}$ point group contains four symmetry operations: the identity, a rotation around the z axis ($\mathrm{C_2}$), and two reflection planes $sigma_{\mathrm{v}}(xz)$ and $sigma_{\mathrm{v}}(yz)$. This group is Abelian and has only two irreducible representations. Its character table is very similar to the one of the inversion group

irrep	E	σ_{h}	linear, rotations	quadratic
A′	$+1$	$+1$	x, y, R_z	x^2, y^2, z^2, xy
A″	$+1$	-1	$z, R_x, R_y,$	yz, xz

(1.12)

The product table for the $\mathrm{C_s}$ group is

$$\begin{array}{c|cc} \times & \mathrm{A}' & \mathrm{A}'' \\ \hline \mathrm{A}' & \mathrm{A}' & \mathrm{A}'' \\ A'' & \mathrm{A}'' & \mathrm{A}' \end{array} \tag{1.13}$$

This group is isomorphic to the inversion group, the $\mathrm{C_i}$ group, and the $\mathrm{C_2}$ group.