

## Symmetry Coordinates and Group Orbitals from Basis Functions

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The gradients of the basis functions of group theory are vector-valued basis functions. When one of the components of such a gradient is evaluated at atomic positions, and the values are summed over a set of equivalent atoms, the result represents a symmetry coordinate and/or a group orbital.

**Key words:** Symmetry coordinates – Group orbitals

The crucial step in the construction of symmetry coordinates or of group orbitals is finding the relative coefficients of the component displacements or orbitals. The two methods commonly used to find these coefficients are 1) projection operators and 2) an intuitive process of orbital “matching” [1]. The first method is straightforward except when the irreducible representation in question is generated more than once by the components, but the procedure is often lengthy and sometimes requires the use of the character table for a subgroup of the true group in order to be tractable. The second approach is limited by one’s intuition, which is risky to rely on in unfamiliar cases.

The intent of this note is to introduce a rigorous way of deriving symmetry coordinates and group orbitals from the basis functions of the irreducible representations. Not only does this approach share the complete reliability of projection operators, but the procedure is generally shorter and faster, always treats the full point group, and is straightforward even in cases where an irreducible representation occurs more than once. The only drawback we can see is the absence of basis functions for several irreducible representations in common character tables, but tables that fill most of those gaps are available [2].

Section 1 is for the reader who is interested in the derivation of the method; he who is more interested in its application may skip to Section 2.

### 1. Derivation

Let  $x_n$  with  $n=1-3$  be one set of Cartesian coordinates  $\mathbf{x}$ . A symmetry operation  $R\mathbf{x}$  produces a second set of coordinates [3]

$$R\mathbf{x} = \mathbf{x}_2$$

whose members are

$$x_{2m} = \sum_{n=1}^3 r_{mn} x_n, \quad m=1-3 \quad (1)$$

and the inverse operation  $R^{-1}\mathbf{x}$  yields a third set

$$R^{-1}\mathbf{x} = \mathbf{x}_3$$

consisting of

$$x_{3k} = \sum_{n=1}^3 r_{nk} x_n, \quad k=1-3 \quad (2)$$

Establish a unit vector  $\mathbf{e}_n$  parallel to each coordinate axis  $x_n$ . The operator  $U_R$  that operates on  $\mathbf{e}_n$  in the same sense that  $R$  operates on  $\mathbf{x}$  is defined in terms of the same matrix elements.

$$U_R \mathbf{e}_n = \sum_{m=1}^3 r_{mn} \mathbf{e}_m \quad (3)$$

Define the operator  $P_R$  for the symmetry operation  $P_R f(\mathbf{x})$  that corresponds to  $R\mathbf{x}$  as follows [3].

$$P_R f(\mathbf{x}) = f(R^{-1}\mathbf{x}) = f(\mathbf{x}_3) \quad (4)$$

Let  $f_i(\mathbf{x})$  and  $f_j(\mathbf{x})$  be basis functions for an  $h$ -dimensional irreducible representation. By definition [3]:

$$P_R f_i(\mathbf{x}) = \sum_{j=1}^h c_{ji} f_j(\mathbf{x}) \quad (5)$$

Now find the gradient of  $f_i(\mathbf{x})$

$$\nabla f_i(\mathbf{x}) = \sum_{n=1}^3 \mathbf{e}_n \frac{\partial f_i(\mathbf{x})}{\partial x_n} = \sum_{n=1}^3 \mathbf{e}_n f_{in}(\mathbf{x}) \quad (6)$$

and note that the result is a vector-valued function; i.e., it defines the gradient vector at every point. We wish to show that the vector functions  $\nabla f_j(\mathbf{x})$ ,  $j=1-h$  are also basis functions for the same irreducible representation as the scalar functions  $f_j(\mathbf{x})$ .

The operators  $U_R$  and  $P_R$  are used to perform a symmetry operation on the gradient function in Eq. (6).

$$U_R P_R \nabla f_i(\mathbf{x}) = \sum_{n=1}^3 \sum_{m=1}^3 \mathbf{e}_m r_{mn} f_{in}(\mathbf{x}_3) \quad (7)$$

But the right-hand side of Eq. (7) is identical to the following result obtained by reversing the order of the gradient and symmetry operators. We use Eqs. (4), (6) and (2) to get

$$\begin{aligned} \nabla[P_R f_i(\mathbf{x})] &= \nabla[f_i(\mathbf{x}_3)] \\ &= \sum_{k=1}^3 \frac{\partial f_i(\mathbf{x}_3)}{\partial x_{3k}} \sum_{n=1}^3 \mathbf{e}_n \frac{\partial}{\partial x_n} r_{nk} x_n \\ &= \sum_{k=1}^3 \sum_{n=1}^3 \mathbf{e}_n r_{nk} f_{ik}(\mathbf{x}_3) \end{aligned} \quad (8)$$

Next we equate the left-hand sides of Eqs. (7) and (8), and from there Eq. (5) yields the desired result.

$$\begin{aligned} U_R P_R \nabla f_i(\mathbf{x}) &= \nabla[P_R f_i(\mathbf{x})] \\ &= \sum_{j=1}^h c_{ji} \nabla f_j(\mathbf{x}) \end{aligned} \quad (9)$$

Comparison of Eqs. (5) and (9) shows that the functions  $f_j(\mathbf{x})$  and their gradients  $\nabla f_j(\mathbf{x})$  are alternative basis functions for the same representation.

When  $\nabla f_i(\mathbf{x})$  is evaluated at  $q$  equivalent points  $p$ , the result is an array of  $q$  vectors. Let us add the vectors in the array, not with the intent of merging them into one total vector, but simply for the purpose of listing them as a composite sum. The set of such sums formed from a set of basis functions is also a basis for the same irreducible representation, as can be seen by summing Eq. (9) over the  $q$  equivalent points  $p$ .

$$U_R P_R \left( \sum_{p=1}^q \nabla f_i(\mathbf{x})_p \right) = \sum_{j=1}^h c_{ji} \left( \sum_{p=1}^q \nabla f_j(\mathbf{x})_p \right) \quad (10)$$

The equivalent points at which Eq. (10) is most useful are the equilibrium positions of the atoms in a molecule. The vibrational displacements of the atoms can be expressed in terms of any set of independent vectors. Let the vectors  $\mathbf{e}_n$  represent unit components of these displacements. *Then the symmetry operand in Eq. (10) can be identified as a symmetry coordinate.*

In the axial point groups [2], each symmetry coordinate can be simplified beyond its form in Eq. (10). For a set of equivalent atoms, the displacement components in the axial direction, say  $\mathbf{e}_3$ , form a set of equivalent vectors apart from the nonaxial components. Consequently, the symmetry coordinates are of two types, one made exclusively of axial vectors, and the other containing only nonaxial vectors. These two types can be separated from their combined form in Eq. (10) to give

$$\sum_{p=1}^q \nabla f_i(\mathbf{x})_p = \sum_{p=1}^q \sum_{n=1}^2 f_{in}(\mathbf{x})_p \mathbf{e}_n + \sum_{p=1}^q f_{i3}(\mathbf{x})_p \mathbf{e}_3 \quad (11)$$

where the two terms on the right each satisfy Eq. (10) independently. Now Eq. (11) does not guarantee that any one set of basis functions will be useful for

finding both axial and nonaxial symmetry coordinates. If  $f_i$  does not belong to one of the irreducible representations generated by the axial vectors, for example, then  $f_{i3}(\mathbf{x})_p$  will be zero and Eq. (10) will be null for that term. This uninformative result usually can be avoided by applying Eq. (10) only to those basis functions whose irreducible representation is generated by the components in question. However, even a generated representation may have one set of basis functions that fails to give nonzero coefficients, and yet have other sets that succeed.

For the nonaxial groups [2], Eq. (11) can be separated further to give three terms that independently satisfy Eq. (10).

$$\sum_{p=1}^q \nabla f_i(\mathbf{x})_p = \sum_{n=1}^3 \left( \sum_{p=1}^q f_{in}(\mathbf{x})_p \mathbf{e}_n \right) \quad (12)$$

Our definition of the unit vectors  $\mathbf{e}_n$  caused the displacements of the atoms to have their respective components all lie in the same direction, but this condition is not necessary. Let us redefine the vectors  $\mathbf{e}_n$ ,  $n=1-3$  to be the unit vectors  $\theta$ ,  $\phi$ , and  $r$ , respectively. Also redefine  $f_{in}$ ,  $n=1-3$  as

$$\frac{1}{r} \frac{\partial f_i}{\partial \theta}, \quad \frac{1}{r \sin \theta} \frac{\partial f_i}{\partial \phi}, \quad \text{and} \quad \frac{\partial f_i}{\partial r},$$

respectively [cf. Eq. (6)]. Then Eqs. (9)–(12) are still valid, but we must remember that  $\mathbf{e}_n$  is now  $\mathbf{e}_n(\mathbf{x})$ . In fact, Eq. (11) now applies to every point group, and Eq. (12) applies to all the axial and nonaxial point groups. The wider applicability of Eqs. (11) and (12) is an important point in favor of this choice of unit vectors, but the most significant advantage was pointed out by Hsu and Orchin [4]: these unit vectors represent not only atomic displacements, but also sigma- and pi-bonding orientations of atomic orbitals.<sup>1</sup> *Therefore Eqs. (11) and (12) represent group orbitals as well as symmetry coordinates.*

## 2. Application

The procedure is outlined in four instructions. 1) To represent each displacement and/or orbital, place a vector of arbitrary length<sup>2</sup> at each atom and align it with one of the unit vectors  $\mathbf{i}, \mathbf{j}, \mathbf{k}, \theta, \phi$ , or  $r$ , as appropriate. 2) Determine the irreducible representations that are generated by these vectors. 3) For each irreducible representation, select a set of basis functions. Take each basis function and find the component of its gradient that contains the unit vector used in step 1). 4) Evaluate this gradient component at each equivalent atom, and add these values to get a symmetry coordinate and/or a group orbital. The result is normalized as usual.

As an aid in step 3), a list of basis functions and their gradients will be published

<sup>1</sup> These authors used slightly different sets of unit vectors, viz.  $-\theta$ ,  $\phi$ , and  $-r$  in some cases and  $-\theta$ ,  $-\phi$ ,  $-r$  in others.

<sup>2</sup> Nonuniform vectors are easier to keep track of during a symmetry operation, especially if the transformation matrix is needed in addition to its character.

elsewhere, but the gradients of  $R_x$ ,  $R_y$ , and  $R_z$  are worth noting here: they are  $yk - zj$ ,  $zi - xk$ , and  $xj - yi$ , respectively.

Steps 1) and 2) are well known, and numerous examples are available [1]. To illustrate steps 3) and 4), we consider the  $E_{1g}$  pi-bonding molecular orbitals of benzene. The molecular plane is  $xy$ , with the  $+x$  axis passing between carbon atoms 2 and 3, and the  $+y$  axis through carbon atom 1. Each  $p_z$  orbital is represented as a vector in the  $k$  direction. Common character tables list two sets of basis functions for  $E_{1g}$ , viz.  $(R_x, R_y)$  and  $(xz, yz)$ , but only one set is needed here. The relative  $(x, y)$  coordinates of carbon atoms 1–6 are  $(0, 2)$ ,  $(\sqrt{3}, 1)$ ,  $(\sqrt{3}, -1)$ ,  $(0, -2)$ ,  $(-\sqrt{3}, -1)$  and  $(-\sqrt{3}, 1)$ , respectively. For  $R_x$ , the  $k$  gradient components at atoms 1–6 are  $k$  times 2, 1,  $-1$ ,  $-2$ ,  $-1$ , and 1, respectively. Hence the normalized wavefunction, neglecting overlap, is

$$\Psi_{E_{1g}}(R_x) = \frac{1}{\sqrt{12}}(2p_{z1} + p_{z2} - p_{z3} - 2p_{z4} - p_{z5} + p_{z6}).$$

For  $R_y$ , the  $k$  gradient components are  $k$  times 0,  $-\sqrt{3}$ ,  $-\sqrt{3}$ , 0,  $\sqrt{3}$ , and  $\sqrt{3}$ , respectively, and the wavefunction is

$$\Psi_{E_{1g}}(R_y) = \frac{1}{2}(-p_{z2} - p_{z3} + p_{z5} + p_{z6})$$

The other basis set,  $(xz, yz)$ , works equally well. The reader can verify that

$$\Psi_{E_{1g}}(xz) = -\Psi_{E_{1g}}(R_y)$$

$$\Psi_{E_{1g}}(yz) = \Psi_{E_{1g}}(R_x)$$

The above change of sign is of no consequence, but the reader is cautioned that some sigma-bonding group orbitals derived by this method for the B orbitals in  $AB_n$  molecules must have their signs reversed in order to have positive overlaps with the A basis orbitals.

In case of multiple occurrence of an irreducible representation, one simply uses the occurrence number of sets of basis functions that are all orthogonal.

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