CHEMISTRY 273

PROJECTION OPERATORS

To determine the symmetry-adapted linear combinations (SALC's) of equivalent a.o.'s from a given basis set, we have been secretly using a simple example of a projection operator. In general, a projection operator is defined by the characteristic property of idempotency:

(1) $$\hat{0}\hat{0}f = \hat{0}f \quad or \quad \hat{0}^2 = \hat{0}$$

A projection operator may also be thought of as an operator which operates on a space spanned by the basis set (f_1,..., f_n) with the following results:

(2) $$\hat{0}^i f_j = f_j \delta_{ij}$$

i.e., the ith projection operator takes f_i into itself but annihilates (takes to zero) any other basis function. Thus if a general function can be expanded in terms of the basis:

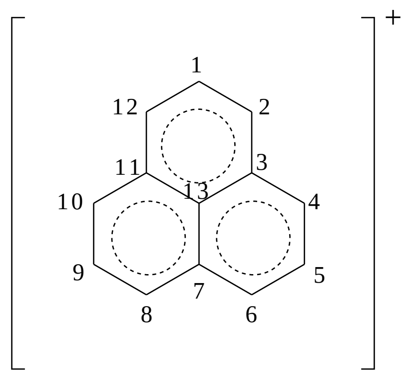
(3) $$g = \sum_j c_j f_j$$

we can recover the ith basis function by application of the projection operator $\hat{0}^i$:

(4) $$\hat{0}^i g = c_i f_i$$

We can use the SALC's of the perinaphthenyl cation as a concrete illustration of projection operators. The three SALC's obtained from the equivalent a.o.'s ϕ_1, ϕ_5 and ϕ_9 are:

$$a_2'' = (\sqrt{1/3})(\phi_1 + \phi_5 + \phi_9)$$
$$e_a'' = (\sqrt{1/6})(2\phi_1 - \phi_5 - \phi_9)$$
$$e_b'' = (\sqrt{1/2})(\phi_5 - \phi_9)$$



We will demonstrate that the projection operator for a function in the ith irreducible representation is:

(5) $$\hat{P}^{(i)} = \frac{\ell_i}{h}\sum_R \chi_i^*(R)\hat{R} = \frac{\ell_i}{h}\sum_R\sum_m (\Gamma_i(R))_{mm}^*\hat{R}$$

Letting $\hat{P}^{(i)}$ operate on f_s^j the sth basis function for the jth irreducible representation, we obtain:

(6) $$\begin{aligned}\hat{P}^i f_s^j &= \frac{\ell_i}{h}\sum_R\sum_{m=1}^{\ell_i}(\Gamma_i(R))_{mm}^*\hat{R}\ \ f_s^j \\ &= \frac{\ell_i}{h}\sum_R\sum_m(\Gamma_i(R))_{mm}^*\left[\sum_i(\Gamma_j(R))_{st}\,f_t^j\right]\end{aligned}$$

Since $$\hat{R}f_s^j = \sum_{i=1}^{\ell_i}(\Gamma_j(R))_{st}\,f_t^j$$

Thus:

(7) $$\hat{P}f_s^j = \sum_m\sum_t f_t^j\sum_R(\Gamma_i(R))_{mm}^*(\Gamma_j(R))_{st}\frac{\ell_i}{h}$$

by the great orthogonality theorem

(8) $$\hat{P}^i f_s^j = \sum_m\sum_t f_t^j\delta_{ij}\ \ \delta_{ms}\ \ \delta_{mt}$$

(9) $$\hat{P}^i f_s^j = \sum_m f_m^j\ \ \delta_{ij}\ \ \delta_{ms} = f_s^j\ \ \delta_{ij}$$

Thus $\hat{P}^i f_s^i = f_s^i$ and $\hat{P}^i f_s^j = 0,\ i \neq j$ as required; and $\hat{P}^i$ operating on any function will give us either a function which transforms as the ith irreducible representation or will give us zero (if c_i in the expansion of the general function g is zero).

As an example of this operation, let us look at the application of symmetry projection operators to the a.o. ϕ_1 (here ϕ_1 is the "general function").

The a.o. can be written as the following linear combination of SALC's:

(10) $$\phi_1 = \left(\sqrt{3}/3\right)a_2'' + \left(\sqrt{6}/3\right)e_a''$$

The projection $\hat{P}^{a_1''} = (1/12)\ (\hat{E} + \hat{C}_3 + \hat{C}_3^2 + \hat{C}_2' + \hat{C}_2'' + \hat{C}_2''' - \hat{\sigma}_h - \hat{S}_3 - \hat{S}_3^2 - \hat{\sigma}_v' - \hat{\sigma}_v'' - \hat{\sigma}_v''')$ on ϕ_1 gives:

$$\hat{P}^{a_1''}\phi_1 = (1/12)\ (\phi_1 + \phi_5 + \phi_9 - \phi_1 - \phi_5 - \phi_9 + \phi_1 + \phi_5 + \phi_9 - \phi_1 - \phi_5 - \phi_9)$$

$= 0$ as required!

The projection $\hat{P}^{a_2''} = (1/12)\ (\hat{E} + \hat{C}_3 + \hat{C}_3^2 + \hat{C}_2' + \hat{C}_2'' + \hat{C}_2''' - \hat{\sigma}_h - \hat{S}_3 - \hat{S}_3^2 - \hat{\sigma}_v' - \hat{\sigma}_v'' - \hat{\sigma}_v''')$ on ϕ_1 gives:

$$\hat{P}^{a_2''}\phi_1 = (1/12)\ (\phi_1 + \phi_5 + \phi_9 + \phi_1 + \phi_5 + \phi_9 + \phi_1 + \phi_5 + \phi_9 + \phi_1 + \phi_5 + \phi_9)$$

$= (1/3)(\phi_1 + \phi_5 + \phi_9) = (\sqrt{3}/3)\ a_2''$ as required!

And the projection $\hat{P}^{e''} = (2/12)\ (2\hat{E} - \hat{C}_3 - \hat{C}_3^2 - 2\hat{\sigma}_h + \hat{S}_3 + \hat{S}_3^2)$ on ϕ_1 gives:

$$\hat{P}^{e''}\phi_1 = (2/12)\ (2\phi_1 - \phi_5 - \phi_9 + 2\phi_1 - \phi_5 - \phi_9)$$

$= (1/3)\ (2\phi_1 - \phi_5 - \phi_9) = (\sqrt{6}/3)\ \ e''$ as required!

Thus we demonstrate that SALC's can be generated by applying symmetry projection operators to an a.o.

This procedure is very well defined in two instances: (1) when a given type of a.o. has only one SALC of a given symmetry and (2) when 1 is satisfied and we desire the SALC for a one-dimensional irreducible representation or a single component of a multi-dimensional irreducible representation. If (1) is not satisfied (e.g., the ϕ_2, ϕ_4, ϕ_6, ϕ_8, ϕ_{10}, ϕ_{12} a.o.'s—equivalent in the perinaphthenyl cation have two e″ irreducible representations), the SALC's must be determined by inspection of the actual matrices (not just the characters) for the symmetry operations. If (1) is satisfied and one desires additional SALC's for multidimensional representations, one may proceed in two ways.

The first method utilizes Abelian subgroups of the full symmetry group to generate projection operators. Thus for the D_{3h} group of perinaphthenyl cation we would try the C_{3h} Abelian subgroup.

Using the complex characters of e″ in C_{3h} we get the two projection operators:

$$\hat{P}^{e_+''} = (1/6)(\hat{E} + \varepsilon\hat{C}_3 + \varepsilon^*\hat{C}_3^2 - \hat{\sigma}_h - \varepsilon\hat{S} - \varepsilon^*\hat{S}_3^2)$$

$$\hat{P}^{e_-''} = (1/6)(\hat{E} + \varepsilon^*\hat{C}_3 + \varepsilon\hat{C}_3^2 - \hat{\sigma}_h - \varepsilon^*\hat{S} - \varepsilon\hat{S}_3^2)$$

Applying these projection operators to ϕ_1, one obtains:

$$e''_{+} = (1/6)(2\phi_1 + 2\varepsilon\phi_5 + 2\varepsilon^*\phi_9)$$

$$e''_{-} = (1/6)(2\phi_1 + 2\varepsilon^*\phi_5 + 2\varepsilon\phi_9)$$

with $\varepsilon = exp(2\pi i/3)$.

Using $\varepsilon + \varepsilon^* = -1$ and $(\varepsilon - \varepsilon^*)/i = \sqrt{3}$ *we can combine* e''_{+} *and* e''_{-} *to get real SALC's for the* e'' *irreducible representation:*

$$e''_{+} + e''_{-} = (1/3)(2\phi_1 - \phi_5 - \phi_9)$$

$$(1/i)(e''_{+} - e''_{-}) = (\sqrt{3}/3)(\phi_5 - \phi_9)$$

When properly normalized, these are just e''_a and e''_b on page 1.

A second method for obtaining components of multidimensional SALC's is to apply the D_{3h} symmetry projection operators to each of the equivalent a.o.'s in a set.

Applying $\hat{P}^{e''}$ *to* ϕ_5 *and* ϕ_9 *would get:*

$$\hat{P}^{e''}\phi_5 = (1/3)(2\phi_5 - \phi_9 - \phi_1)$$

$$\hat{P}^{e''}\phi_9 = (1/3)(2\phi_9 - \phi_1 - \phi_5)$$

These two SALC's plus e''_a are not linearly independent. However, one can take a linear combination of the two vectors above to get e''_b as on page 1. The foolproof (take note) method for producing a set or orthogonal (therefore linearly independent) functions from a non-orthogonal set is an application of the Schmidt orthogonalization procedure, which is the subject for another day!