Corrections to Cotton, p. 124

MH_6 example on pp. 123-4 is in error:

$$\hat{P}^{T_1}(\sigma_1) = 3\sigma_1 + (2\sigma_1 + 2\sigma_2 + 2\sigma_2) - (\sigma_1 + 2\sigma_2)$$
$$- (\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + 2\sigma_2)$$
$$= 4\sigma_1 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 \qquad ?$$

$$\hat{P}^{T_1}(\sigma_2) = 4\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$

This should read:

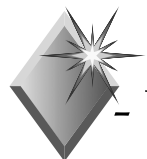| O	E	$8C_3$	$3C_2$ $(= C_4^2)$	$6C_4$	$6C_2$
T_1	3	0	–1	1	–1

$$\hat{P}^{T_1}(\sigma_1) = 3\sigma_1 + (-1)(\sigma_1 + 2\sigma_2)$$
$$+ (1)(2\sigma_1 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$
$$+ (-1)(2\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$
$$= 4(\sigma_1 - \sigma_2)$$

Symmetry-Adapted Linear Combinations

- ✿ We have examined many cases where sets of functions serve as bases for IRs.
- ✿ We need a prescription for how to construct such basis functions.
- ✿ We turn to the use of *projection operators* to construct *Symmetry-Adapted Linear Combinations* (*SALC*s)

Projection Operators - Why and How to Use Them

- ✿ For beginners, *Projection Operators* can seem formalistic and complicated - so we shall first try to understand how they come about.
- ✿ After becoming familiar with "how projection operators operate" we shall look at explicit formulas - then try to demystify them.
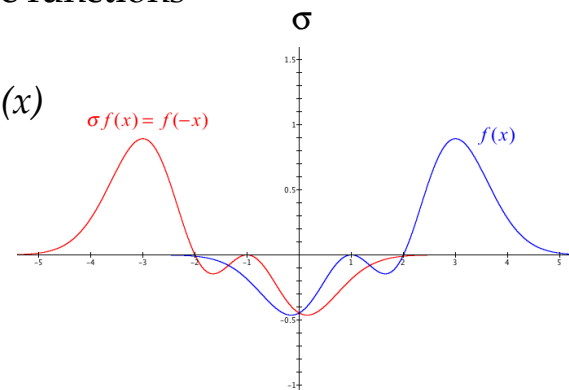
How do we get a "Recipe" for Symmetry Adapted Functions?

Consider the functions

$f(x)$,

$f(-x) = \sigma f_1(x)$

Finding the "Recipe" …

$f_1(x) = f_2(-x)$ or $f_2(x) = \sigma f_1(x)$

$g(x) = (f_1(x) + f_2(x))/2$ - an even function

$h(x) = (f_1(x) - f_2(x))/2$ - an odd function

$g(x)$ and $h(x)$ can be obtained <u>using the</u> <u>symmetry operators of the C_s group:</u>
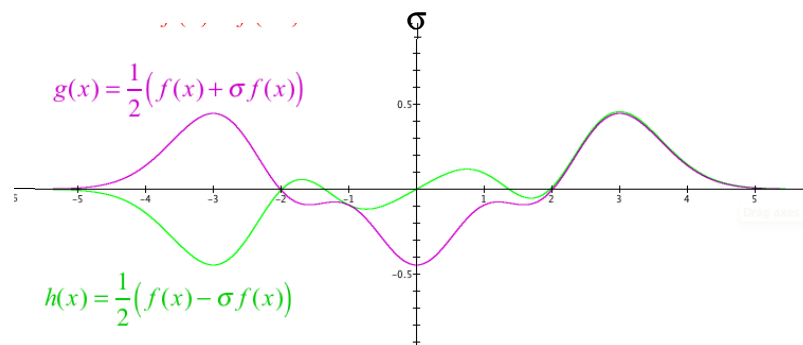
$g(x) = (1/2)[(1)\mathbf{E} + (1)\sigma]\, f_1(x)$

$h(x) = (1/2)[(1)\mathbf{E} + (-1)\sigma]\, f_1(x)$

"Symmetry Adapted" Results

$g(x)$ and $h(x)$ are respectively even and odd.

$$g(x) = \frac{1}{2}\left(f(x) + \sigma f(x)\right)$$

$$h(x) = \frac{1}{2}\left(f(x) - \sigma f(x)\right)$$

Intuitive Approach

✿ Let's consider some examples that give us an idea of how to "build-in" symmetry into our basis-functions:

- the O-H stretching vibrations of H_2O
- the O-H σ bonding orbitals of H_2O
- the π orbitals of the formate (HCO_2^-) ion
- the Pt-Cl stretching vibrations of $PtCl_4^{2-}$
- the π orbitals of the cyclopentadienyl ion, $C_5H_5^-$

Rigorous Approach: Projection Operators

✿ The method used to handle previous examples point to a more general prescription of building SALCs

✿ For nondegenerate IRs, the formula for a projection operator for the jth IR can be guessed (try it out on earlier examples):

$$P^j = \frac{l_j}{h}\sum_R \chi^*(R)^j \hat{R}$$

✿ For degenerate IRs, more care is needed

Slide 1

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Slide 2

Full Projection Operators

✿ For degenerate representations, to get SALCs directly, we use the so-called <u>full</u> projection operators:

$$P_{st}^j = \frac{l_j}{h} \sum_R [\Gamma(R)_{st}^j]^* R$$

"diagonal" operators ($s = t$) are most important:

$$P_{tt}^j = \frac{l_j}{h} \sum_R [\Gamma(R)_{tt}^j]^* R$$

✿ To construct full projection operators, we need the complete matrices for the representation, not just the characters.

Slide 3

Incomplete Projection Operators from Full Operators

Even for degenerate representations, "incomplete" projection operators are useful. These are obtained by summing the "complete" projection operators over the diagonal:

$$P^j = \sum_t P_{tt}^j = \frac{l_j}{h} \sum_t \sum_R [\Gamma(R)_{tt}^j]^* \hat{R}$$

$$= \frac{l_j}{h} \sum_R \left\{ \sum_t [\Gamma(R)_{tt}^j]^* \right\} \hat{R}$$

$$P^j = \frac{l_j}{h} \sum_R \chi^*(R)^j \hat{R}$$

Slide 4

Two Examples revisited

✿ Projection operators for two cases that were not obvious with the "intuition":
  • the Pt-Cl stretching vibrations of $PtCl_4^{2-}$
  • the π orbitals of the cyclopentadienyl ion, $C_5H_5^-$

✿ Another example:
  • SALCs for hydrogen 1s orbs of NH_3

D_{4h} character table

D_{4h}	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

D_{5h} character table

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2'	1	1	1	−1	1	1	1	−1	R_z	
E_1'	2	$2\cos 2\pi/5$	$2\cos 4\pi/5$	0	2	$2\cos 2\pi/5$	$2\cos 4\pi/5$	0	(x, y)	xy
E_2'	2	$2\cos 4\pi/5$	$2\cos 2\pi/5$	0	2	$2\cos 4\pi/5$	$2\cos 2\pi/5$	0		(x^2+y^2, z^2)
A_1''	1	1	1	1	−1	−1	−1	−1		
A_2''	1	1	1	−1	−1	−1	−1	1	z	
E_1''	2	$2\cos 2\pi/5$	$2\cos 4\pi/5$	0	−2	$-2\cos 2\pi/5$	$-2\cos 4\pi/5$	0	(R_x, R_y)	(xz, yz)
E_2''	2	$2\cos 4\pi/5$	$2\cos 2\pi/5$	0	−2	$-2\cos 4\pi/5$	$-2\cos 2\pi/5$	0		

Example, NH₃

Example, NH_3
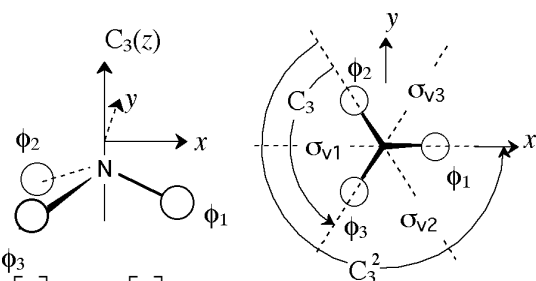
Basis Functions: $\hat{\mathbf{x}} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ $\hat{\mathbf{y}} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$ (same as p_x and p_y)

$E: \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ $C_3: \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$ $C_3^2: \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$

$\sigma_{v1}: \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ $\sigma_{v2}: \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$ $\sigma_{v3}: \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$