

Corrections to Cotton, p. 124

MH₆ example on pp. 123-4 is in error:

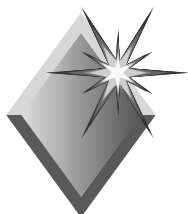
$$\begin{aligned}\hat{P}^{T_1}(\sigma_1) &= 3\sigma_1 + (2\sigma_1 + 2\sigma_2 + 2\sigma_2) - (\sigma_1 + 2\sigma_2) \\ &\quad - (\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + 2\sigma_2) \\ &= 4\sigma_1 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6\end{aligned}\quad ?$$

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

This should read:

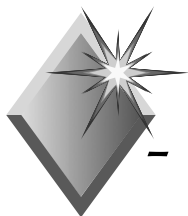
$$\begin{aligned}\hat{P}^{T_1}(\sigma_1) &= 3\sigma_1 + (-1)(\sigma_1 + 2\sigma_2) \\ &\quad + (1)(2\sigma_1 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \\ &\quad + (-1)(2\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \\ &= 4(\sigma_1 - \sigma_2)\end{aligned}$$

<i>O</i>	<i>E</i>	$8C_3$	$3C_2$ ($= C_4^2$)	$6C_4$	$6C_2$
<i>T₁</i>	3	0	-1	1	-1



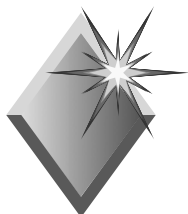
Symmetry-Adapted Linear Combinations

- ✿ 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 (SALCs)*



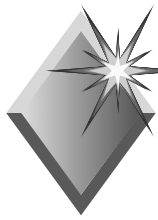
Projection Operators *- Why and How to Use Them*

- ✿ 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.



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^-

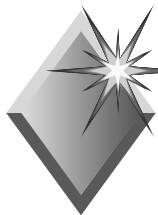
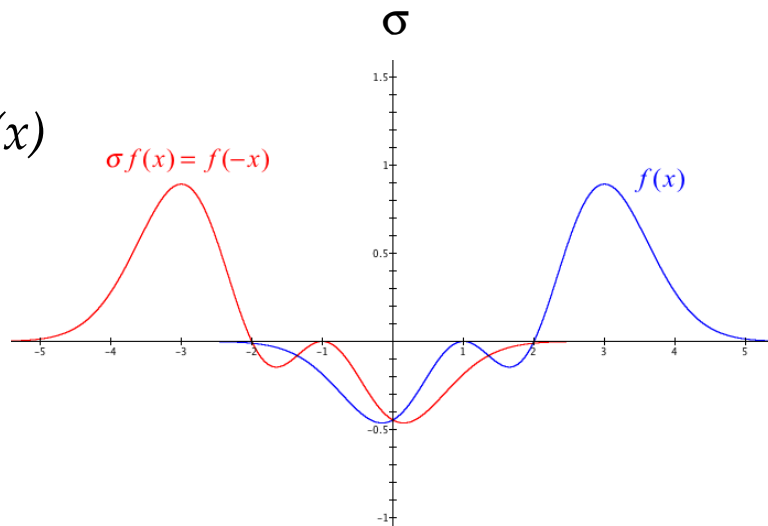


How do we get a "Recipe" for Symmetry Adapted Functions?

Consider the functions

$$f(x),$$

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



Finding the "Recipe" ...

$$f_1(x) = f_2(-x) \text{ or } f_2(x) = \sigma f_1(x)$$

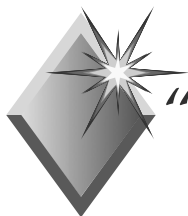
$$g(x) = (f_1(x) + f_2(x))/2 - \text{an even function}$$

$$h(x) = (f_1(x) - f_2(x))/2 - \text{an odd function}$$

$g(x)$ and $h(x)$ can be obtained using the symmetry operators of the C_s group:

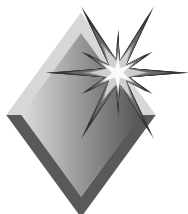
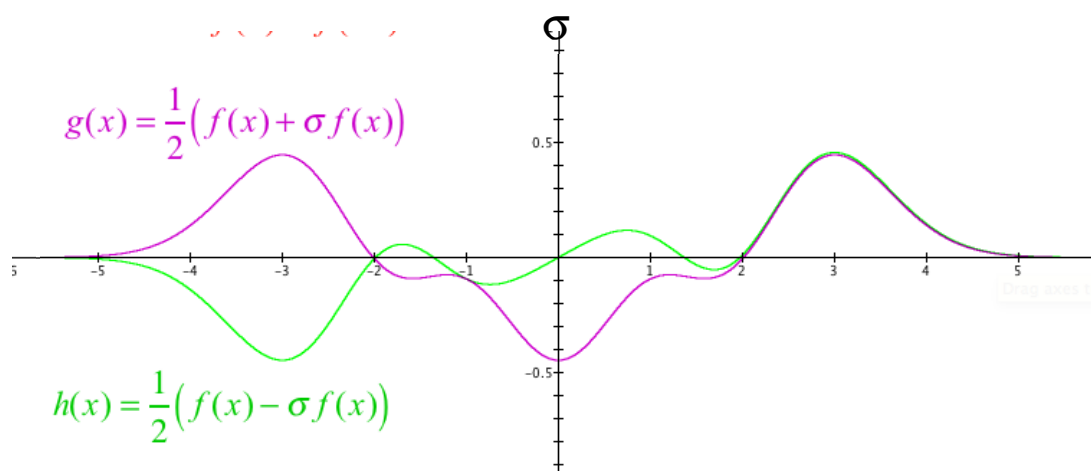
$$g(x) = (1/2)[(1)E + (1)\sigma] f_1(x)$$

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



"Symmetry Adapted" Results

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

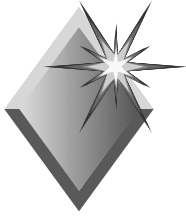


Rigorous Approach: Projection Operators

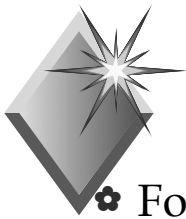
- ✿ The method used to handle previous examples point to a more general prescription of building SALCs
- ✿ For nondegenerate IRs, the formula for a projection operator for the j^{th} IR can be guessed (try it out on earlier examples):

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

- ✿ For degenerate IRs, more care is needed



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	



Full Projection Operators

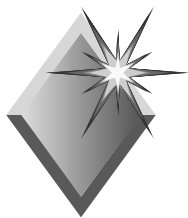
- For degenerate representations, to get SALCs directly, we use the so-called full projection operators:

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

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

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

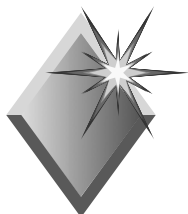
- To construct full projection operators, we need the complete matrices for the representation, not just the characters.



Incomplete Projection Operators from Full Operators

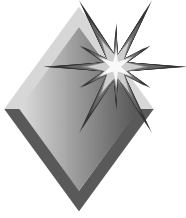
Even for degenerate representations, “incomplete” projection operators are useful. These are obtained by summing the “complete” projection operators over the diagonal:

$$\begin{aligned} P^j &= \sum_t P_{tt}^j = \frac{l_j}{h} \sum_t \sum_R [\Gamma(R)_{tt}^j]^* \hat{R} \\ &= \frac{l_j}{h} \sum_R \left\{ \sum_t [\Gamma(R)_{tt}^j]^* \right\} \hat{R} \\ P^j &= \frac{l_j}{h} \sum_R \chi^*(R)^j \hat{R} \end{aligned}$$

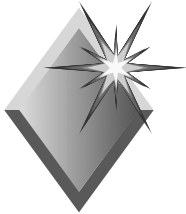


Two Examples revisited

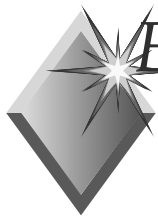
- ❖ Projection operators for two cases that were not obvious with the “intuition”:
 - the Pt-Cl stretching vibrations of PtCl_4^{2-}
 - the π orbitals of the cyclopentadienyl ion, C_5H_5^-
- ❖ Another example:
 - SALCs for hydrogen 1s orbs of NH_3



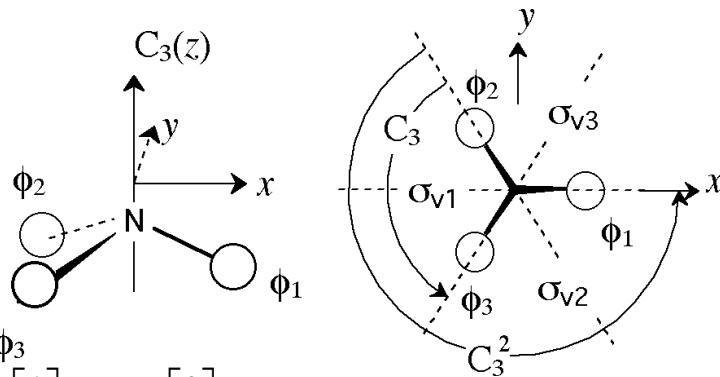
D_{4h}	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		$x^2 - y^2$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		(xz, yz)
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	z	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
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}	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	R_z	$x^2 + y^2, z^2$	
A_2'	1	1	1	-1	1	1	1	-1		xy	
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)	
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	z		
A_2''	1	1	1	-1	-1	-1	-1	1			
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, NH_3



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

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

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