TPC 30 jan 2018

Tuesday, January 30, 2018 2:26 PM

- Consider a molecule of ammonia and a basis set of atomic orbitals composed by the the sp^3 hybrids of the N atom valence shell, as schematically represented in Fig. 1. We indicate with sp^3_z the orbital directed along the c_3 symmetry axis of the molecule and with sp^3_A, sp^3_B and sp^3_C the other three orbitals. Construct a *matrix representation* of the symmetry group of ammonia with these atomic orbitals, then compute the *characters* of the representation.

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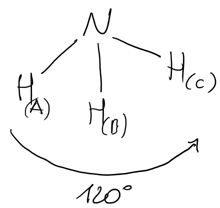
$$\begin{array}{c} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \begin{array}{l} sp^3_z \\ sp^3_A \\ sp^3_B \\ sp^3_C \end{array}$$

E

$\chi(E)=4$

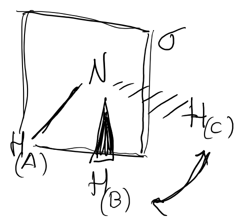
$$\begin{array}{cccc} \tilde{sp}^3_z & \tilde{sp}^3_A & \tilde{sp}^3_B & \tilde{sp}^3_C \end{array}$$
$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix} \begin{array}{l} sp^3_z \\ sp^3_A \\ sp^3_B \\ sp^3_C \end{array}$$

$\chi(C_3)=1$ C_3



$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{array}{l} sp^3_z \\ sp^3_A \\ sp^3_B \\ sp^3_C \end{array}$$

σ $\chi(\sigma)=2$



- We define a symmetry–adapted linear combination of the atomic orbitals defined above, by performing the unitary transformation

$$\phi^N_1 = sp^3_z \tag{1}$$
$$\phi^N_2 = sp^3_A + sp^3_B + sp^3_C \tag{2}$$
$$\phi^N_3 = 2\, sp^3_A - sp^3_B - sp^3_C \tag{3}$$
$$\phi^N_4 = sp^3_B - sp^3_C \tag{4}$$

Construct the matrix representation of the symmetry group with this new basis and check that the characters are left unchanged by the transformation. Now inspect the matrix representation: explain why it is in an *irreducible form* and check what type of *irreducible representations* ("irreps") are spanned by the orbitals.

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E

$$\begin{bmatrix} \boxed{1} & 0 & 0 & 0 \\ 0 & \boxed{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(E)=4$

$$C_3 \quad \left\{ \begin{array}{l} sp^3_A \to sp^3_B \\ sp^3_B \to sp^3_C \\ sp^3_C \to sp^3_A \\ sp^3_z \to sp^3_z \end{array} \right.$$

$$\phi^N_1 \to \phi^N_1$$

$$\phi^N_2 \to sp^3_B + sp^3_C + sp^3_A = \phi^N_2$$

$$\phi^N_3 \to 2sp^3_B - sp^3_C - sp^3_A = -sp^3_A + 2sp^3_B - sp^3_C$$

$$\phi^N_4 \to sp^3_C - sp^3_A = -sp^3_A + sp^3_C$$

$$\tilde{\phi}^N_3 = -sp^3_A + 2sp^3_B - sp^3_C$$

$$\phi^N_3 = 2sp^3_A - sp^3_B - sp^3_C$$

$$\phi^N_4 = sp^3_B - sp^3_C$$

$$\tilde{\phi}^N_3 = -\frac{1}{2}\phi^N_3 + \frac{3}{2}\phi^N_4$$

$$\tilde{\phi}^N_4 = -sp^3_A + sp^3_C = -\frac{1}{2}\phi^N_3 - \frac{1}{2}\phi^N_4$$

$$\begin{bmatrix} \boxed{1} & 0 & 0 & 0 \\ \end{bmatrix}$$

$$= -sp_n^3 + sp_c^3$$

$$\begin{bmatrix} \boxed{1} & 0 & 0 & 0 \\ 0 & \boxed{1} & 0 & 0 \\ 0 & 0 & -1/2 & +3/2 \\ 0 & 0 & -1/2 & -1/2 \end{bmatrix} \qquad \chi(C_3) = 1$$

σ

$$\phi_1^N \to \phi_1^N$$
$$\phi_2^N \to \phi_2^N$$
$$\phi_3^N \to \phi_3^N$$
$$\phi_4^N \to -\phi_4^N$$

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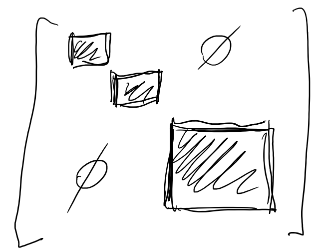
$$\begin{bmatrix} \boxed{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \qquad \chi(\sigma) = 2$$

common block diagonal structure



- Now compute the irreps spanned by the orbitals by projecting onto the irreps characters (so–called "representation reduction") and check that the results agree with the block–diagonal structure of the matrix representation.

E	C_3	σ
4	1	2

Table 5.5 The C_{3v} character table

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0

A_1) $\frac{1}{6}(4\times 1 + 2\times 1\times 1 + 3\times 2\times 1) =$

$$= \frac{1}{6}(4+2+6) = \frac{1}{6}\cdot 12 = 2$$

A_2) $\frac{1}{6}(4\times 1 + 2\times 1\times 1 + 3\times 2\times(-1)) =$

$$= \frac{1}{6}(4+2-6) = 0$$

E) $\frac{1}{6}(4\times 2 + 2\times 1\times(-1) + 3\times 2\times 0) =$

$$= \frac{1}{6}(8-2+0) = \frac{1}{6}\cdot 6 = 1$$

$$\langle \varphi_i | \mathcal{H} | \varphi_j \rangle = 0$$

$$\underbrace{A_1 \quad A_1 \quad E}$$