February 20, 2007

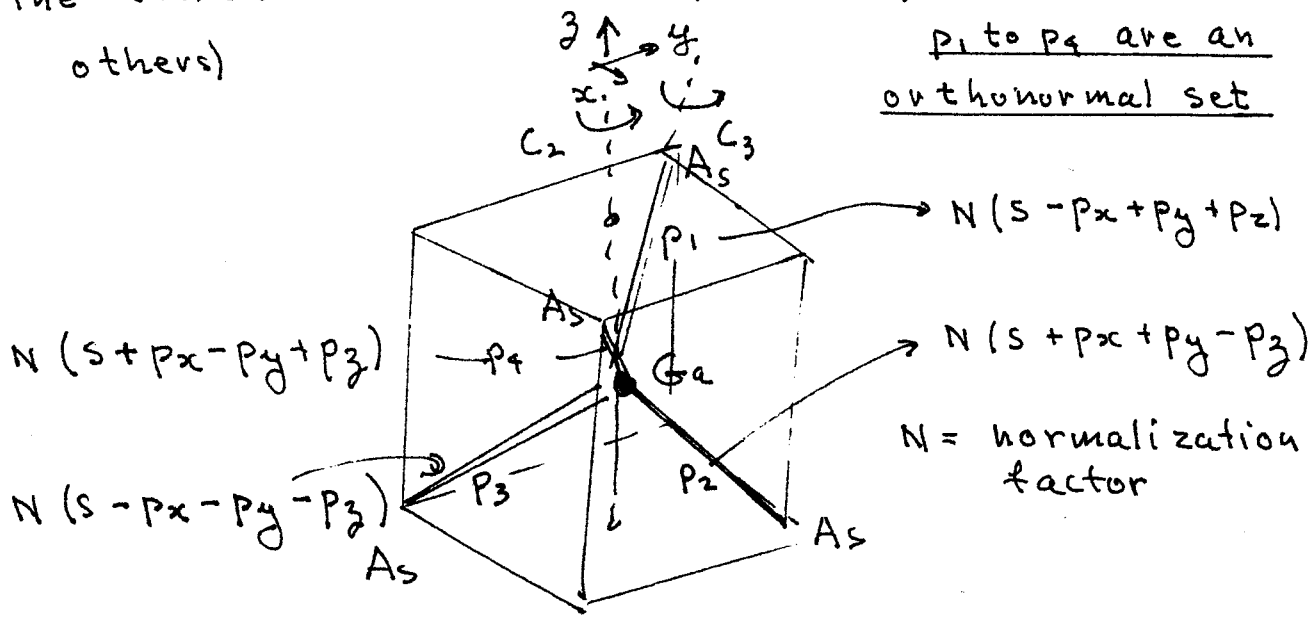
LECTURE #14

Symmetry and Super Position States
(Tetrahedral 4-Fold and Planar 3-Fold Super Positions)

Character Analysis of Tetrahedral Bonding and Vibrational Oscillations (comments on Phonons)

(Burns has a similar example of $s-p^3$ hybridyzation)

The tetrahedral Bond - one possibility (There are others)



p_1 to p_4 are an orthonormal set

N = normalization factor

Symmetries of the Tetrahedron

(Reference Kettle, Symmetry and Structure)

Two different Things!

Note this notation!

	E	$4C_3$	$4C_3^2$	$3C_2$	basis fns
A	1	1	1	1	$x^2+y^2+z^2$
E	1	ϵ	ϵ^*	1	
	1	ϵ^*	ϵ	1	
T	3	0	0	-1	$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ $\begin{pmatrix} xy \\ yz \\ zx \end{pmatrix}$
Γ	4	1	1	0	

$\epsilon = e^{i2\pi/3}$

1 bond does not change position

0 ← all bonds change position

For The Tetrahedron

4 bonds do not change positions

$\therefore \Gamma = T \oplus A$ - Thus the tetrahedral bond consists of a T basis and an A basis.

The A - basis has the character of the s - state

The T - the character of either $\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}$ or 3 of the 5 - d - states

Gatts

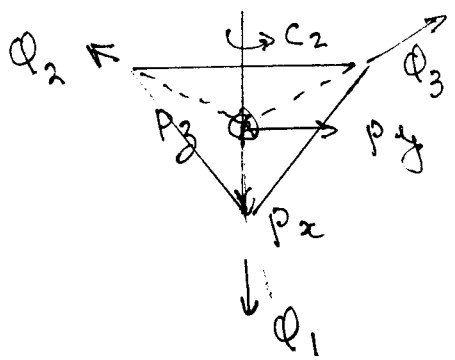
Si

$p_1 \cdots p_4$ above can be found by projection - however they are rather obvious if one realizes they have the vector character of F

s is necessary for the orthonormal character.

A more easily solvable problem Quartz, Ethane (1)

D_3	E	$2C_3$	$3C_2$	basis
A_1 (M_1)	1	1	1	s
A_2 (M_2)	1	1	-1	p_z (out of plane)
E (M_3)	2	-1	0	$\begin{pmatrix} p_x \\ p_y \end{pmatrix}$



Under C_2 $p_x \to p_x$

$p_y \to -p_y$

$$\begin{matrix} p'_x \\ p'_y \end{matrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix}$$

↳ Trace = 0

Under C_3

$$\begin{matrix} p'_x \\ p'_y \end{matrix} = \begin{pmatrix} -1/2, & -\sqrt{3}/2 \\ \sqrt{3}/2, & -1/2 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix} \begin{cases} p_x \to -\frac{\sqrt{3}}{2} p_y - \frac{1}{2} p_x \\ p_y \to +\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y \end{cases}$$

↳ Trace = -1 (det = 1) (unitary)

Note the three bonds $\varphi_1, \varphi_2, \varphi_3$ transform with matricies having Traces

	E	$2C_3$	$3C_2$	
Γ	3	0	1	← remains the same

↑ All three remain the same

↳ all three change

Note $\Gamma = \Gamma_1 + \Gamma_3$ → so the bonds must be a linear combination of s p_x and p_y s necessary for orthogonality

p_x and p_y are <u>orthonormal</u> angular parts of the wave functions (spherical harmonics)

In this case we can use the vector character of (2) p_x and p_y to obtain the bonds

$$Q_1 = A\, p_x + B\, s \qquad \langle Q_1 | Q_1 \rangle = 1 \quad (A^2 + B^2 = 1)$$

$$Q_2 = A\Big(\underbrace{-\tfrac{p_x}{2} + -\tfrac{\sqrt{3}}{2} p_y}_{\text{this is orthogonal}}\Big) + B\, s \qquad (A^2 + B^2 = 1)$$

$$Q_3 = A\left(p_y \tfrac{\sqrt{3}}{2} - \tfrac{p_x}{2}\right) + B\, s \qquad (A^2 + B^2 = 1)$$

Note have also used p_x orthogonal to p_y and p_y orthogonal to s.

If they are to be orthonormal as well

$$\langle Q_1 | Q_2 \rangle = 0 \qquad -\frac{A^2}{2} + B^2 = 0 \Rightarrow \frac{3}{2} A^2 = 1$$

$$A = \sqrt{2/3}$$

$$B = \sqrt{1/3}$$

Reference (Burns

What if the geometry is not so clear! How do we formally find the linear combinations we know the bonds are linear combinations of p_x, p_y and s

Let
$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \begin{pmatrix} a, & b, & c \\ d & e & f \\ g & h & i \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}$$

Two ways to proceed,

a) Apply symmetry constraints

b) Use "projection operators" (will do that later)

a) C_3 $\quad Q_1 \to Q_2 \to Q_3$

s does not change (spherically symmetric)

thus $a = d = g$

so only have to deal with $\begin{pmatrix} b & c \\ e & f \\ h & i \end{pmatrix}$

For convenience change basis from p_x and p_y to $p_1 = p_x$ and $\left(p_y \frac{\sqrt{3}}{2} - p_x/2\right) = p_2$

$$\begin{matrix} Q_1 \\ Q_2 \\ Q_3 \end{matrix} = \begin{pmatrix} as + b' p_1 + c' p_2 \\ as + e' p_1 + f' p_2 \\ as + h' p_1 + i' p_2 \end{pmatrix}$$

(forget the primes)

Under C_3

$$p_1 \to -p_2 - p_1 = p_x/2 - \frac{\sqrt{3}}{2} p_y$$

$$p_2 \to p_1$$

Forget the o-terms for this since we know they are completely symmetric

Thus $Q_1 \to b(-p_2 - p_1) + c p_1$

$\downarrow$

$Q_2 = e p_1 + f p_2$ (Thus $e = -b + c$; $[f = -b]$

$Q_2 \to e(-p_2 - p_1) + f p_1$

$\downarrow$

$Q_3 = h(p_1) + i p_2$ (Thus $h = f - e$; $[i = -e]$

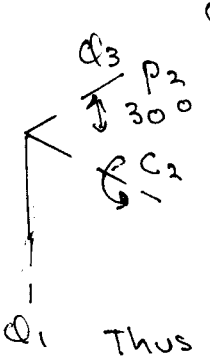
$Q_3 \to h(-p_2 - p_1) + i p_1$

$\downarrow$

$Q_1 = b p_1 + c p_2$ (Thus $b = -h + i$; $c = -h$

Under C_2

$Q_3 \to Q_1 \quad p_2 \to p_1$



$Q_3 \to h p_2 + i p_1$

$\downarrow$

$Q_1 = b p_1 + c p_2$

[or $h = 0$]

[gives $h = 0$]

(Thus $h = c$; $b = i$

$= 0$

Thus bonds are of form

$$Q_1 = as + \overset{\overset{i}{\shortparallel}}{b} p_1 - i$$

$$Q_2 = as + e p_1 + f p_2 \qquad f = -b = -i$$

$$Q_3 = as + i p_2$$

or

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = a \begin{pmatrix} s \\ s \\ s \end{pmatrix} + \begin{pmatrix} b p_1 \\ -b p_1 - b p_2 \\ b p_2 \end{pmatrix}$$

Note $p_1 + p_2 = p_y \frac{\sqrt{3}}{2} + \frac{1}{2} p_x$ which is normalized

thus as before $a^2 + b^2 = 1 \qquad a^2 - b^2/2 = 0 \leftarrow$ orthogonality

As discussed in class

a) prove $J_x J_y - J_y J_x = i\hbar J_z$

b) $\bar{p}_{op} = \hbar/i \, \nabla$

c) $H = \bar{p}_{op} \cdot \bar{p}_{op}/2m + V(x,y,z)$ ← potential

d) Schroedinger $H\psi = i\hbar \frac{\partial \psi}{\partial t}$

(use plane waves to argue this)

If E is an energy eigenvalue $H(\psi) = E(\psi)$

$\psi = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_n \end{pmatrix}$ n-fold degenerate, then ψ is a basis

for the symmetry group of H (what is meant by this?). Let $\psi' = R\psi = M(\psi)$ matrix representation of R

↳ symmetry operation

Thus

$$RH\psi = E R\psi \quad \text{or} \quad (RHR^{-1})R\psi = ER\psi$$

↑ diagonal constant

a) $RHR^{-1} = H$ (as def of symmetry group of H.

Assuming the R's and I form a group)

↳ unit operation

b) if ψ is an eigen function then $R\psi$ is an eigen function. Thus ψ forms a basis for a rep. of the group $R\psi = M\psi$

matrix can be used to describe what R does

Note $R_1 R_2 \psi = R_1(M_2 \psi) = M_1 M_2 \psi = R\psi$

Thus the M's form a valid representation

c) If part of the basis space can be made independent of the rest (it breaks up into 2 or more parts (i.e. $M(\psi) = \begin{pmatrix} (\;) & 0 \\ 0 & (\;) \end{pmatrix} (\psi)$ for all M) then we call it reducible

d) The character tables give the only irreducible representations