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-p² hybridization)

The tetrahedral Bond - one possibility (There are others)

\[ p_1 \text{ to } p_4 \text{ are an orthonormal set} \]

\[ N(S - p_x + p_y + p_z) \]

\[ N(S + p_x - p_y - p_z) \]

\[ N(S + p_x + p_y - p_z) \]

\[ N = \text{normalization factor} \]

Symmetries of the Tetrahedron

(Reference Kettle, Symmetry and Structure)

Two Different Things

A

<table>
<thead>
<tr>
<th>E</th>
<th>C₃</th>
<th>C₃²</th>
<th>3C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Note this notation! \{ E, C₃, C₃² \}

T

<table>
<thead>
<tr>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x, y)</td>
<td>(x, 2y)</td>
<td>(y, -2x)</td>
<td>(2x, y)</td>
<td></td>
</tr>
</tbody>
</table>

For the Tetrahedron:

1 bond does not change position

4 bonds change positions

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 \( (\frac{p_x}{p_z}) \) or 3 of the S-d-states \( S_i \).

\( p_1 \text{ to } p_4 \) 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  

\[ D_3 \quad E \quad 2C_3 \quad 3C_2 \quad \text{basis} \]

| \( A_1 (M_1) \) | 1 | 1 | 1 | \( S \) |
| \( A_2 (M_2) \) | 1 | 1 | -1 | \( p_y \) (out of plane) |
| \( E (M_3) \) | 2 | -1 | 0 | \( \begin{pmatrix} p_x \\ p_y \end{pmatrix} \) |

\[ \Phi_2 \quad \Phi_3 \quad \Phi_1 \]

Under \( C_2 \)  
\[ p_x \rightarrow p_x \]  
\[ p_y \rightarrow -p_y \]  
\[ p'_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix} \]  
\[ \text{Trace} = 0 \]

Under \( C_3 \)  
\[ \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix} \]  
\[ p_x \rightarrow -\sqrt{3}/2 p_y - 1/2 p_x \]  
\[ p_y \rightarrow +\sqrt{3}/2 p_x - 1/2 p_y \]  
\[ \text{Trace} = -1 \ (\text{det} = 1) \ (\text{unitary}) \]

Note the three bonds \( \Phi_1, \Phi_2, \Phi_3 \) transform with matrices having traces

\[ E \quad 2C_3 \quad 3C_2 \]

\[ \Pi \quad 3 \quad 0 \quad 1 \quad \text{remains the same} \]

\[ \text{All three} \quad \text{all three} \quad \text{remain the change same} \]

Note \( \Pi = \Pi_1 + \Pi_3 \rightarrow \) 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 orthonormal angular parts of the wave functions (spherical harmonics)
In this case we can use the vector character of \( p_x \) and \( p_y \) to obtain the bonds

\[
Q_1 = A \, p_x + B \, s \quad \Rightarrow \quad \langle Q_1, Q_1 \rangle = 1 \quad (A^2 + B^2 = 1)
\]

\[
Q_2 = A \left(- \frac{p_x}{2} - \frac{\sqrt{3} \, p_y}{2}\right) + B \, s \quad (A^2 + B^2 = 1)
\]

This is orthogonal

\[
Q_3 = A \left( p_y \frac{\sqrt{3}}{2} - p_x \right) + B \, s \quad (A^2 + B^2 = 1)
\]

Note have also used \( p_x \) orthogonal to \( p_y \)
and \( p_y \) orthogonal to \( s \).

If they are to be orthonormal as well

\[
\langle Q_1, Q_2 \rangle = 0 \quad - \frac{A^2}{2} + B^2 = 0 \quad \Rightarrow \quad \frac{3}{2} A^2 = 1
\]

\[
A = \frac{\sqrt{2}}{3} \quad B = \frac{1}{3}
\]

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

\[
\begin{pmatrix}
Q_1 \\
Q_2 \\
Q_3
\end{pmatrix} =
\begin{pmatrix}
a & b & c \\
c & e & f \\
h & i & j
\end{pmatrix}
\begin{pmatrix}
p_x \\
p_y \\
p_z
\end{pmatrix}
\]

Two ways to proceed,

a) Apply symmetry constraints
b) Use "projection operators" (will do that later)

a) \( C_3 \) \( Q_1 \rightarrow Q_2 \rightarrow Q_3 \)

\( s \) does not change (spherically symmetric)

Thus \( a = d = g \)
Thus as before
\[ \mathbf{a} \cdot \mathbf{b} = \mathbf{c} \cdot \mathbf{d} \]

Thus bounds are of form
\[ \mathbf{b} = \mathbf{a} \pm \mathbf{c} \]

(Thus \( \mathbf{b} = -\mathbf{a} \))

Note \( \mathbf{b} \) \( \mathbf{c} \) \( \mathbf{d} \) \( \mathbf{a} \) normalised

For (a) change basis from \( \mathbf{p} \) and \( \mathbf{q} \) such that

\[ \begin{align*}
\mathbf{e} &= \mathbf{a} + \mathbf{b} + \mathbf{c} + \mathbf{d} \\
\mathbf{f} &= \mathbf{a} + \mathbf{b} + \mathbf{c} \\
\mathbf{g} &= \mathbf{a} + \mathbf{b} + \mathbf{d} \\
\mathbf{h} &= \mathbf{a} + \mathbf{c} + \mathbf{d} \\
\mathbf{i} &= \mathbf{b} + \mathbf{c} + \mathbf{d} \\
\mathbf{j} &= \mathbf{a} + \mathbf{b} + \mathbf{c} + \mathbf{d} - \mathbf{a} \\
\mathbf{k} &= \mathbf{a} + \mathbf{b} + \mathbf{c} + \mathbf{d} - \mathbf{b} \\
\mathbf{l} &= \mathbf{a} + \mathbf{b} + \mathbf{c} + \mathbf{d} - \mathbf{c} \\
\mathbf{m} &= \mathbf{a} + \mathbf{b} + \mathbf{c} + \mathbf{d} - \mathbf{d} \\
\end{align*} \]
As discussed in class

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

b) $\tilde{P}_{\text{op}} = t_x v$

c) $H = \tilde{P}_{\text{op}} \cdot \tilde{P}_{\text{op}} + V(x, y, z)$

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

(Use plane waves to argue this)

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

$\psi = (\psi_1) \ n\text{-fold degenerate}$, then $\psi$ is a basis

for the symmetry group of $H$ (what is meant by this?)

Let $\psi' = R \psi = H(\psi')$ matrix representation

Thus $R H \psi = E R \psi$ or $(R H R^{-1}) \psi = E \psi$

da) $R H R^{-1} = H$ (as $R$ is a symmetry of the group)

b) if $\psi$ is an eigenfunction then $R \psi$ is an eigenfunction. Thus $\psi$ forms a basis for a rep. of the group $R \psi = \tilde{R} \psi$

Matrix can be used to describe what $R$ does

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

Thus the $R$'s form a valid representation

If part of the basis space can be made

-independent of the rest (it breaks up into 2 or more parts (i.e. $M(\psi) = (1 \ 0) \psi \neq \psi$ for all $M$) then we call it reducible

The character tables give the only irreducible representations