

## TOM and TEV:

TOM: molecular orbital theory

TEV: valence bond theory.

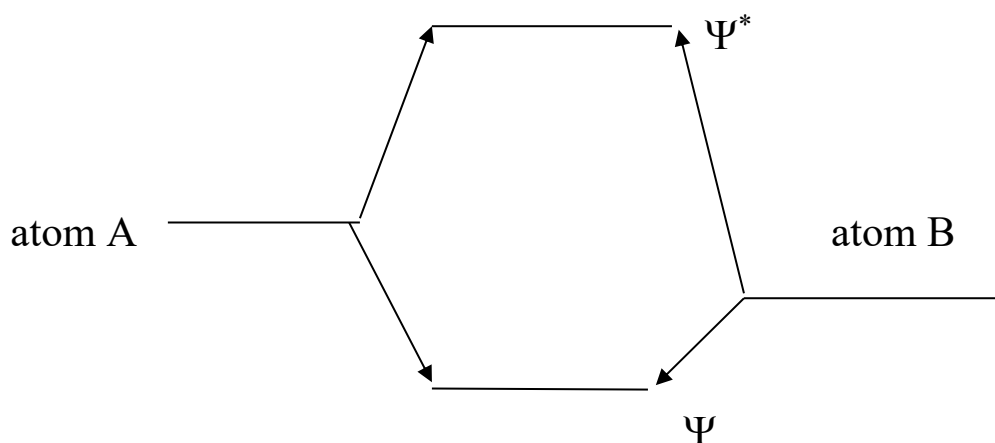
Hybridization: combination of  $\Psi$  the central atom.

Let us recall that each orbital is described by a wave function or  $\Psi$ .

Definition of orbital: the wave function ( $\Psi$ ) defines the probability of finding the  $e^-$  in a given region of space, while the orbital is the representation of each point in space;  $\Psi$  it can be represented in polar or Cartesian coordinates.

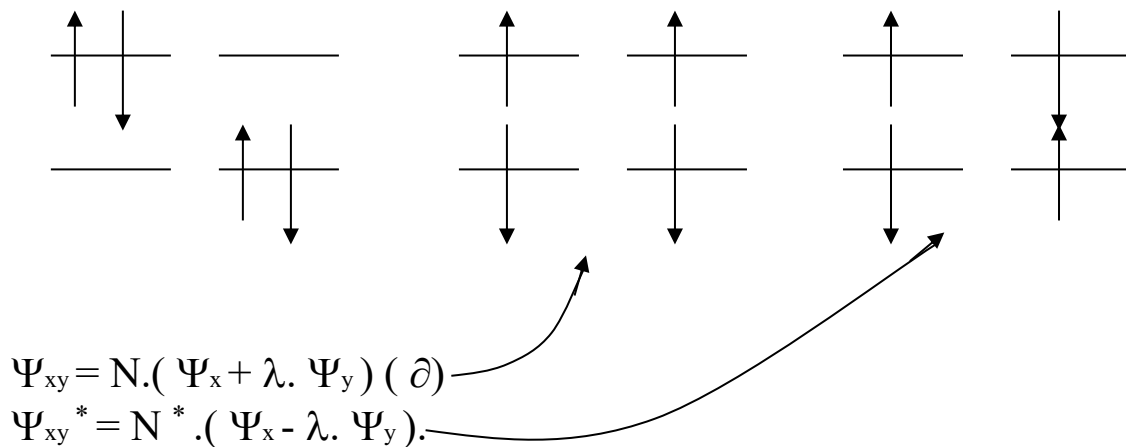
We are talking about **wave functions applied to bond theory**; As you may already know, each  $\Psi_{\text{om}}$  contains those  $\Psi$  of each atom or  $\Psi$  involved in the bond (TOM) whereas in TEV everything revolves around the central atom and its hybridization (which must be geometric, that is, linear, trigonal, tetrahedral, and other combinations that we can see in VSEPR).

We find that in the case of a bond between 2 atoms (both  $H_2$ , and  $NO, \dots$ ) all 2 atoms or orbitals that represent each atom (as we will see in  $\partial$ ) have equal importance, and both TEV and TOM give equal expressions ( $A_2$  or  $AB$ ).



In the TOM there is a coefficient called **the mixing coefficient ( $\lambda$ )** that gives the idea of **polarity** or where the present electron density is found in greater probability (it turns out that if  $\lambda$  is 1, both orbitals have equal majority, on the other hand if it is  $>1$  it represents that one  $\Psi$  is found in the majority. (fig.16).

Fig. 16:



Where XY represents AB or A<sub>2</sub> and

- Since OM number = OA number, it is necessary to visualize that there are two ways of seeing an  $\Psi_{om}$  : **linking and antilinking** , and ultimately it can be observed that the numbers agree.
- It turns out that we have *bonding and antibonding orbitals* , and the bonding ones are filled first.
- OMs must be formed from **equal symmetry, equal E's, and constructive overlap.**

TEV	TOM				
sp	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$		
sp <sup>2</sup>	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	
sp <sup>3</sup>	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$

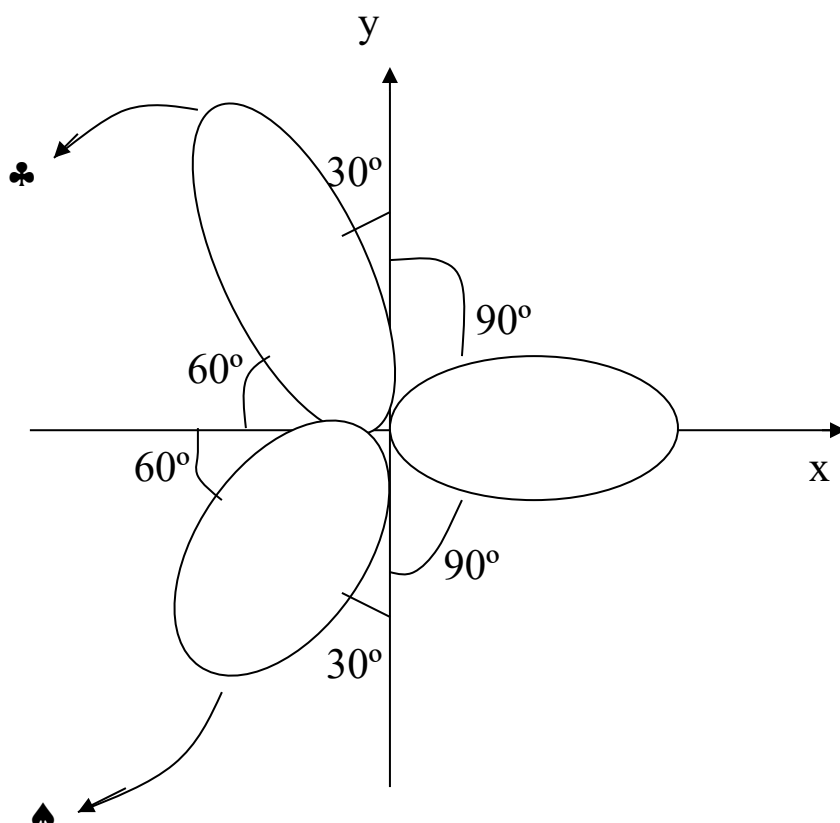
which represents A    B    B'    B''    B'''

$$N_A^2 + N_B^2 + N_{B'}^2 + N_{B''}^2 + N_{B'''}^2 = 1$$

Where the signs of the **normalization factors** are not taken into account because they are squared.

In the case of a *trigonal molecule* we have the following representation (fig.17).

Fig. 17:



and the upper part, which we define as ( ♣ ) it can be deduced that for the 360° angle there is 1/3 of the proportion, while for the 30° there is 2/3, then the contribution is already found.

The lower part ( ♠ ) is also found: 2/3 for y and 1/3 for x then 2/3 multiplied by 2/3 gives 0.44, and 1/3 multiplied by 2/3 gives 0.22; what is missing is 1/3, a value that is included in the s orbital, which contributes to each of the *hybrids* (TEV).

$$\Psi_{sp^2} = \sqrt{1/3} \cdot \phi_s + \sqrt{2/3} \cdot \phi_{px}$$

$$\Psi_{sp^2} = \sqrt{1/3} \cdot \phi_s - \sqrt{2/9} \phi_{px} + \sqrt{4/9} \phi_{py}$$

$$\Psi_{sp^2} = \sqrt{1/3} \phi_{yes} - \sqrt{2/9} \phi_{px} - \sqrt{4/9} \phi_{py}$$

Note that in the *tetrahedral molecule* it is not so easy to deduce the contribution of the angles; we have analyzed this below in ( ▽ ).

In this case the s orbital present in each of the 4 hybrids is always worth 1/4; however *the x,y,z components of each of the 4 hybrids* is a calculation of the 0.75 that are missing to obtain the normalization.

Let us remember that the normalization is:

$$\int_{-\infty}^{\infty} \Psi^2 dx = 1 = \int_{-\infty}^{\infty} (N_a \cdot \phi_a + N_b \cdot \phi_b + \dots + N_n \cdot \phi_n) \cdot (N_a^* \cdot \phi_a^* + \dots + N_n^* \cdot \phi_n^*) dx$$

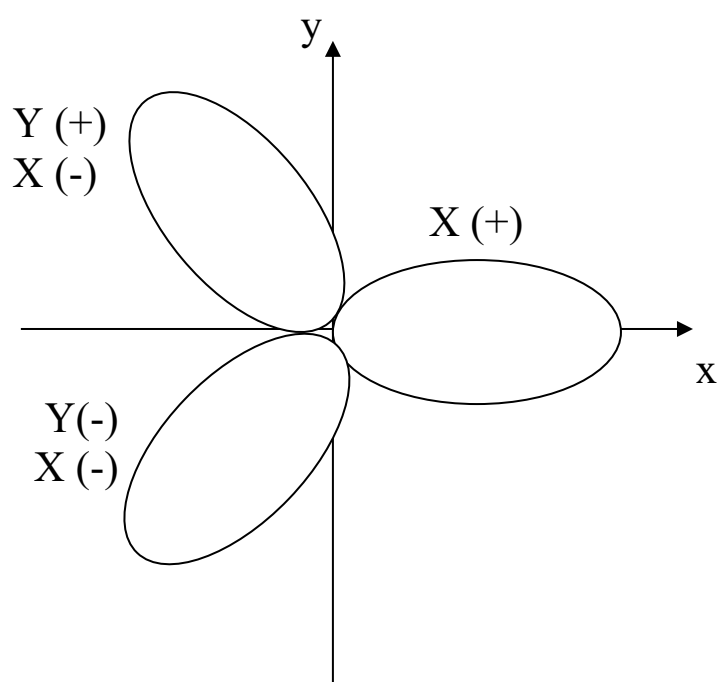
$$= N_a^2 + N_b^2 + \dots + N_n^2 = 1 = \int_{-\infty}^{\infty} \Psi \cdot \Psi^* dx$$

$$\int_{-\infty}^{\infty} \Psi_i \cdot \Psi_i^* dx = 1 \text{ since there is } \textit{overlap} \text{ . Instead:}$$

$$\int_{-\infty}^{\infty} \Psi_i \cdot \Psi_j dx = 0 \text{ since there is no } \textbf{interpenetration}$$

It turns out that in this case the signs are not important. They only become essential when we are not trying to discover the normalization factors  $N$ 's but the signs of each  $\phi$  of the **hybrid**  $\Psi_{sp^2}$ ,  $\Psi_{sp^2}$ ,  $\Psi_{sp^2}$ . So, we will analyze the trigonal hybrid, which is easier. (fig.18).

Depending on the quadrants, the signs of each component of the  $\Psi_{\text{hybrid}}$  ( $s, p_x, p_y$ ) vary as follows:



Orbital "s" is always positive.

( ∇) if we define the angles that each of the 4 hybrids draws with respect to the x,y,z axes we can see that:

$$\begin{array}{l} 80^\circ \longrightarrow y \\ 40^\circ \longrightarrow x \\ 20^\circ \longrightarrow z \end{array}$$

Then we add them and get  $140^\circ$ . Knowing that by doing the % we get that:

$$80/140 = 0'57$$

$$40/140 = 0'28$$

$$20/140 = 0'14$$

$$\frac{\quad}{1} +$$

From here we will make the 0'75 be 100, and each of the values obtained above ( i ) will be the one that gives the contribution of each axis that represents the  $\Psi_{sp^3}$ .

Like this:

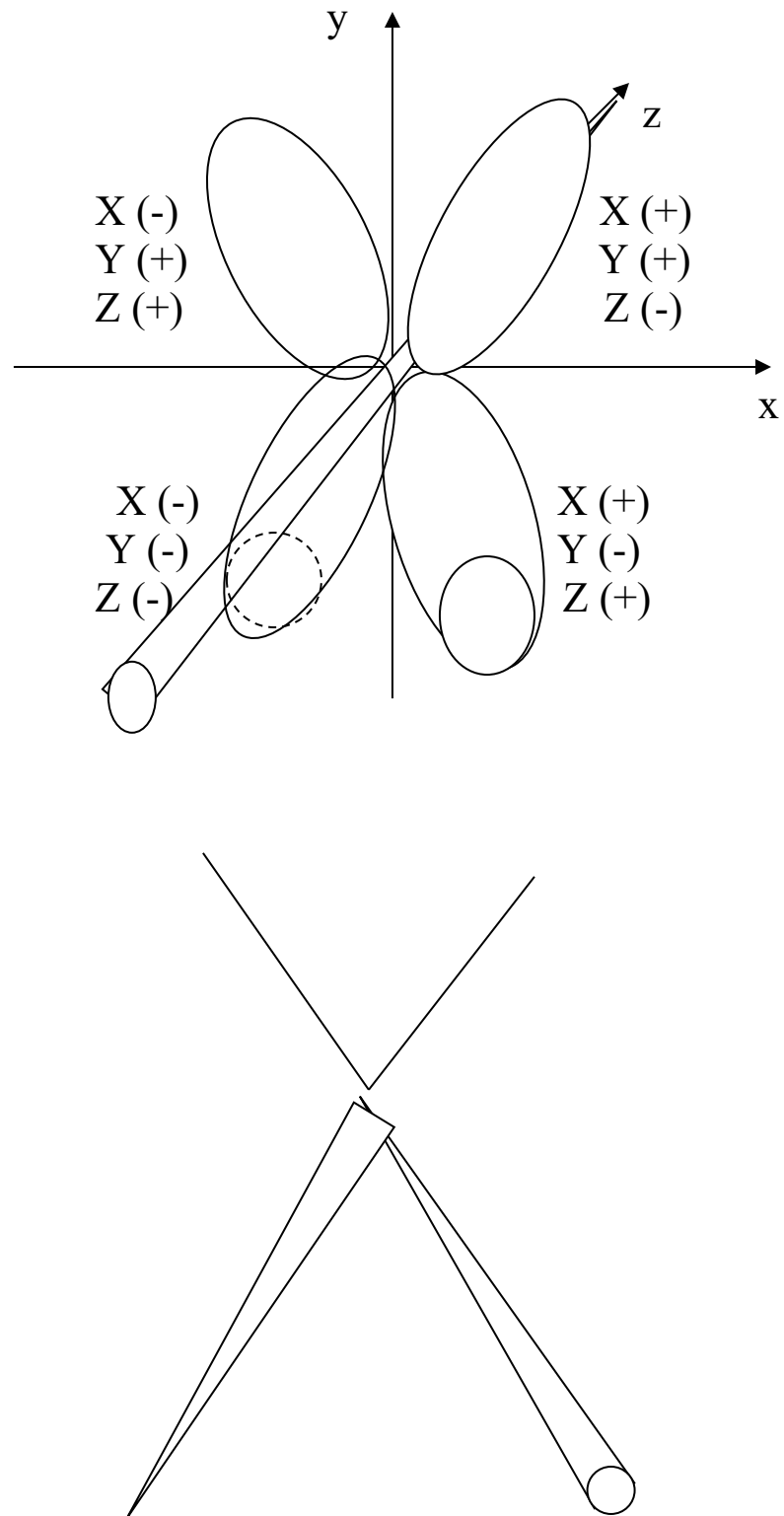
$$\begin{array}{l} 100 \longrightarrow 0'75 \\ 28 \longrightarrow x_y \text{ where } x_y = 0'21 \end{array}$$

$$\begin{array}{l} 100 \longrightarrow 0'75 \\ 57 \longrightarrow x_x \text{ where } x_x = 0'42 \end{array}$$

$$\begin{array}{l} 100 \longrightarrow 0'75 \\ 14 \longrightarrow x_z \text{ where } x_z = 0'15 \end{array}$$

and we see that  $\sqrt{0'4}(px) + \sqrt{0'2}(py) + \sqrt{0'15}(pz) + \sqrt{1/4}(s) =$  the normalization factors of an  $\Psi_{sp^3}$ , and they are equal to 1. Each of the 3  $\Psi$  missing will have different values depending on the angles it draws with the x, y, z axes. (fig.19).

Fig. 19:



On the other hand, to find the N of the  $\Psi_{\text{TOM}}$  's it is necessary to see the contribution of each atomic wave function (not molecular) or in other words, as an example, if we deal with  $\text{AB}_2$ , the N of  $\Psi_{\text{A}}$  will be double that of each  $\Psi_{\text{B}}$  (remember **Aufbau**), that is:

$$\Psi = \sqrt{1/2}\Psi_{\text{A}} + \sqrt{1/4}\Psi_{\text{B}} + \sqrt{1/4}\Psi_{\text{B}'}$$

And in the case of  $\text{AB}_3$  the triple:

$$\Psi = \sqrt{1/2}\Psi_{\text{A}} + \sqrt{1/6}\Psi_{\text{B}} + \sqrt{1/6}\Psi_{\text{B}'} + \sqrt{1/6}\Psi_{\text{B}''}$$

**VSEPR** is a mechanism that allows the geometry of the central atom to be elucidated from secondary atoms.

**Exchange e** : additional force to find the posterior stability in the form of an  $e^-$  in each space (or atom).

**Bond order** =  $(n^\circ \text{ bonding orbitals} - n^\circ \text{ antibonding orbitals})/2$ .

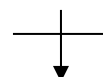
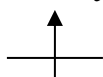
**Pauli exclusion principle**, which states that no two electrons will ever have the same quantum numbers (due to electronic repulsion).

*The main atom, A, is always in the middle.*

According to *the sign of the axes* it is obvious that there must be the opposite in all case:



They are oriented differently in space:

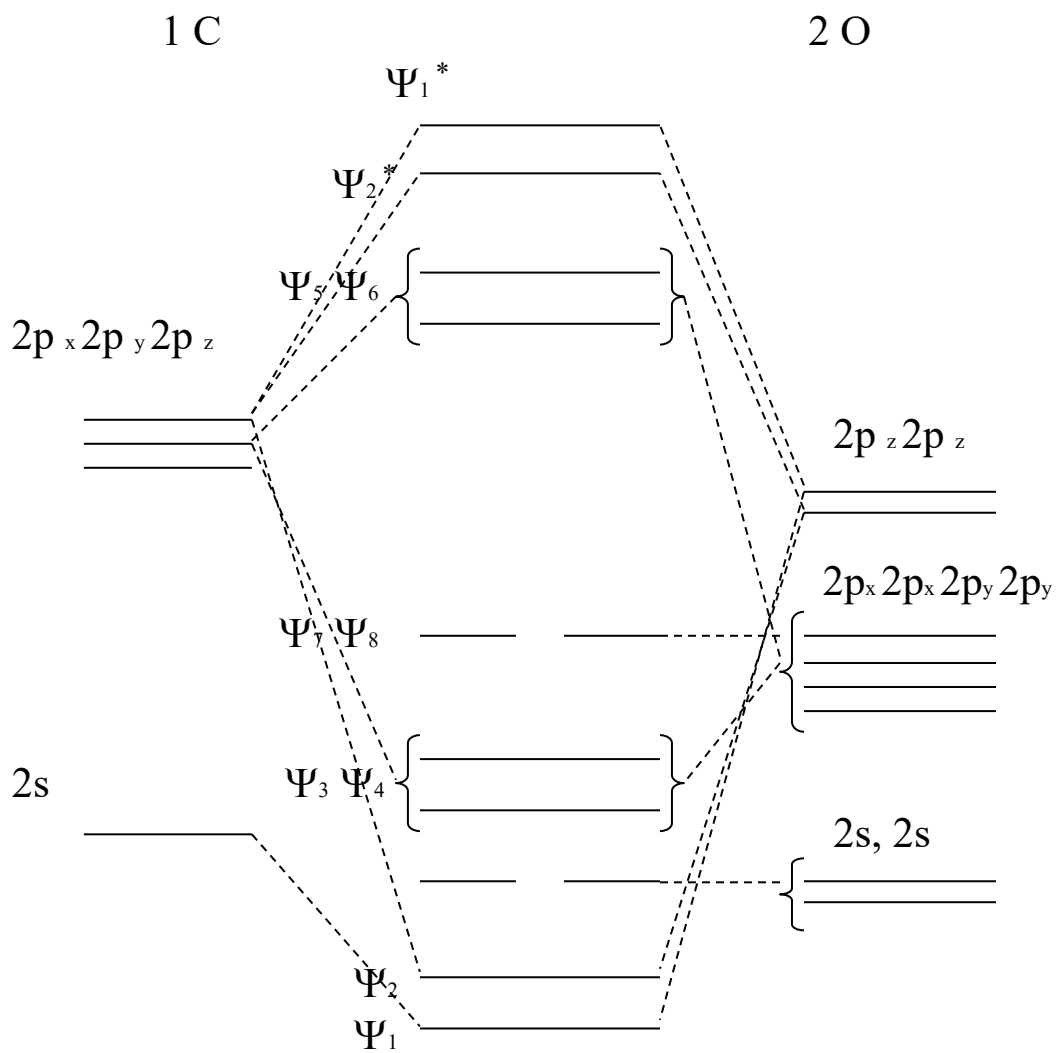


In terms of TOM:

In the case of  $AB$ , we repeat, we have the following graphic representation: (where the orbitals that are missing to achieve that  $n^\circ OM = n^\circ OA$  are those corresponding to the “s” orbital).

While in the case of  $AB_2$ , (for example  $CO_2$ ), we have the representation of fig.20

Fig. 20:



“REFISHING”:

TOM AB<sub>4</sub>:

$\Psi = N. \phi A2s+N'. \phi B2px+N''. \phi B2px+ N'''. \phi B2px + N^{IV}. \phi B2px$   
 $\Psi^* = N. \phi A2s-N'. \phi B2px-N''. \phi B2px-N'''. \phi B2px- N^{IV}. \phi B2px$   
 $\Psi' = N. \phi A2px+N'. \phi B2px+N''. \phi B2px+ N'''. \phi B2px+ N^{IV}. \phi B2px$   
 $\Psi^{*'} = N. \phi A2px-N'. \phi B2px-N''. \phi B2px- N'''. \phi B2px- N^{IV}. \phi B2px$

$\Psi_1 = N. \phi A2s+/-N'. \phi B2py+/-N''. \phi B2py+/- N'''. \phi B2py+/- N^{IV}. \phi B2py$   
 $\Psi_2 = N. \phi A2s+/-N'. \phi B2pz+/-N''. \phi B2pz+/- N'''. \phi B2pz+/- N^{IV}. \phi B2pc$   
 $\Psi_3 = N. \phi A2px+/-N'. \phi B2py+/-N''. \phi B2py+/- N'''. \phi B2py+/- N^{IV}. \phi B2py$   
 $\Psi_4 = N. \phi A2px+/-N'. \phi B2pz+/-N''. \phi B2pzy+/- N'''. \phi B2pz+/- N^{IV}. \phi B2pc$   
 $\Psi_5 = N. \phi A2py+/-N'. \phi B2py+/-N''. \phi B2py+/- N'''. \phi B2py+/- N^{IV}. \phi B2py$   
 $\Psi_6 = N. \phi A2py+/-N'. \phi B2pz+/-N''. \phi B2pz+/- N'''. \phi B2pz+/- N^{IV}. \phi B2pc$   
 $\Psi_7 = N. \phi A2pz+/-N'. \phi B2py+/-N''. \phi B2py+/- N'''. \phi B2py+/- N^{IV}. \phi B2py$   
 $\Psi_8 = N. \phi A2pz+/-N'. \phi B2pz+/-N''. \phi B2pz+/- N'''. \phi B2pz+/- N^{IV}. \phi B2pc$

$\Psi'' = N. \phi A2py+ N'. \phi B2px+ N''. \phi B2px+/- N'''. \phi B2px+/- N^{IV}. \phi B2px$   
 $\Psi^{*''} = N. \phi A2py- N'. \phi B2px- N''. \phi B2pz-/- N'''. \phi B2pz-/- N^{IV}. \phi B2pc$   
 $\Psi''' = N. \phi A2pz+/-N'. \phi B2px+/-N''. \phi B2px+ N'''. \phi B2px+ N^{IV}. \phi B2px$   
 $\Psi^{*'''} = N. \phi A2pz+/-N'. \phi B2px+/-N''. \phi B2px- N'''. \phi B2px- N^{IV}. \phi B2px$

Where  $\Psi_1$  to  $\Psi_8$  are non-linkers