Walsh Diagram

In 1953 Walsh actually calculated the energies of molecular orbitals of a reference geometry and its several distortions for simple triatomic molecules.

Walsh correctly predicted the actual geometries of a number of simple triatomic molecules like H_3^+, H_2O, BeH_2 etc.

By plotting a graph between the calculated energies of molecular orbitals of the refrence geometry and those of the distorted geometries of a molecule Vs the distortion parameter i.e. bond angle,

the position of minimum energy of the filled molecular orbitals in the graph indicated the most stable geometry of the molecule. Such graphs are known as Walsh diagrams.

Walsh Diagram for triatomic molecules like BeH_2

BeH_2 molecule in gaseous state is linear.

It has $D_{\infty h}$ symmetry and contains σ bonds only.

It is obvious from symmetry considerations, the atomic orbitals of Be capable of forming σ bonds in BeH_2 molecule are 2s and $2p_z$ orbitals.

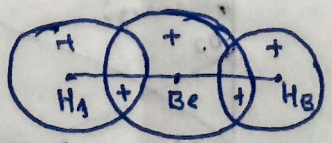
The p_x and p_y orbitals of Be are not suited for forming σ bond.

The orbitals of two H atoms which are capable of forming σ bonds are 1s atomic orbitals.

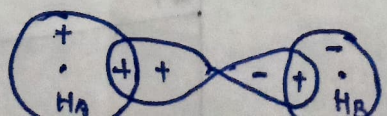
The two linear combination of 1s atomic orbitals of H which are capable of forming σ bonds with 2s and $2p_z$ orbitals of Be are $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$ and $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$.

The bonding and antibonding linear combinations of these orbitals are shown below. The bonding combinations have a net positive overlap of orbitals whereas antibonding combination have a net negative overlap.

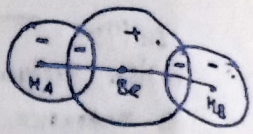
$$\sigma_1 \text{ (Bonding)} = a[\psi_{2s}(Be)] + b[(\psi_{1s}(H_A) + (\psi_{1s}(H_B)]$$



$$\sigma_2 \text{ (Bonding)} = a[\psi_{2p_z}(Be)] + b[\psi_{1s}(H_A) - \psi_{1s}(H_B)]$$



σ_3 (antibonding) = $b[\psi_{2s}(Be)] - a[\psi_{1s}(H_A) + \psi_{1s}(H_B)]$



σ_4 (antibonding) = $d[\psi_{2s}(Be)] - c[\psi_{1s}(H_A) - \psi_{1s}(H_B)]$

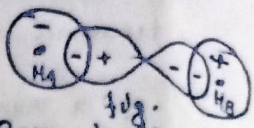
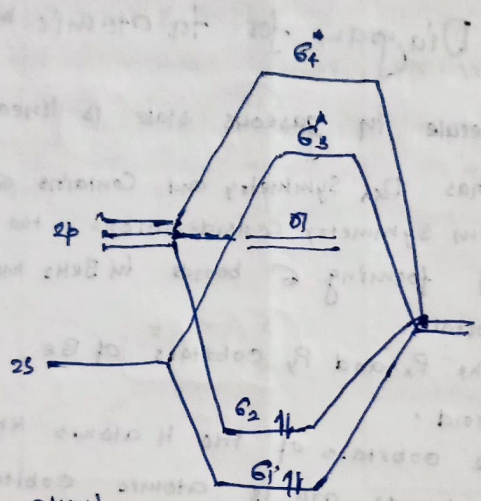


fig.

The molecular orbital energy level diagram of BeH_2 is shown in the above figure

The four valence electrons occupy σ_1 and σ_2 bonding molecular orbital.

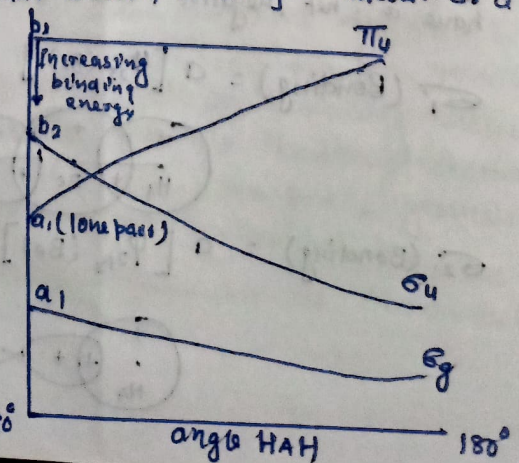
The above simple molecular orbital treatment does not explain the equivalence of the two Be-H bonds which is experimentally established & to explain the above facts the concept of hybridisation has to be introduced.



Walsh diagrams are known as angular co-ordinate diagram or Correlation diagrams

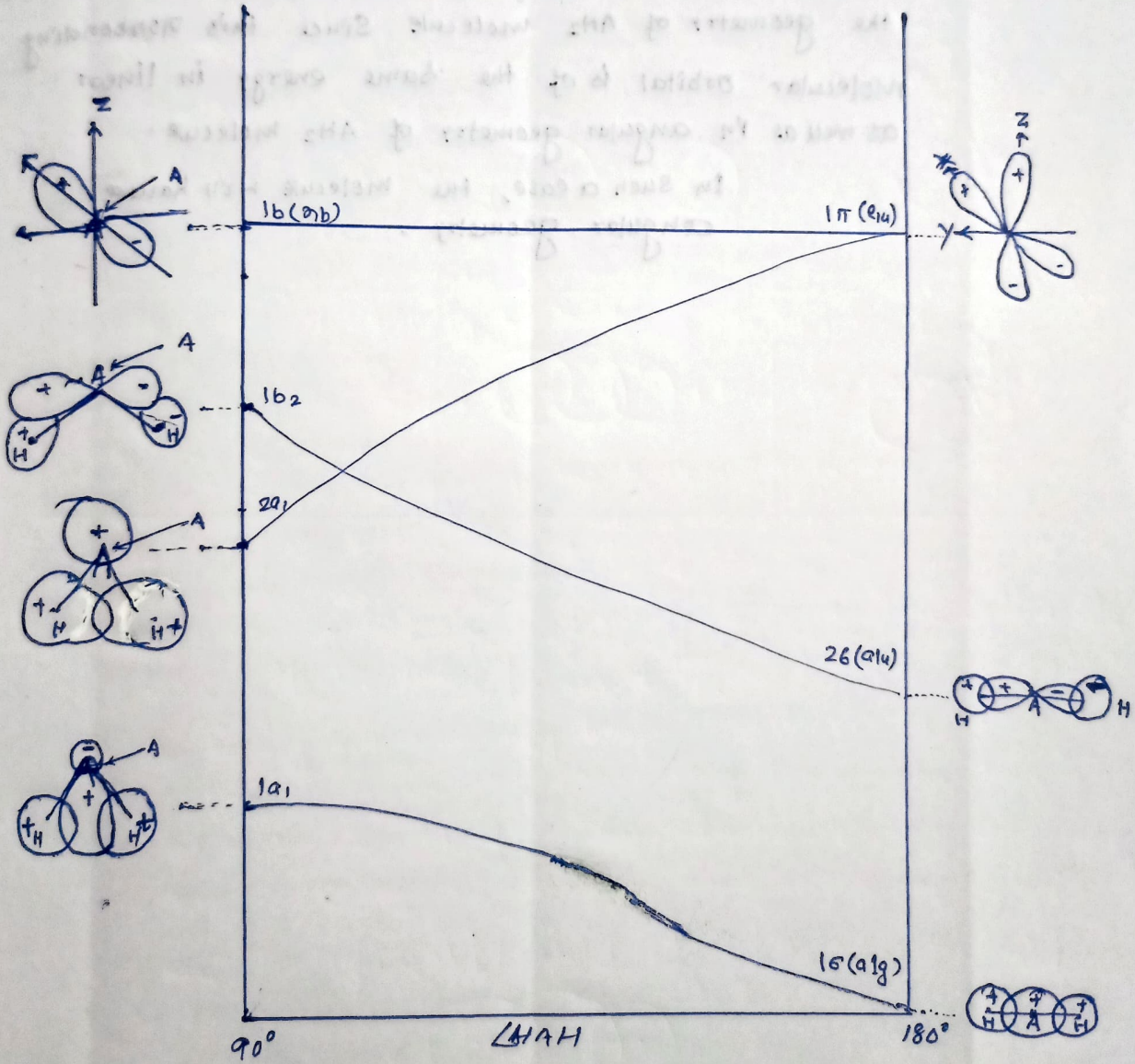
It is a representations of calculated orbital binding energies of a molecule versus a distortion co-ordinate (Bond angle), It is used for making quick predictions about the geometry of the small molecules.

This geometry of small molecules can be predicted by plotting the change in molecular orbital levels of a molecule as a function of geometrical change.



The various orbitals which take part in molecular orbital formation of AH_2 molecule are 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of 'A' [a second Period element] and two 1s orbitals of Hydrogen atoms. Thus Six molecular orbitals are formed out of which the four lower energy molecular orbital are shown in fig given below.

The four molecular orbitals can accommodate Eight Valence electrons which is the maximum numbers of electron that are present in AH_2 molecule [Where A is element of the second Period of P.T]



If follows from the Walsh diagram of AH_2 molecules that a linear geometry of BeH_2 would be more favourable than the angular geometry. It is because the two filled lower energy Molecular orbitals of linear geometry of BeH_2 are of lesser energy than the two lower energy molecular orbitals of angular geometry of BeH_2

In order to decide if there are only 4 electrons to be accommodated in molecular orbitals of the molecule AH2 (to form), the molecule would have a lower energy linear geometry

If however the number of electrons to be accommodated in molecular orbital is more than 4 (four) for example if it is 5 or 6 the third molecular orbital has to be occupied it would have lower energy in angular AH2 molecule than the linear AH2 molecule.

The filling of the third non bonding molecular orbital is of no consequence in determining the geometry of the molecule since this non bonding molecular orbital is of the same energy in linear as well as in angular geometry of AH2 molecule.

In such a case, the molecule will have angular geometry.