Walsh diagram (complete note)

Note for
M.Sc. Chemistry (sem. –I)
Inorganic chemistry

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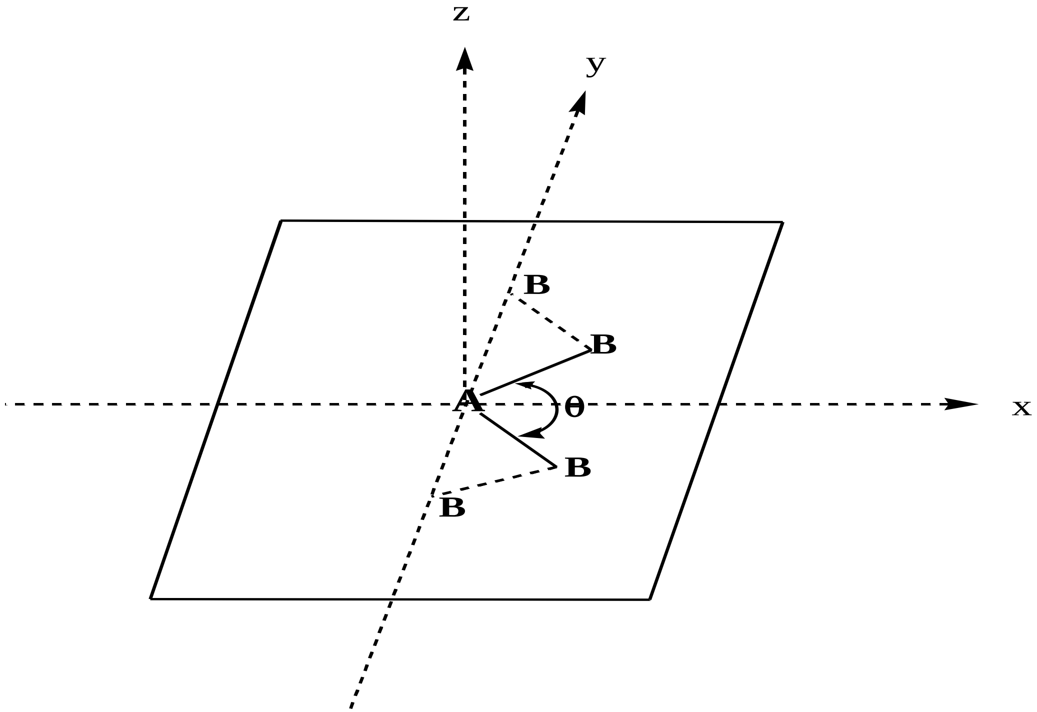
❖Walsh diagram is given by A.D. Walsh (1953).

❖In Walsh diagram **``orbital binding energies'' plotted against bond angles**. The primary idea is that the total energy is the sum of all the orbital binding energies; therefore, by considering the stabilization or destabilization of all the orbital by a change in the angle, one can predict (roughly) the equilibrium bond angle for a given state of a molecule. Walsh diagrams, often called **angular coordinate diagrams or correlation diagrams**, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making rapid predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations.

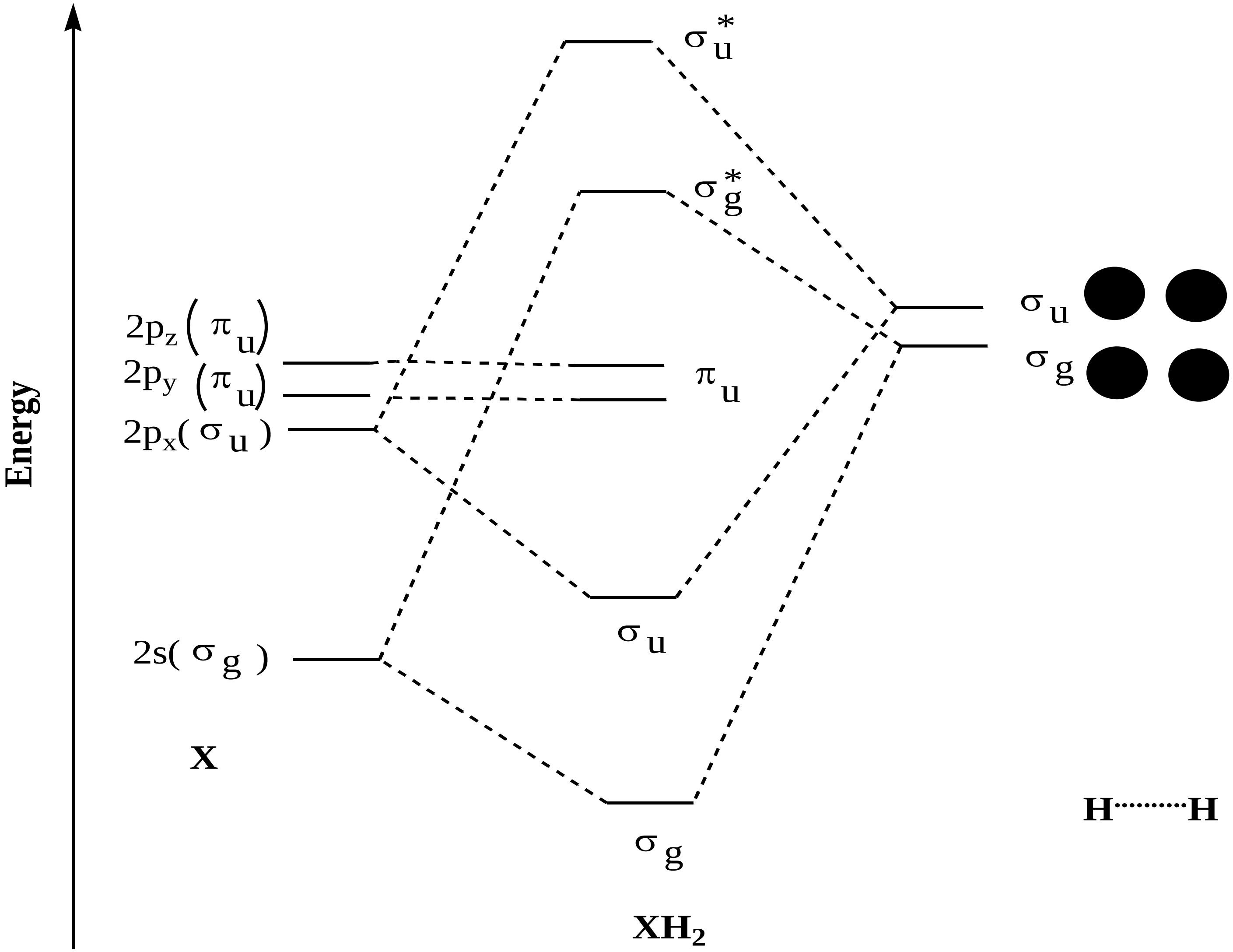
(He explain why water adopts a bent conformation.)

Application to Triatomic Molecules

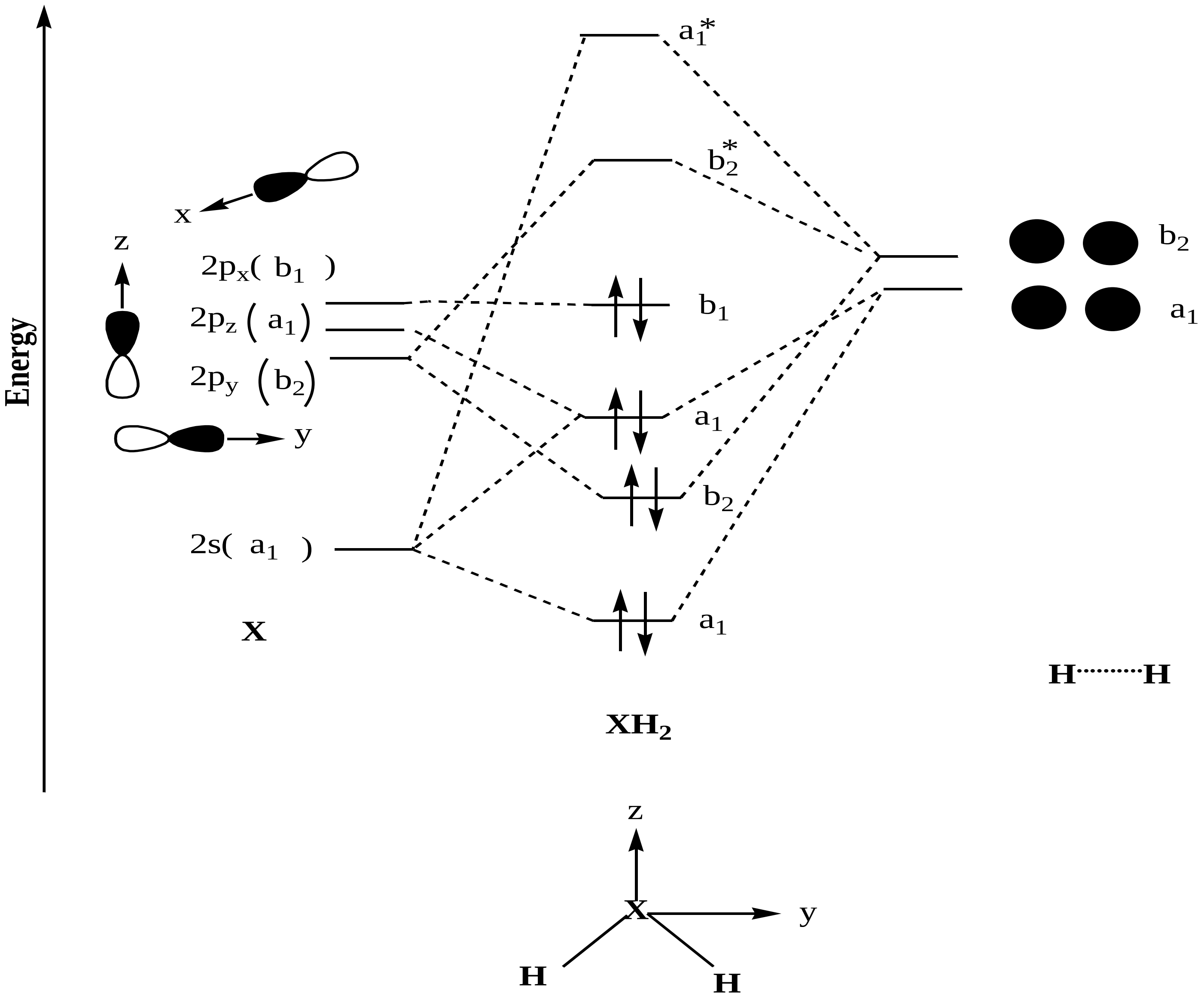
The coordinate system for the AB2 molecule is shown in given below Figure. The AB2 molecule has C2v symmetry when it is bent but when linear it has $D_{\infty h}$ symmetry. To simplify notations, however, the linear configuration is considered to be simply an extremum of the C2v symmetry. Therefore the labels given to the orbitals through the range $90^o \leq \theta < 180^o$ are retained even when $\theta = 180^o$. The symbols used to label the orbitals are derived from the orbital symmetry properties in a systematic way, but a detailed explanation is not given here. For present purposes, these symbol may be treated simply as labels and please go to symmetry unit for details.



A linear XH_2 molecule belongs to the $D_{\infty h}$ point group. A qualitative molecular orbital diagram for the formation of linear XH_2 from atom X and two H atoms is shown below.



A bent XH2 molecule belongs to the C2v point group. A general qualitative molecular orbital diagram for the formation of bent XH2 from atom X and two H atoms is shown below.



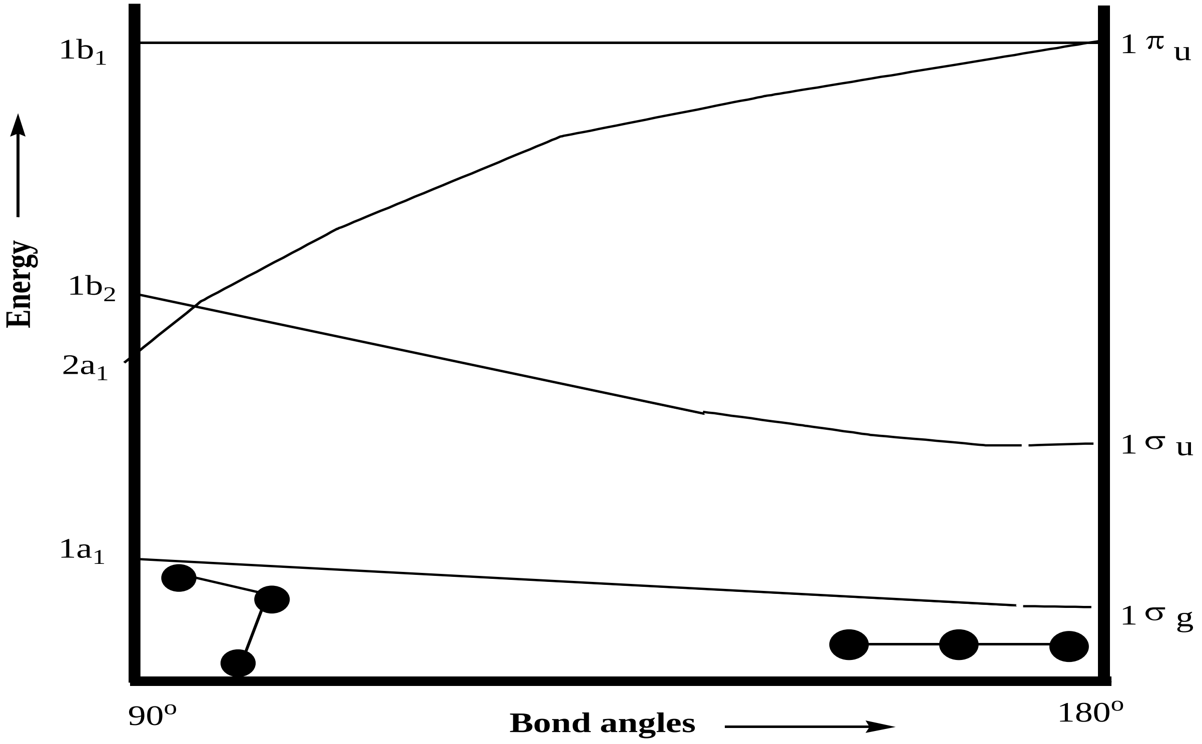
❖It is found that an AB_2 molecule (without lone pairs) is more stable when linear than when bent. The 1b2 orbital drops steadily in energy form $\theta = 90^o$ to 180^o; while the energy of the 1a1 orbitals is fairly insensitive to angle. This is shown for BeH2 in next slide.

❖For an AB2L molecule the results are ambiguous, because the trend in the energy of the 2a1 orbital approximately offsets that of the 1b2 orbiral.

❖For AB2L2 molecules, the result should be the same as for AB2L. Since the energy of b1 orbirtal is independent of the angle. Thus it is not clear in this approach that AB2L2 molecules should necessarily be bent, but it is clear that it exist in bent form..

Example- BeH2 molecule

For BeH2 molecule walsh diagram is shown below. Electronic configuration of BeH2 in linear form is **(2σg)2 ,(1σu)2** whereas in bent form it is **$(2a1)^2$,$(1b2)^2$**. The energy of the 1a1 orbitals is nearly constant that fairly insensitive to angle. Consider (2σg) orbital which is constructed from atomic wave function that are everywhere positive and hence on bending there will be increase in overlap since the two H- atoms wave function will overlap to slightly greater extent. The energy of 2σg is lowered somewhat. It is now labelled as 2a1. In contrast the energy of the 1σu increases on bending. This is because the sign of wave function changes and overlap of H- atoms will be to lesser extent. 1σu is now labelled as 1b2. Since 1b2 loses more energy than 2a1 gains, therefore BeH2 is linear , not bent.



Example H2O Molecule

Let us consider a simple molecule, H2O. It has eight electrons in its valance shell and its molecular configuration in linear is **$(2\sigma g)^2, (1\sigma u)^2, (1\pi u_x)^2, (1\pi u_y)^2$** and in bent is **$(2a1^2\ 1b2^2\ 3a1^2\ 1b1^2)$.** 2σg (2a1) is stabilized in bent form somewhat and 1πu (3a1) is stabilized in greater extent in bent form than 1σu (1b2) destabilized**.** As result of this bent form exist than linear.