

Walsh Rule

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According to Walsh, the following facts are generally true regarding the shapes of the molecules: —

- (i) Molecules with 16 valency electrons are linear in their ground states.
- (ii) Molecules with 17 to 20 valency electrons are bent in their ground states, the apex angle decreasing markedly from 16 to 17 and from 17 to 18-electron molecules and less markedly from 18 to 19 and from 19 to 20 electron molecules.
- (iii) Molecules with 22-electrons are linear or nearly linear in their ground states.

These are the main postulates of Walsh Rule —

- (i) Electrons are completely delocalized in molecules. Further, they move in MOs extending over the entire molecular framework.
- (ii) Only the valence electrons should be considered for properties, which can be

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explained by qualitative M.O Theory.

- (III) Linear combinations of atomic orbitals can form satisfactory molecular orbitals.
- (IV) The molecular orbitals for each type of molecular framework must be qualitatively similar, the individual molecules may differ only in no. of valence electrons occupying the common M.O system.
- (V) The total energy of the molecule is the sum of the orbital energies of the valence electrons.
- (VI) The electron-electron or nuclear-nuclear repulsions are not considered in this simple model.
- (VII) The symmetry restrictions limit the particular AOs to combine and form MO. Molecular orbitals must be either symmetric or anti-symmetric with respect to the symmetry operation of the molecule.
- (VIII) ~~It~~ It is possible to draw picture of the MOs and to establish the approximate order of energies from the properties of AOs.
- (IX) The changes in the molecular shape accompany the lowering of energy of MO resulting from an in-phase overlap between two or more AOs. Conversely, the raise the energy of the MO is observed when AOs overlap in an out of phase manner.