Chapter 3. The Molecular Orbital-Valence Bond Theory of Excited States.

The original monograph introducing qualitative Valence Bond (VB) and Molecular Orbital Valence Bond (MOVB) theory to the chemical community was entitled "Unified Valence Bond Theory of Electronic Structure".¹,² In this work, we begin to justify the use of the adjective "unified" by showing how the same MOVB concepts that are applicable to ground state chemistry can be applied to excited state chemistry. In particular, we shall use the MOVB theory and the accessory conceptual tools developed before in order to elucidate the energetic interrelationships of the low lying excited states of a given system and discover ways in which the energy ordering of these states can be altered. After reading the chapter describing the Induced Deexcitation model and this one, it is hoped that the reader will have no difficulty seeing that the energy ordering of different molecular states at fixed geometry and the energy ordering of different ground state geometrical structures are analogous problems which can be handled by the same MOVB concepts.
I. Theory

According to MO theory, the ground state of a closed shell n-electron molecule is constructed by utilization of the Aufbau Principle, i.e., by "feeding" electrons to the MO's starting from the lowest energy MO and proceeding up the ladder until the n/2 lowest energy MO's have been filled. Singly excited states are constructed by promoting one electron from an occupied to an unoccupied MO, doubly excited states by promoting two electrons, and so on. Of course, these are only approximate monodeterminantal descriptions which must be improved by inclusion of Configuration Interaction (CI). Nonetheless, this is the way in which a chemist who is trained in MO theory thinks, in a qualitative sense, about molecular states. According to MOVb theory with core-ligand dissection, the ground state of a closed-shell n-electron system is constructed by generating the maximum number, P, of two-electron multicenter bonds linking core and ligands. MOVb excited states corresponding to the singly excited states of MO theory are of two types:

a. States having P-1 two-electron bonds plus one zwitterionic (singlet) or radicaloid (triplet) antibond.

b. States having P-2 two-electron bonds plus one one-electron and one three-electron bond consistent with singlet or triplet multiplicity.

MOVb excited states corresponding to the doubly excited states of MO theory belong to various types such as the following:

a. States having P-1 two-electron bonds plus a "delocalized antibond".

b. States having P-2 two-electron bonds plus a four-electron antibond.

c. States having P-4 two-electron bonds plus four bonds of the odd-electron variety.

The MOVb states defined in this way are only approximate molecular states.

The MOVb representation of molecular states is the main topic of this chapter and the description given above will be discussed, clarified, and illustrated in