

valence bond (VB) theory

A method of approximating the total wavefunction of a molecule as a linear combination of functions related to certain pairings of electron spins. Each such function is given by a product of the atomic orbitals of the separated atoms. As a first approximation the covalent pairing scheme is employed, in which pairs of electrons between the atoms have their spins paired as much as possible. To account for electron correlation effects, mixing in of functions representing ionic pairing schemes, in which some of the separated atoms are replaced by positive and negative ions, is employed. The VB and MO methods, if carried out with the same basis set of orbitals, are entirely equivalent if all possible ionic structures are included in the VB and all possible configurations in the MO.

1999, 71, 1967