Answer on Question #49538 – Chemistry – Inorganic Chemistry

Question:

Discuss variation method of valence.

Answer:

Valence bond method: A quantum mechanical approximation method used to describe bonding in molecules. In contrast to the Molecular orbital theory (see), the V. is based on the assumption that atomic orbitals are largely retained in the molecule, and is usually applied only to the valence electrons. Different possible distributions of these electrons among the atomic orbitals of a molecule produce different valence structures. These determinant wavefunctions (see Antisymmetry) can be constructed mathematically from the occupied atomic orbitals, and represented symbolically by valence dash formulas. The total wavefunction Ψ of the molecule is approximated in the V. by a linear combination of valence structures: $\Psi = \Sigma C_I \varphi_I$, where φ_I is the wavefunction of valence structure I. The coefficients C_I are determined using the variation method to minimize the total energy. Valence structures do not actually exist, but are only a device used to represent the true bonding state. For the hydrogen molecule, the linear combination of the covalent valence structure H_A-H_B with the two ionic valence structures $\overset{\oplus}{H_A}\ \overset{\ominus}{H_B}$ and $\overset{\ominus}{H_A}\ \overset{\oplus}{H_B}$ gives a good description of the bonding state; in it, the covalent valence structure makes the greatest contribution. The bonding in benzene can be represented in simplified form as a combination of the Kekulé formulas K_1 and K_2 plus the Dewar formulas D_1, D_2 and D_3 (see Resonance). It has been calculated that each Kekulé structure contributes about 39% of the total wavefunction, and each Dewar structure, about 7.3%. If only one valence structure makes a significant contribution to the energy of the ground state, one speaks of approximately localized valency; otherwise, it is nonlocalized valency. The calculations for larger molecules using the V. are complicated by the large numbers of valence structures which have to be taken into acount. The method is therefore most important for qualitative interpretation of molecular bonding.