



Charge Distributions and Chemical Effects: A New Approach to the Electronic Structure and Energy of Molecules

S. Fliszar

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The energy of a molecule can be studied with the help of quantum theory, a satisfactory approach because it involves only basic and clearly identified physical concepts. In an entirely different approach, the molecular energy can be broken down into individual contributions reflecting chemical bonds plus a host of subsidiary "effects", like γ -gauche, skew pentane, ring-strain, etc. , giving an overall picture in terms of topological characteristics. The latter approach can be successful, particularly if a sufficient number of particular topological situations have been parametrized (which is an empirical way of "understanding" chemistry), but also contains the seed for difficulties. Indeed, the danger exists of unduly ascribing a physical meaning to corrective terms whose function is primarily to account in an empirical fashion for discrepancies between "expected" and observed results. The link between this type of empirical approach and the knowledge that the ground state energy is uniquely determined by the electron density is lost somewhere along the road, although some of the "steric effects" are here and there vaguely traced back to electronic effects. The approach presented in this monograph goes back to the fundamentals in that it is exclusively based on interactions involving nuclear and electronic charges. Confining the study to molecules in their equilibrium geometry, the problem of molecular energies is reduced to its electrostatic aspects, explicitly involving local electron populations.

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