DENSITY MATRICES AND THE INTERFERENCE ENERGY ANALYSIS

Marco Antonio Chaer do Nascimento
Instituto de Química
Universidade Federal do Rio de Janeiro, Brazil
chaer01@gmail.com

Density matrices play a fundamental role in many areas of physics and chemistry. In particular its usage in quantum chemistry was considerably enhanced by the seminal Ruedenberg paper on the "Physical Nature of the Chemical Bond" [1]. Arguing that the energy as well as all other observable quantities are completely determined by the first and second order density matrices, he chose these two quantities, and the related energy components, as the starting point for an interpretative analysis on the nature of chemical bonds. Based on this premise and using the MO language, Ruedenberg was able to identify that quantum interference effects are responsible for the formation of a chemical bond and that this effect manifests itself, from the energetic point of view, as a reduction of the kinetic energy of interference and an increase of the potential energy of interference as the bond is being formed.

Recently we have shown that by casting Ruedenber's proposal in the VB language it is possible to calculate the interference contributions of individual chemical bonds, or groups of bonds, to the total energy of a system using GVB wave functions. This is possible because for SCGVB wave functions, the second-order reduced density matrices can be blocked by groups of electrons whose contributions to the interference energy can be separately analyzed. Another great advantages of using this type of wave function for the Interference Energy Analysis (IEA) is that the atomic orbitals are uniquely defined within a given basis set (avoiding the arbitrariness involved in the choice of atomic orbitals in the MO analysis) and also that the total interference energy and density per bond are automatically obtained. There is another extremely important reason to use GVB (and SCVB) wave functions to study many electrons systems and that has to do with the fact that only these wave functions are basis for the symmetric (or permutation) group as required by the permutation symmetry of the many-electrons Hamiltonian [2].

In this talk we will present the results of the Interference Energy Analysis for molecules exhibiting distinct bonding patterns. Diatomic and polyatomic molecules, with single double and triple bonds, with different degrees of polarity, linear or branched cyclic or not, conjugated and aromatics, 2c-2e, 2c-1e, 3c-2e bonds have been considered [3]. In all cases the conclusion was exactly the same: for each bond of a diatomic or polyatomic molecule the results of the energy partitioning into interference and quasi-classical contributions pointed that the main contribution to the depth of the potential wells comes from the interference term, showing that EAI analysis provides a unified view of the chemical bond [4]. (CNPq, FAPERJ)

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