Local Approach to Delocalized Electronic Systems : An Investigation Tool for Cohesive Energies and Gap Evaluations

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Starting from strongly localized N-electron functions built from either pure Atomic Orbitals or fully localized bond Molecular Orbitals, it is possible to evaluate the ground state energy of aperiodic lattice ruled by a tight-binding or Hubbard Hamiltonians without explicitly introducing the mono-electronic crystal orbitals. The method consists of a self-consistent perturbation of the zeroth-order wave-function which incorporates high order effects and offers reasonable convergence properties. Along this framework, a single variable per bond type is introduced, namely the amplitude of the charge transfer. The method leads to a set of coupled equations which can be numerically solved, if not analytically. Short-range delocalization effects under periodic conditions are explicitly taken into account and relatively accurate cohesive energies are estimated for regular homoatomic and heteroatomic 1D-chains as well as for honeycomb lattices. In addition, good agreement with experiment for the distortion amplitude in polyacetylene is obtained. This exploratory tool may be easily extended to more sophisticated Hamiltonians, to investigate ring current contributions (see Figure 1), for which the solutions are not accessible. Since our approach only introduces short-range delocalization effects, its performance questions the importance of the specifically collective delocalization effects.

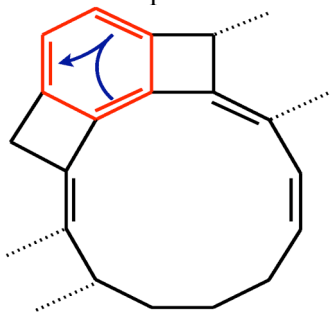

Fig. 1: Relative ring currents contributions to the cohesive energy of 2D zeolithe-type architectures: towards the concept of aromaticity in 2D networks.

[1] J. P. Malrieu et al., J. Chem. Phys., 120 (2004) 7374.
[2] A. Boullanger et al., Eur. Phys. Lett., 6 (2005) 906.