4E12

Stress tensor description of chemical bonds

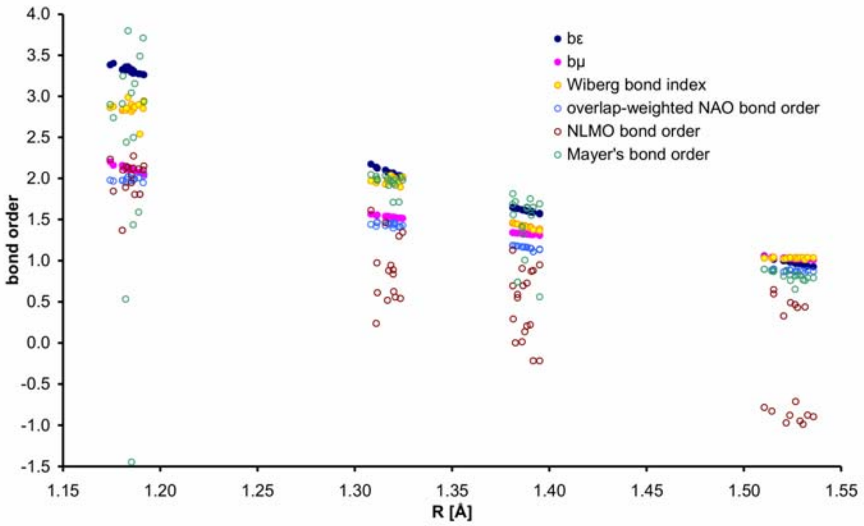
and New Bond Order Concept

（京都大院工）
○Paweł Szarek and 立花明知

【Introduction】The interpretative mathematical model (consistent with postulates of Quantum Mechanics and valid for exact wavefunctions) of chemical bond should rely on observable quantities. The geometrical representation of bonding in real space is intimate and advantageous to our perception or world. Therefore theoretical description of Lewis ideas in geometrical space should arise from density distribution, since objects like molecular orbitals or valence bond structures (without physical significance) appear as intermediates upon solving the Schrödinger equation. The first Hohenberg-Kohn theorem binds electron density distribution with corresponding number of electrons N and external potential (i.e. distribution of nuclei), for a given ground state, providing complete chemical information about the system. The essential in chemistry a chemical bond concept by Lewis, despite its simplicity, urges one to search between atomic centers for a localized electron pairs and, following Pauling, to explore associated forces that lead to stabilization of an aggregate. This work attempts to bridge practical chemistry and quantum mechanics and seek for physical explanation for chemical bonding in terms of energy density and electronic stress tensor analysis.

【Result and Discussion】The regional DFT rigged QED electronic stress tensor analysis of distribution of electrons in atoms and molecules is innovative tool aiding understanding of chemical bonding and giving new prospective. On first sight this concept might seem “strange”, however a deeper reflection will bring one to conclusion that it is natural to explore the electronic structure of chemical bonding in terms of internal forces acting on electrons. The stress tensor subsumes such local indicators of “electron pairing” based on local kinetic energy density like electron localization function [1], local temperature of “nighness” functional [2], local entropy measures [3] or localized orbital locator [4]. The Bader’s Atoms-In-Molecules theory [5] show some analogies with theory presented here. However the fundamental difference between these two methods is the means in which electrons are treated: topological analysis of charge density by Bader and dynamical approach which takes into account quantum mechanical forces acting on electron distribution. The idea and role of stationary point of charge density, defined by dynamical forces acting on electrons in molecules, in bonding region, so called “Lagrange point” has been explained. The relations between forces acting on electron distribution, through electronic stress tensor and corresponding energy density were found. We have introduced new non-classical bond orders based on electronic properties (local electronic energy density and local chemical potential derived from electronic stress tensor) of stationary point of electron density. Systematic analysis of bond orders of simple diatomic, homonuclear molecules, the properties associated with Lagrange point, was made. Along with new bond orders, changes in the energy density due to interaction between bonding atoms are locally pictured in real tri-dimentional space representation and confronted against corresponding deformation of charge density. The extended discussion on bonding in terms of stress tensor and new bond orders is provided using simple organic molecules as an example. Different aspects of bonding are considered, like different multiplicity of bonds (different number of electron pairs in corresponding Lewis structure), conjugation and hyperconjugation effects as well as the stability of isomers and conformers, substitution effects and the dependency of electronic properties on electronegativity of bonded atoms. The correlation of new indices with interatomic distance and with commonly used overlap or population based bond orders was made. The stability of the method against different theory levels is discussed as well. The reactivity and stability might be expressed in terms of local electronic chemical potential and interaction energy density.

Fig 1. The correlation of carbon-carbon bond order indices with bond length for group of organic compounds (C_2H_nA - with different functional groups). The stress rooted bond orders bε and bμ are blue and pink dots, NBO bond orders: Wiberg's indexes (yellow dot), atom-atom overlap NAO bond order (blue ring) and NLMO bond orders (brown ring), and Mayer's bond order is represented by green rings.



【References】

[1] (a) A. D. Becke and K. E. Edgeecombe, *J.Chem.Phys.* **92**, 5397 (1990), (b) M. Kohout, *Int. J. Quantum Chem.* **97**, 651 (2004), (c) A. Savin, n, A. D. Becke, J. Flad, R. Nesper, H. Preuss, and H. G. Vonschnering, *Angew. Chem.* **30**, 409 (1991), (d) A. Savin, R. Nesper, S. Wengert, and T. F. Fassler, *Angew. Chem.* **36**, 1809 (1997).

[2] P. W. Ayers, R. G. Parr, and A. Nagy, *Int. J. Quantum Chem.* **90**, 309 (2002).

[3] P. K. Chattaraj, E. Chamorro, and P. Fuentealba, *Chem. Phys. Lett.* **314**, 114 (1999).

[4] (a) H. L. Schmider and A. D. Becke, *J.Mol.Struc.Theochem* **527**, 51 (2000), (b) H. L. Schmider and A. D. Becke, *J. Chem. Phys.* **116**, 3184 (2002).

[5] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory.* (Clarendon, Oxford, 1990).