# Methodology of bonding analysis

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The analysis of chemical bonding in molecules and solids is performed utilizing bonding indicators specially designed for this task. Each of the indicators yields an additional specific view into this explicitly theoretical investigation. The development of bonding indicators is an important aspect in order to gain new insights into chemistry.

The methods of chemical bonding analysis are strongly connected to the availability of suitable descriptors. The development of new descriptors on the basis of recent theoretical founding is an ongoing process [1].

#### Curvature of the electron position uncertainty

The investigation of chemical bonds in real space is closely related to the atomic shell structure and, thus, to the piecewise exponential decay of the electron density. This property, which is reflected by the change of the function  $\nabla \rho / \rho$ , was utilized to propose a real space bonding indicator termed the position uncertainty curvature PUC [2]. The spread of the electron density can be described by the information entropy which is a mean value of  $-\log \rho$ , that can be interpreted as the uncertainty of the prediction of the electron position. The Laplacian of  $-\log \rho$  defines PUC. In case of free atoms the PUC unravel the atomic shell structure by a sequence of maxima. The electron populations in a subsequent shells bounded by PUC minima are close to the ones given, for instance, by the electron localizability indicator ELI-D [2].

The structuring of PUC for molecules is exemplary shown in Fig. 1 for cyclopropane. Beside the atomic cores of the carbon atom (blue colored spheres) there



Fig.-1: PUC for the  $C_3H_6$  molecule. Yellow colored: isosurfaces PUC = 4.3; blue colored: isosurfaces PUC = 3.3.

are separate localization domains (also colored blue) that can be attributed to the bonding between the carbon atoms. As different from the ELI-D description the bonding is marked by two separate topological objects because the PUC maxima are closer to the nucleus than the ELI-D maxima. This feature is especially pronounced in case of the C-H bonding, for which PUC shows not only the spherical objects around the hydrogen atoms but also the remainder of the carbon valence shell.

#### Bonding analysis of molecules and solid state

The established methods of real space bonding analysis, like the quantum theory of atoms in molecules (QTAIM), the utilization of delocalization indices, possibly decomposed in terms of Fermi orbitals, and ELI-D based analysis was applied to many molecular systems. The whole arsenal of methods was used, for instance, to elucidate the bonding situation in systems with dative N-B bond with associated O-B interaction [3].

The methods of domain-averaged Fermi-hole (DAFH) analysis were used to gain new insight into the peculiar bonding situation of the carbon dimer [4]. Additionally, the covalent bond order based on localized natural orbitals was compared to the results of DAFH analysis.

To utilize any of the above mentioned real space analysis for solid state systems, the electron density as well as all the (still) orbital dependent fields need to be computed first. To accomplish this, a chosen solid state code needs to be interfaced to make the wavefunction available. Further more, all the routines computing the fields necessary for the evaluation of the bonding descriptors must be implemented to serve the periodic conditions. This work was realized for the solid state program FHI-aims [5].

The availability of the solid state wavefunction was utilized in the analysis of the bonding situation in the thorium compound  $ThPt_{3+x}Be$  [6]. The most surprising result of the ELI-D analysis were the pronounced Be-Pt bonding interactions showing that the Be atoms serve to build the skeleton of the compound by bonding,



Fig.-2: Bonding situation in  $ThPt_{3+x}Be$ . Yellow colored isosurfaces ELI-D = 1.21; blue objects: QTAIM basins colored according the electron density values.

instead of a simpler view assuming ionic interactions for Be cations, cf. Fig. 2.

## **Decay rate of delocalization measures**

The delocalization indices (DI) evaluated over QTAIM basins were utilized to analyze the decay of the electron sharing with the distance between the basins. The procedure was applied to cyclic chains of hydrogen atoms of different length [7]. The oscillations of DIs with distance due to mesomeric effects can nicely be observed. The influence of electron correlation (up to CISD) on the decay of the DIs was analyzed.

The DIs for periodic systems were further investigated for hydrogen lattices applying the one-particle reduced density matrix functional theory [8]. The spatial decay of the DIs was investigated for 1D to 3D hydrogen lattices with unit cell parameters ranging from 3-8 a.u. The oscillations found for the 1D case disappear for the higher dimensional cases. Moreover, they are strongly damped by the electron correlation.

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