

Quantum Chemical Tools for Bonding Analysis

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The chemical bonding situation in molecules and solids can be analyzed in several ways depending on the chosen viewpoint as well as on the underlying quantities used in their interpretation. Roughly spoken, two routes are utilized: On one hand, the composition (in a broader sense) of the wave function is analyzed, i.e., orbital dependent indices are created and interpreted, like orbital populations, orbital overlap integrals or various transformations of orbitals are examined. On the other hand, functions derived from density matrices based on the total wave function serve as the source for further examination. In the following we will focus on tools for the bonding analysis evaluating integrals of density matrices and operating in real (coordinate) space.

Obviously, stable molecules and solids can be prepared. This means that a more or less strong influence is needed to disturb the physical state of the compound (for instance the composition, configuration, etc.). The compounds are thought to be composed of individual atoms held together by attractive forces. The whole situation is described by the notion of chemical bonding. Especially in case of molecules the pairwise interaction between atoms or fragments seems to be a favorable concept to represent the chemical bonding. The situation becomes more complicated when collective interactions, i.e., with more participants, are apparently responsible for the bonding, respectively in cases where the individuality of the atoms is strongly disturbed. This is often the case for solid state compounds.

Bonding Indicators in Real Space

As the chemical bond is not explicitly given by a corresponding quantum mechanical operator different suitable descriptors were created in the past and are still under development [1–3]. Focusing on the bonding indicators in real space the 2-matrix can conveniently be utilized as the basis for the investigation. The 2-matrix is given by the squared modulus of the wave function after integrating the coordinates of all electrons but 2 over the whole

space. The diagonal part of the 2-matrix is the electron pair density. The 2-matrix can be further reduced to the 1-matrix, the diagonal part of which is the electron density.

The electron density and its derivatives are the central objects of the so-called Bader analysis [4]. The electron density gradient field determines the critical points, i.e., the minima (repellers), maxima (attractors) and saddle points, given as the spatial positions of zero density-gradient, respectively as the end points of the gradient field lines (trajectories) in case of attractors located at the nuclear position. The pair of trajectories starting from a chosen saddle point and connecting two attractors defines a bond path. The diagram showing all the bond paths connecting the saddle points with the attractors (in case of the electron density usually the nuclei) describes the so-called molecular graph. Additionally, regions given by all trajectories terminating at the same attractor are so-called basins. In Bader's approach the basin around a nucleus is used to define an atom.

Figure 1 shows the 0.125-localization domains of the electron density for MgB_2 (regions surrounded by isosurfaces for the density value 0.125 bohr^{-3}).

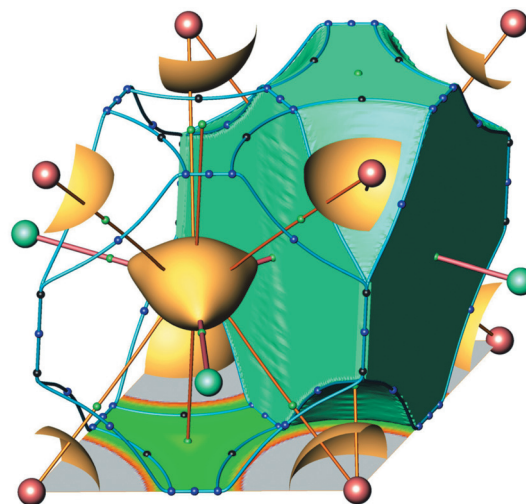


Fig. 1: Molecular graph of MgB_2 . Mg: red, B: green. Small spheres: saddle points in green, ring points in blue, minima in black. Electron density localization domains and the boron basin (large green object) are also shown.

The wave function was computed with the solid state DFT program Elk [5]. The calculation of the electron density and the determination of the critical points, the bond paths as well as the basins for the solid state was performed with the program DGrid [6,7]. The atoms in the unit cell are connected by bond paths – light brown lines – starting from the density saddle points (small green spheres). Thus, each boron atom is connected to the 3 neighboring boron atoms and the 6 closest Mg atoms (above and below the boron plane). Additionally, there are bond paths to the 2 boron atoms in the surrounding boron planes. There is no bond path between the Mg atoms (however, already a small change in the density distribution in the Mg plane could give rise to a saddle point between the Mg atoms). The (non-spherical) shape of the atomic basin of boron gives an impression of the spatial demand of the atomic species (in contrast, the atomic basins of Mg are almost spherical – the shape can be guessed by the “holes” in the boron basin). For a deeper analysis the density Laplacian as well as the energy density at the saddle points can be evaluated.

For the analysis of the correlative effects between the electrons various indicators based on the electron pair density can be utilized. For instance, the electron localizability indicator (ELI) is determined by integrals of the pair density over very small, compact non-overlapping regions. One of the ELI forms (triplet ELI-D [1]) is given by the distribution of populations of triplet-coupled electrons over regions enclosing a fixed amount of electron pairs coupling to a triplet. High ELI-D values are found for regions where it is not favorable for the electrons to couple to a triplet pair, i.e., where high electron population is needed to form such a pair. The ELI-D distribution is rich of structures that can be used as signatures of atomic shells, bonds and lone pairs. The field can be searched for critical points and corresponding interconnection lines (trajectories starting from saddle points to the attractors, in case of ELI-D not necessarily connected with bonds between atoms). The integration of the electron density in the ELI-D basins yields the basin population that can be interpreted further.

The evaluation of the electron density of MgB_2 presented in Figure 1 can be extended by the inspection of the ELI-D functional, cf. Figure 2. High ELI-D values are found in the core regions of

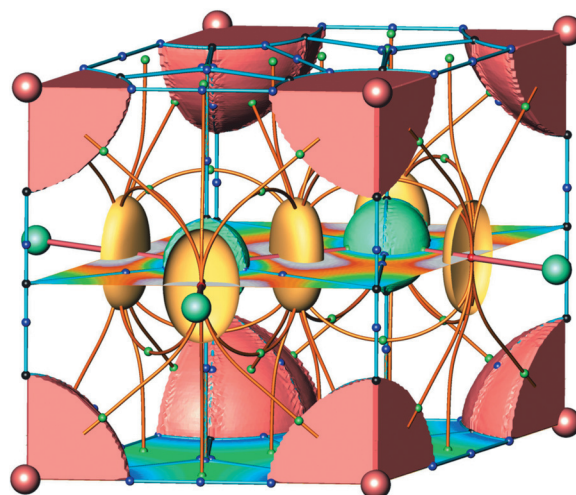


Fig. 2: ELI-D interconnection graph for MgB_2 . Mg: red, B: green. Saddle points are presented in green, ring points in blue, minima in black. ELI-D localization domains together with the B and Mg core basins (large green and red objects) are shown.

the atoms as well as in the bonding region between the boron atoms. For the ELI-D attractors in the core regions the corresponding basins (in case of Mg grouped together into superbases) were determined. The basins are shown in Figure 2 as large green (B core) and red (Mg core) objects populated by 2 and 10 electrons, respectively. The attractors of ELI-D positioned at the midpoints of the shortest B-B distances can be viewed as the signatures of bonds. The interconnection lines linking chosen ELI-D bond attractor with other attractors (via ELI-D saddle points) bridge that bond attractor not only with the 2 closest boron core attractors but also with the 4 closest Mg cores. Additionally, the interconnection lines are bridging the bond attractor with the 4 closest bond-attractors in the boron plane and 2 bond attractor from the neighboring boron planes.

Delocalization Indices

The electron pair density is a spatial function depending on the coordinates of two electrons. The integral of the pair density over a chosen region yields the number of electron pairs within. The integration can also be performed in such a way that each electron is confined to a separate region, giving the number of pairs between the regions.

For convenience, the number of pairs can be decomposed into the product of electron populations and a part connected with exchange-correlation effects. It is the latter part of the pair density integrals that is utilized for the bonding analysis. The exchange part of the pair density integral computed between two regions A and B is termed the delocalization index $\delta(A, B)$ [8]. With the basins for the electron density or ELI-D at hand the delocalization indices between the basins can be evaluated. In case of density basins for diatomic molecules the $\delta(A, B)$ index can be connected with the bond order [9].

The determination of the delocalization indices in DGrid was interfaced with the solid state program Elk, and a selected set of compounds was examined [10]. The dense packing in solid state compounds favors long range pairing of electrons. Accordingly, significant values of the delocalization index were found between more distant density basins, for instance for graphite or the metals Na and Cu. Thus, in *fcc* Cu an atomic basin (i. e., determined by electron density) shares 0.66 electron pairs with all the basins other than the closest neighbors (there are $12 \times 0.26 = 3.12$ electron pairs shared with the 12 closest atomic basins; this can be contrasted with the single electron pair found for the Cu_2 dimer).

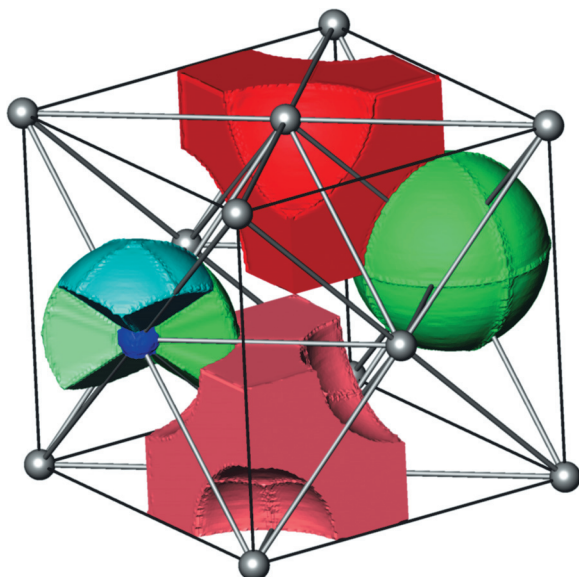


Fig. 3: ELI-D basins for *fcc* Cu. Red: basins in the bonding region. Blue sphere: core basin surrounded by 3rd shell basins. Green sphere: 3rd shell basin set.

ELI-D for *fcc* Cu shows, besides the concentric atomic shells, attractors in the bonding region (outside the 3rd ELI-D shell of Cu). The corresponding bonding basins are presented in Figure 3 as red objects, each enclosing 1.1 electrons. For the 3d transition elements it is useful to merge the basins of the two innermost atomic shells into the inner-core superbasis (the small blue-colored basin in Figure 3 enclosing 10.5 electrons) and analyze the 3rd shell basins separately. In *fcc* Cu each inner-core basin is surrounded by six 3rd shell basins. Interestingly, these 3rd shell basins (each populated by 2.7 electrons) share electron pairs mainly with the other basins of the same 3rd shell and the inner-core basin. This supports the idea of merging the 3rd shell basins into a single basin set forming nearly a sphere (cf. the large green sphere in Figure 3; the whole 3rd shell ELI-D basin set is populated by 16.4 electrons). For each Cu site the 3rd shell basin set shares $8 \times 0.26 = 2.10$ electron pairs with the 8 closest bonding basins (even the inner-core basin still shares $8 \times 0.018 = 0.144$ pairs with the bonding basins). The sharing indices allow for deeper inspection of the pairing interactions between specific regions.

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