Chemical Bonding in Intermetallic Phases

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The four topics included in this report are given in a certain logical order. We start with a theoretical electron-density (ED) reconstruction study [1] suitable for QTAIM analysis via a tuneable Fourier synthesis approach. The second topical report [2] presents a study where the relation between computed QTAIM atomic charges of Pt atoms in binary Pt-Al intermetallic phases and experimental HAXPES results on Pt core level shifts is resolved within the ED-ELI approach [3]. The third topic [4] reports a computational study, that relates the QTAIM atomic charges in 8-valence electron main-group compounds of the TiNiSi type of structure to polar-covalent bonding conceptually described by an $8–N^{\mathrm{eff}}$ octet-rule implemented within the ED-ELI approach. The fourth topical study [5] on multicenter bonding describes the results of a new quantum chemical approach using delocalization ratios to analyze multi-center bonding situations in prototype *closo* borane clusters in a way that can be related to, but also goes beyond, the classical Lipscomb *styx* concept. In a purely conceptional study [6] the octet-rule fulfillment in this type of clusters is analyzed with a novel approach based on a topological octet-rule implementation (TORI).

The mission of this 22-years project was the development and application of mutually interrelated position-space chemical bonding approaches in order to decipher the complex chemical bonding scenarios in intermetallic phases, while still staying basically grounded by observable physical quantities.

Based on the foundational theorems of Hohenberg and Kohn, the electron density (ED) distribution of a chemical system like a molecule or a solid can be considered as one of the most fundamental scalar quantum fields that is experimentally accessible. The static ED distribution is the key ingredient for the exhaustive partitioning of 3D position space into atomic regions in the QTAIM (Quantum Theory of Atoms in Molecules) [7] approach.

The 1-particle distributions of the ED and its Laplacian also play the role of local bonding indicators. The ED itself constitutes part of the "Interacting Quantum Atoms" approach in crystals [8] for total energy partitioning into intraatomic self-energies and interatomic interaction energies in position space where it yields the Coulombic interaction energy between QTAIM atoms. This is complemented by the exchange-correlation interaction energy between two QTAIM atoms using explicit information from the electronic pair density.

The 2-particle properties of the electron distribution are closely related to the local chemical bonding indicators ELI (electron localizability indicators) for singlet and triplet coupled electron pairs [9] as well. The complementary information contained in electronic 1- and 2-particle distributions are combined in the ED-ELI approach [3].

Electron density reconstruction via a tuneable Fourier synthesis approach

The fact that it is possible to reconstruct ED distributions for crystalline solids from high-end x-ray diffraction experiments makes it an interesting research topic to work on systematically improving the ED reconstruction quality. The earliest and unbiased way for ED reconstruction is the Fourier "back-transformation" of experimental structure factors, which typically needs some additional smoothing function to prevent series truncation artefacts. Many experimental ED-reconstruction studies nowadays employ the Hansen-Coppens (HC) type of density multipole fitting, which may not be free of a certain basis set bias. This uncertainty may prevent it from challenging quantum chemical methods for electronic structure calculation.

The topic of this pilot study is the development and detailed evaluation of a tuneable Fourier-synthesis approach solving the task of extracting static ED and ED Laplacian distributions sufficiently precise for a QTAIM analysis from a finite data set of static all-electron or valence-electron ED structure factors [1]. The quantum chemically (DFT) computed ED distribution and the derived static ED structure factors of the compound CaB_6 crystallizing in a cubic *cP*7-type of structure have been exemplarily chosen for this study. The choice of a theoretical ED distribution as a reference for the synthesized distributions enabled a detailed error and convergence analysis of the Fourier synthesis methods employed.

For the purpose of getting rid of non-nuclear maxima (NNM) artefacts, a new strategy has been introduced to supplement each weighting *method* (6 methods either from the literature or newly developed) with a suitable smoothing factor *exponent*, such that the final weighting functions used were of the type *method*(*exponent*) (ME approach). The *exponent p* was adjusted to take the smallest possible value ($p \geq 1.0$) leading to ED distributions without occurrence of NNM artefacts. The smaller p values led to smaller norm deviations of the synthesized EDs. Using higher *exponents* within each *method*, eventual resolution-dependent ED Laplacian contour ripples can be systematically smoothed out as well, however at the expense of increased ED norm deviations, such that a compromise is to be found. As a result, a Fourier synthesis approach has been presented, which yields a systematic reconstruction-quality improvement of ED and ED Laplacian distributions from both, valence-electron and all-electron static structure factors with increasing resolution $(\sin(\theta)/\lambda)_{\max}$. The decisive issue is the application of tuneable weighting functions to avoid series termination artefacts while extracting the maximum amount of chemical bonding information.

Convergence of the ED and ED Laplacian distributions with respect to the corresponding reference DFT-based distributions with increasing resolution $(\sin(\theta)/\lambda)_{\max}$ was clearly demonstrated by analysis of norm deviations of the synthesized distributions, QTAIM effective charge deviations, and ED and ED Laplacian value deviations at chemically important ED critical points. The criteria for successful and sufficiently precise reproduction of the characteristic ED and ED Laplacian features important for chemical-bonding arguments were based on qualitative relations of values between different critical points rather than on absolute value convergence. Based on this type of criteria, successful reconstruction of the val-ED and its Laplacian from valence-electron structure factors is found for resolutions ≥ 1.2 Å^{-1} and for all-ED structure factors $\geq$ 2.0 Å^{-1}.

Calculation of static ED distributions within the Hansen-Coppens model using the multipole parameters corresponds to an extrapolation of the experimental data set to infinite resolution. Conversely, in the framework of Fourier synthesis, the application of mathematical weighting functions decaying with increasing $\sin(\theta)/\lambda$ until $(\sin(\theta)/\lambda)_{\max}$ corresponds to systematically down-weighted contributions of the higher reflections, which could be considered as an under-interpretation of these data. Therefore, as a general strategy for robust experimental ED studies it is suggested to consider both approaches in parallel.

QTAIM charges and HAXPES core level shifts

Besides the x-ray scattering method mentioned above, many spectroscopic methods are widely used to probe the electronic structure of compounds. Such measurements also provide data through which the validity of computational electronic structure methods can be assessed. Chemical bonding information like the effective atomic charges is directly contained already in the experimental ED distribution. Moreover, there exist also concepts that derive related chemical information from spectroscopic results. Sometimes, interesting cases show up where the concepts established in many previous case studies seemingly run into contradictions.

A particular case was presented by studying seven binary Al_nPt_m intermetallic compounds. The electronic structure was investigated by hard x-ray photoelectron spectroscopy (HAXPES) using elemental Pt as a reference [2]. It was found that the Pt 4*f* core levels shift towards higher binding energies (BE) as Al content increases. This seems to be in contradiction to the electronegativity scales. The charge transfer is expected to be from Al to Pt such that Pt should get more negative as Al content increases, which was confirmed by the effective QTAIM [7] atomic charges. The more negative the Pt charge, the higher the 4*f* BE was found. These results cannot be reconciled within the standard "chemical shift" approach which argues that core levels shift to higher BE if the atom is positively charged. The shifts to higher 4*f* BE measured imply that Pt should be increasingly positively charged, which contradicts the standard explanation.

A reasonable explanation can be found by considering the basic idea behind the standard reasoning and combining the QTAIM approach with the complementary position-space chemical bonding indicator ELI-D within the ED-ELI approach [3]. The basic idea is about electronic screening of the nuclear Coulomb potential, and the valence electrons most effective in providing this screening are the electrons belonging to the penultimate atomic shell. QTAIM analysis yields the total number of electrons inside the atomic basin. Part of these electrons are engaged in chemical bonding interactions, and their main ED contributions typically lie in the interatomic regions and, to a lesser extent, in intraatomic core region. However, this is not the case for transition-metal *d*-electrons having a dual character [10,11]. For Pt, the number of electrons in the

5th (penultimate) shell may be more effective in the screening than those in 6th shell valence region. Note that, the 5*d* electrons mainly belong to the 5th shell, and 5*d* occupancy changes from compound to compound. In an ELI-D analysis, the number of core electrons can be obtained by integrating the electron density inside the ELI-D core basin region (1st to 5th atomic shell). Since ELI-D analysis places the 5*d* electrons in the core (penultimate shell), the changes in the core basin population is ascribed only to changes in the 5*d* occupancy. This way, for each compound, the number of 5*d* electrons in the Pt 5th shell is calculated by $n_{5d} = n_{core} – 68$ (total number of core electrons for Pt according to the *aufbau* principle).

The calculations reveal a surprising result: the higher the charge transfer $|Q^{eff}|$ to Pt, the lower is n_{5d}. The relative deviation of the 5*d* occupancy for the binary intermetallic compounds, $\delta n_{5d}(Al_nPt_m) = n_{5d}(Pt) – n_{5d}(Al_nPt_m)$, shows a qualitative correlation with relative 4*f* core level shifts: it has a large (small) value if the shift is large (small). Moreover, $\delta n_{5d}(Al_nPt_m)$ was found to correlate with $n_{5d}(Pt)$. With increasing Al content, the amount of charge transferred to Pt also increases, but $\delta n_{5d}(Al_nPt_m)$ decreases, so that there are fewer electrons available for screening the 4*f* core hole causing 4*f* core levels to shift towards higher BE.

Highly negative effective charges accompanied by unexpected XP core level shifts to higher BE were observed earlier in intermetallic systems Ga_nPd_m[12], and Be_5Pt [13]. Yet, only the Al-Pt system with reasonable number of compounds and complete spectroscopic data, was studied in detail. The general validity of the explanation for the counterintuitive core level shifts is to be checked in future studies on other systems.

8–N^{eff} rule for 8 ve TiNiSi type compounds

The QTAIM atomic charges represent effective charges different from conceptual ones, i.e. formal charges or oxidation states. The question arises, how to relate the effective charges to a conceptual picture, and how can the deviations from the non-polar conceptual picture be incorporated into a more realistic conceptual model of chemical bonding taking bond-polarity effects into account?

The study [4] represents an extension of the bonding analysis on polar, conceptually 4-bonded frameworks in cubic half-Heusler (MgAgAs) type compounds of main-group elements [14]. In these studies, a covalent bonding preference of zinc blende type of one partial structure over the other one has been found which seemed to corroborate the classical Lewis-type bonding picture of maximally four covalent bonds per main-group element. In contrast, the orthorhombic TiNiSi type of structure features a much higher geometrical flexibility to optimally arrange metal atoms of different sizes and types. The bonding analysis of 8 ve main-group compounds $AA'E$ ($A = A^{(1,2)}$, $A' = A'^{(1,2)}$, $E = E^{(14\text{-}16)}$) revealed a gradual transition towards a non-Lewis type of bonding scenarios of species E with 9 or 10 polar-covalently bonded metal atoms A, A.

The semiconducting main-group compounds $AA'E$ with 8 ve/f.u. crystallizing in the TiNiSi structure family can be understood within a charge-compensated Zintl-like scheme $A^{x+}A'^{y+}$ ([8–N^{eff}]b)$E^{(x+y)–}$, even for the non-integer charge transfers x and y obtained in the position-space bonding analysis. The total heteroatomic covalency of the compounds, as measured by the amount of covalent bonds N_{cb} of species $E^{(x+y)–}$ according to 8–$N^{eff}(E)$, increases from chalcogenides towards tetrelides according to $N_{cb}(E^{16}) < N_{cb}(E^{15}) < N_{cb}(E^{14})$. This increase is consistent with the associated EN(E) decrease. Noteworthy, the most covalent polar-bonding situations (2b', 2lp') appearing with the $E^{(14)}$ anions and large A^2, A^{2}' cations are also those for which the band gap closes. It may indicate that the (2b', 2lp') situation could be an upper boundary for multiatomic polar-covalent bonding systems understandable within the charge-compensated Zintl scheme. Further studies of this interesting issue are necessary.

Different views of the two competing MgAgAs and TiNiSi crystal structure types of $AA'E$ main-group compounds have created a conceptual gap between them. This difference is caused by the identification of a diamond type of partial structure in the former, and the absence of such a tempting coordination in the latter. Thus, while the TiNiSi type main-group compounds are usually treated with the predictive type of approach, e.g. CaMgSn is formally considered as Ca^{2+} Mg^{2+} (0b)$Sn^{4–}$, the MgAgAs type ones are often interpreted in the framework of the analytical type of approach emphasizing one covalently bonded zinc-blende type partial structure, i.e. a compound like LiAlGe is formally considered as Li^{+} (4b)$Al^{–}$ (4b)Ge^{0} rather than as Li^{+} Al^{3+} $Ge^{4–}$. The current study on TiNiSi type main-group compounds closes the conceptual gap between those and the MgAgAs type of main-group compounds by analysis of polar-covalent bonding within the 8–N^{eff} scheme.

Neither the crystal chemical nor the bond-polarity analysis of the 8 ve/f.u. main group compounds of the TiNiSi-type (*AA'E*) studied support the familiar notion of a '[NiSi]' = [*A'E*] type of network with filler atoms of type 'Ti' = *A* in the voids. The present study yields a basic understanding of differences in nonmetal–metal coordination from the viewpoint of bonding polarity for the polar multi-atomic bonds found already in the semiconducting main-group compounds. It forms a basis for future studies of TiNiSi-type compounds with transition metals.

Multicenter Bonding

The special feature which 2-center polar bonding and multicenter non-polar bonding have in common is the occurrence of fractional covalent bond orders. Bonding scenarios become conceptually intricate, if both types of bonding effects occur simultaneously. This is typical for many intermetallic phases like the ones of the AlB_2 structure type [15]. To disentangle both effects, studies focusing on each effect separately by selecting suitable chemical systems is the appropriate strategy. The study of non-polar multicenter bonding is the topic of the present section.

a) Multi-center bonding analysis: styx and beyond

Closo-boron hydrides $B_nH_n^{2-}$ (n = 5 to 12) are a conceptually well understood class of compounds. For these and a few related prototype compounds, both the local and the global picture of 3-center bonding are extracted from position-space quantities based on the electron density and the pair density [5]. For this purpose, three-center delocalization indices between QTAIM atoms are used to develop a consistent set of local bond- and triangle-, as well as global cluster-delocalization ratios (*DR*s), which are quantitatively compared to conceptual Γ values derived from the *styx* code for each cluster. Combination of the cluster *DR*s with associated effective numbers of skeletal electron sharing (*SES)* for selected cluster surface edges, triangles or the whole cluster yields effective *styx* values describing the trend – and even the size – of the conceptual *styx* codes for *closo*-boranes $B_nH_n^{2-}$ and related systems with increasing cluster size n reasonably well. For non-uniform cluster topologies, the different skeletal vertex degrees are shown to cause systematic 3-center wise delocalization effects for the associated topologically different edges and triangles of different average vertex degrees.

The possibility to proceed beyond the initial *styx* restrictions by triangulation of the full-skeleton electron delocalization seamlessly opens the perspective of bonding investigations of endohedral clusters with multiple atomic shells. The successfully established chemical interpretation of the local edge, triangle, and global cluster *DR*s with their associated *SES* values constitutes the basis for systematic investigations of mixed 2- and 3-center bonding scenarios in intermetallic and related cluster compounds in the future.

b) Topological Octet Rule Implementation

The octet rule represents one of the most basic principles of the science of chemistry. In the large class of main-group element Zintl phases, the octet rule plays an immediately visible role only in the Zintl-type polyanions following the pseudo-atom concept in the framework of the 8–*N* rule. In the conceptual framework of the Wade's type of clusters, the relations to the octet rule are less obvious. This issue is addressed in [6] for the class of the most delocalized *closo*-type main-group clusters by generalizing the basic ideas behind the Lipscomb's *styx* code. A complementary topological implementation of the octet rule (TORI) is introduced which is based on the average topology of the deltahedral cluster skeletons and the fractional bond distributions of the delocalized bonding scenario obtained after resonance averaging of Lewis type 2-electron bond allocations. For the same skeletal electron pair count SEP^{closo}, TORI yields values similar to (0, t, y, 0) of the *styx* code. In contrast to the *styx* concept, in the TORI approach two hierarchically different types of octet-rule fulfillment are identified, the local one and the cluster-wise one. The local octet-rule fulfillment always implies the cluster-averaged one, while the converse is not true. This way, seemingly isoelectronic deltahedral clusters with different skeletal topologies and identical *SEP* count can be distinguished by their specific way satisfying the cluster-wise and local octet-rule. The main difference to the 8–*N* type of partial structures identified is the more flexible way of octet-rule fulfillment in the Wade's type of clusters which does not prevent them from realizing the same cluster topology with different *SEP* counts. In contrast, the 8–*N* rule for Zintl-Klemm type of polyanions allows only one unique electron count for a specific partial structure.

External Cooperation Partners

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