Heteropolar Bonds and a Position-Space Representation of the 8−*N* Rule

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The chemical bonding of main-group Zintl phases, MgAgAs-type and zinc-blende-type compounds is analyzed with the aid of quantum chemical position-space indicators.[1] The 8−*N* rule - basis for the formal description of chemical bonding in Zintl phases - is reformulated in position space and extended for the quantitative and consistent description of heteropolar bonding present in the compounds of the MgAgAs and zinc-blende type. Heteropolar bonds (p) are understood as a superposition of a nonpolar covalent part (b') and a polar hidden lone-pair part (lp') according to (p) = (*x*b',[1-*x*]lp'). The particular ratio of nonpolar and polar part depends on the atoms' contributions to heteropolar bond similar to a classical Lewis formula (Figure 1). A covalent bond is characterized by an equal electronic contribution of the bonding partners, a lone pair is characterized by a component's complete ownership of the electron population. The intermediate bonding situations represent heteropolar bonding.

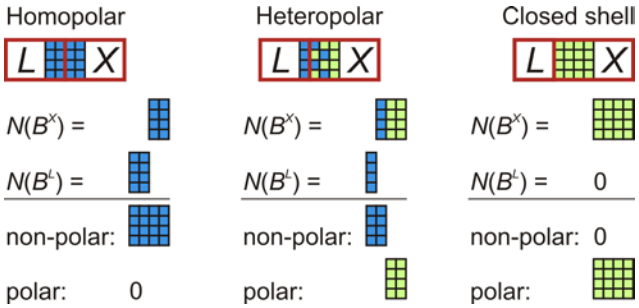

Figure 1: Thick red lines represent atomic boundaries of the atoms *L* and *X*. The valence region *B* between the atoms is represented by 16 colored minisquares: blue indicates nonpolar, green indicates polar bonding. Each square represents an equal fraction of the electronic population of the valence region $N(B)$. Atomic contributions to the valence region: $N(B^L)$ and $N(B^X)$.

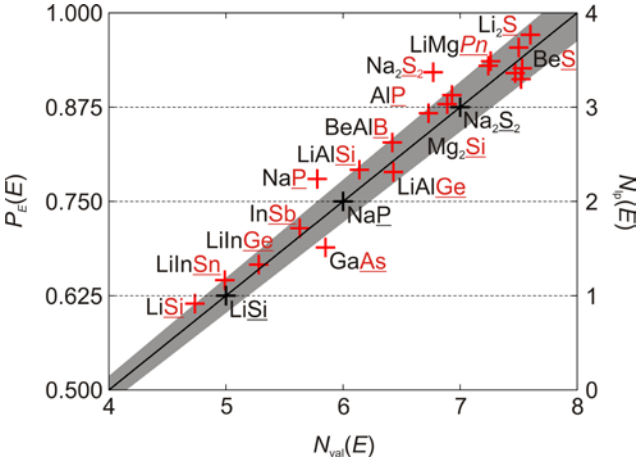

Figure 2: 8−*N* rule from a position-space perspective (red crosses). Black line and crosses represent the formal 8−*N* rule. Valence electron number $N_{val}(E)$ and charge claim $P_E(E)$ of the anions *E* yield the number of lone pairs $N_{lp}(E)$.

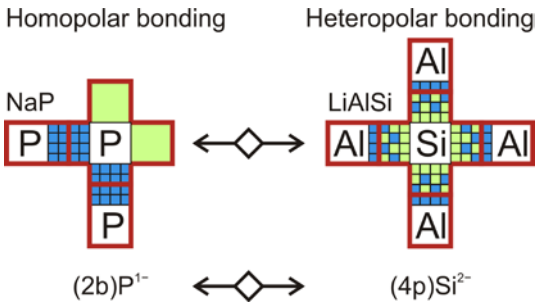

Figure 3: Analogy of compounds with homopolar and heterpolar bonding is indicated by the arrow symbol.

The access electron number $N_{acc}(E)$, the valence electron number $N_{val}(E)$, and the charge claim $P_E(E)$ recover the 8−*N* rule in position space and allow the treatment of heteropolar bonding according to the presented model (Figure 2). The equal treatment of compounds with homopolar and heteropolar bonding leads to an interesting analogy of the bonding situations (Figure 3).
Additionally, the position space variant of the 8–N rule provides a new framework for analysis of non-tetrahedral partial structures and even compounds with non-octet atomic species.

[1] D. Bende, F. R. Wagner, Yu. Grin, *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.5b00135.