

performance in electronegativity equalization methods discussed [9]. Finally, based on Hirshfeld-I derived density matrices [10], an AIM is formulated in momentum space.

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**Keywords:** density, quantum, charge

### MS.34.3

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#### Relativistic effects on the topology of the electron density

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The topological analysis of electron densities obtained either from X-ray diffraction experiments or from quantum chemical calculations provides detailed insight into the electronic structure of atoms and molecules. Of particular interest is the study of compounds containing (heavy) transition-metal elements, which is still a challenge for experiment as well as from a quantum-chemical point of view.

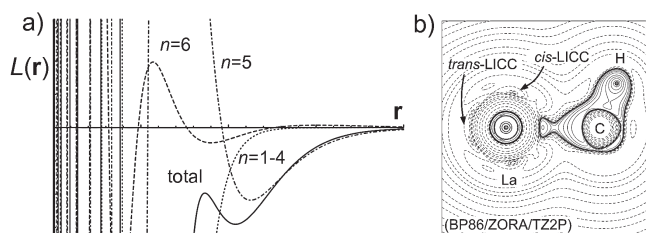
Accurate calculations on such systems need to take relativistic effects into account explicitly. Regarding the valence electron density distribution, these effects are often only included indirectly through relativistic effective core potentials. But as different variants of relativistic Hamiltonians have been developed all-electron calculations of heavy elements in combination with various electronic structure methods are feasible. In a previous study on the topology of the total electron density distribution of model systems  $M(C_2H_2)$  ( $TM = Ni, Pd, Pt$ ) calculated in different relativistic approximations we have compared several relativistic Hamiltonians with respect to their effect on the electron density in terms of a topological analysis [1].

In the present work we extended these studies to model systems containing lanthanide elements (for example  $[La(CH_3)_2]^{2+}$  and  $La(CH_3)_3$ ). Besides the investigation of relativistic effects on the topology of the electron density, we concentrated on two additional aspects: We analyzed the general polarization pattern of lanthanide atoms in metal organic complexes as revealed by the Laplacian of the electron density,  $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ , and the Electron Localization Function (ELF). For  $L(\mathbf{r})$  it is known for example from studies on isolated La atoms that starting from  $n = 5$  the valence shells can only be resolved as local maxima with  $L(\mathbf{r}) < 0$  (see Figure a) [2].

The results of our study indicate that the general pattern of local charge concentrations (LCCs) in the valence region of 6<sup>th</sup> row elements can still be observed in  $L(\mathbf{r})$  and that in the case of the Lanthanum model complexes investigated this pattern shows a clear effect of the 4f-orbital contributions to the bonding molecular orbitals (see Figure b).

The second aspect of the present study concerns the possibility to recover the polarization patterns of such heavy elements by a multipolar refinement of structure factors calculated from electron density distributions obtained by relativistic density functional theory calculations. The results indicate that several independent sets of multipolar functions at one atomic site are required in order to fully

recover the electron density distributions in the model-systems under investigation.



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### MS.34.4

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#### Electron Deficient and Polycenter Bonds in $\gamma$ -B<sub>28</sub>

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The recently established superhard high-pressure  $\gamma$ -B<sub>28</sub> polymorph of boron has grown a resurgence of interest in this element [1]. The crystal structure of  $\gamma$ -B<sub>28</sub> consists of cubic closest packed icosahedral B<sub>12</sub> units with B<sub>2</sub> dumbbell units placed on the octahedral sites. A charge-density study has been carried out in order to understand the nature of chemical interactions within  $\gamma$ -B<sub>28</sub>. Charge densities of  $\gamma$ -B<sub>28</sub> have been obtained by the multipole refinement using the computer program XD2006 [2] against low-temperature, high-resolution, single-crystal synchrotron X-ray diffraction data. Interpretation of the electron density with the aid of Bader's quantum theory of atoms in molecules (QTAIM) [3] reveals the existence of an one-electron-two-center bond between B<sub>12</sub> units, which explains the covalent bonding mechanism in  $\gamma$ -B<sub>28</sub>. The charge separation previously reported has been found to be a local phenomenon, driven by a unique polar-covalent two-electron-three-center bond between two boron atoms of the B<sub>12</sub> unit and one boron atom of the B<sub>2</sub> unit.

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**Core and valence electron density distribution in a Ga<sup>I</sup> NHC-analogue**