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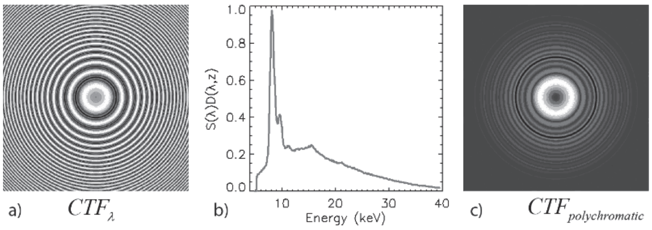
Quantitative phase imaging with polychromatic sources

Mac B. Luu,[a,b] Chanh Q. Tran,[a,b] Andrew G. Peele.,[a,b,d] [a]*Department of Physics, La Trobe University, Victoria 3086, (Australia).* [b]*Center of Excellence for Coherent X-ray Science, (Australia).* [d]*Australian Synchrotron, (Australia).* E-mail: bmluu@students.latrobe.edu.au

In most laboratories, X-ray sources are polychromatic. To date, X-ray absorption contrast imaging with polychromatic sources has produced good qualitative results when it is used for high absorbing objects. However, the application of the absorption based technique to weakly absorbing objects remains limited.

Phase contrast imaging has been widely recognized as a unique tool to study weakly absorbing objects [1], [2], [3]. A phase retrieval algorithm based on the so-called Contrast Transfer Function (CTF) approach [4] has been demonstrated to quantitatively reconstruct the thickness of weakly absorbing homogeneous samples using monochromatic sources. The technique can be applied to propagation distances ranging from the near field to the holographic regions.

In this work we propose an extension of the CTF algorithm to polychromatic sources [3]. Principles and simulated results of the new technique will be presented. We will discuss quantitative experimental results for homogeneous samples using (a) synchrotron radiations with a significant harmonic content; and (b) a laboratory X-ray source. The experimental results indicate highly potential applications of the technique to quantitative studies of both 2D and 3D samples.



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Keywords: polychromatic source, contrast transfer function, X-rays phase imaging

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An account on multicenter bonding and its relationship with aromaticity

Eduard Matito,[a] Ferran Feixas,[b] Miquel Solà,[b] [a]*Kimika Fakultatea, Euskal Herriko Unibertsitatea, Donostia, Euskadi (Spain).* [b]*Institut de Química Computacional, Universitat de Girona, Catalonia (Spain).* E-mail: ematito@gmail.com

There has been renewed interest in the calculation of different indices based on the electron density matrices to account for multicenter bonding [1-6]. Some of these quantities have also been used as aromaticity indices, providing very good results as compared to other aromaticity indicators [7], [8]. Multicenter indices are thus perfect candidates to account for aromaticity from the electron delocalization perspective. The general formula for the calculation of the multicenter index involves the very intuitive *n*-order central moment of the electron population used in probability theory [9], [10]:

Unfortunately, the calculation of this quantity is not trivial, especially in correlated methods for which the computation of the *n*-density matrix is necessary. In this talk we review the concept of multicenter bonding and its application to aromaticity. First we present I_{ring} [1], *MCI* [2] and their recently introduced normalized variants, I_{NG} and I_{NB} [3]. We analyze the different formulations suggested in the literature, either in terms of the corresponding *n*-density matrix or its simplified version in terms of the first-order density matrix. An analysis of the differences between these approaches is performed and we suggest new formulae, which approximate the *n*-density matrices in different ways.

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Keywords: aromatic, multiple, bonding

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The hirshfeld-i method: atoms in molecules and chemical bonding perspective

Patrick Bultinck, *Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Gent, (Belgium).* E-mail: Patrick.Bultinck@UGent.be

The Hirshfeld method for the atom in the molecule (AIM) was born from crystallography and relies on the use of a so-called promolecule [1]. The promolecule is composed of all atoms in their respective locations in the molecule and a promolecular density is obtained as the sum of all isolated atomic densities. At every point in space, the share of an (isolated) atom in the promolecular density can be easily computed via their ratio and the key element of the Hirshfeld method is that this ratio is then used to extract an AIM density from the molecular electron density . That is:

$$D(A_1,\ldots,A_n) \sim \left\langle \left(\hat{N}-\overline{N}\right)^n \right\rangle_{A_1,\ldots,A_n}$$

Unfortunately, the results of Hirshfeld analysis depend heavily on the isolated atom states used to compute the AIM weight functions. In the improved Hirshfeld-I method, the Hirshfeld process is repeated until self consistency is reached. In other words: the charge on the AIM and the isolated atom are the same. In this presentation the information theoretic context of Hirshfeld-I is sketched, performance of the method compared to regular Hirshfeld analysis discussed, its impact on the nature of atom condensed Fukui functions described, and its use for good quality monopole approximation electrostatic potentials is shown [2-6].

Electron delocalization indices, as obtained using the Hirshfeld-I method, are described [7] and the excellent Hirshfeld-I AIM charge 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

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Relativistic effects on the topology of the electron density

Georg Eickerling, Kilian Batke, Wolfgang Scherer *Institut für Physik, Universität Augsburg, Universitätsstrasse 1, 86159 Augsburg, (German*y). E-mail: georg.eickerling@physik.uni-augsburg.de

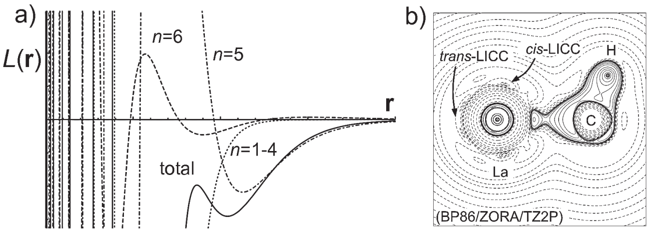
The topological analysis of electron densities obtained either from X-ray diffraction experiments or from quantum chemical calculations provides detailed insight into the electronic structure of atoms and molecules. Of particular interest is the study of compounds containing (heavy) transition-metal 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 $[La(CH_3)]^{2+}$ 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 6th 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 4*f*-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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Keywords: electron density, topology, relativistic effects

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Electron Deficient and Polycenter Bonds in γ-B$_{28}$

Swastik Mondal,[a] Sander van Smaalen,[a] Andreas Schönleber,[a] Yaroslav Filinchuk,[b] Dmitry Chernyshov,[b] Sergey I. Simak,[c] Arkady S. Mikhaylushkin,[c] Igor A. Abrikosov,[c] Evgeniya Yu. Zarechnaya,[d] Leonid Dubrovinsky,[d] Natalia Dubrovinskaia,[a] [a]*Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth (Germany).* [b]*Swiss-Norwegian Beam Line, ESRF, 38043 Grenoble (France).* [c]*Theory and Modeling Division, IFM, Linköping University, 581 33 Linköping (Sweden).* [d]*Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth (Germany).* E-mail: swastik.mondal@uni-bayreuth.de

The recently established superhard high-pressure γ-B$_{28}$ polymorph of boron has grown a resurgence of interest in this element [1]. The crystal structure of γ-B$_{28}$ consists of cubic closest packed icosahedral B$_{12}$ units with B$_2$ 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 γ-B$_{28}$. Charge densities of γ-B$_{28}$ 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$_{12}$ units, which explains the covalent bonding mechanism in γ-B$_{28}$. 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$_{12}$ unit and one boron atom of the B$_2$ unit.

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Keywords: X-ray_diffraction, charge_density, boron

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Core and valence electron density distribution in a Ga^{I} NHC-analogue