Quantum Crystallography
Online Meeting 2020
QCrOM2020

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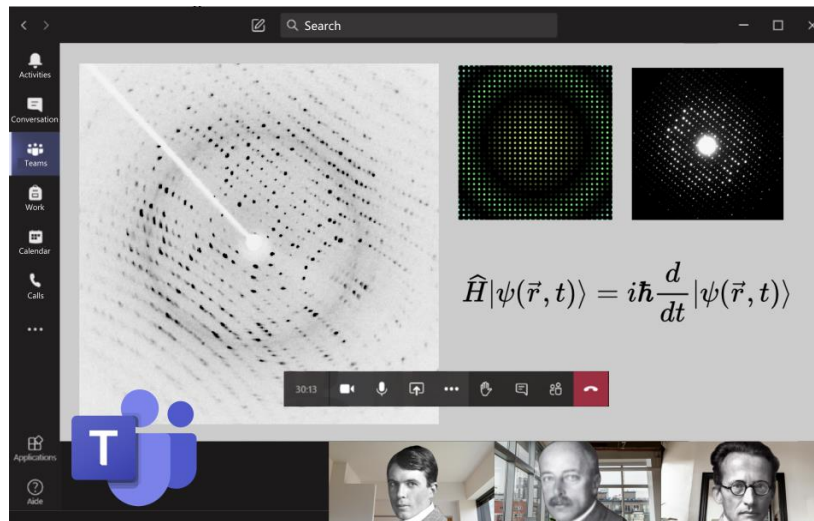
Book of Abstracts

Commission on Quantum Crystallography of IUCr

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A meeting in memory of
E.D. Stevens, Dirk Feil and Wolf Weyrich

Edwin David Stevens died in May 2020. He was a leading high-resolution X-ray diffraction expert (especially TDS). As one of the pioneers in electron densities, collaborating with P. Coppens, E.D. Stevens had a profound impact on quantum crystallography as we know it today. He is remembered as a very generous collaborator always willing to help the young researchers, for example in discovering the Kappa-refinement subtleties. Among other contributions, he was the first to give an estimate of d-orbital populations while studying a cobalt phtalocyanine. *An obituary page was created by the University of New Orleans in honour of E.D. Stevens[1].*

Dirk Feil passed away in April 2020. He was a deep-thinking scientist who has served the charge density community in a number of ways during the second half of the twentieth century. Dirk was active in many aspects of charge density and, later in his career, worked on intermolecular interactions. He had the well-deserved reputation of an enthusiastic professor in Twente and a fantastic speaker in all the conferences he participated. Dirk Feil was very active when experimental charge density modelling took off, an earlier user of the quantum theory of atoms in molecules and collaborated on many occasions with Bob Stewart and Philipp Coppens. *An obituary article was published by Grant and Barbara Moss in J. App. Cryst.* **53(4), 2020,** *pp1167-1168.*
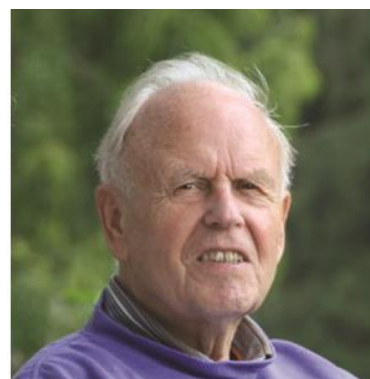
Wolf Weyrich passed away in April 2019. Wolf was a modest and quiet scientist who had a valuable contribution in the momentum space aspects of charge (and spin) density. He was a very rigorous and careful experimentalist who successfully explored the possibilities of gamma-rays then synchrotron radiation to bring new insights from the momentum space analysis to chemical bonds. Quite naturally, without always intending to do so (the density matrices workshop in Brest was a crucial step) Wolf educated some of us to the importance of density matrices, and the complementarity of position and momentum representation approaches. *A nice recollection of Wolf's work was published on his 60th birthday by M. Springborg in Zeitschrift für Physikalische Chemie* **220(7) 2006 pp 793-796.**

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[1] https://www.uno.edu/news/2020-05-14/in-memoriam-chemistry-prof-edwin-david-stevens.

Welcome to QCrOM2020

Quantum Crystallography Online Meeting 2020 is not the recurrent Summer meeting which we all cherish. It bears no resemblance to the conferences we have been taken to by our PhD advisor ever since we first stared at an electron deformation density map. There is little chance that ten years from now, we might rediscover a group photo taken on the stairs of the conference centre. We will not remember having spilt our coffee on our neighbour while rushing to the snack table during a short break.

However, we will remember that this meeting was held at the end of a very peculiar summer, which followed a no less awkward, if not painful, academic semester. For the first time the IUCr meeting, planned to be held in Prague late August, was postponed by a year. We all had scheduled a trip there and were anticipating new exciting discussions. We were looking forward to hearing about the progress of our colleagues and friends. We were devising the most appropriate way to explain our latest results. For all of us, this change meant a sudden lack of scientific interaction, less opportunity to get feedback from the community and fewer opportunities to receive advice from more experienced researchers. It was bound to have a significant impact on the work of the youngest of our colleagues. The flow of ideas, boosted by scientific meetings, could not be interrupted without any harm. Some alternative had to be put forward. Soon enough, it dawned on us that the most natural way was to replace direct photon-mediated face-to-face interaction by electron-based transmission. Internet was the easiest way to go. Ten years down the road, we will probably still have in mind how much time during the lockdown, we had to sit in front of our camera. We will remember having mildly attended meetings, trying to make students interact during lectures and, most importantly, worrying and caring about our elders. And, yet, before starting a new academic year while the uncertainties around the pandemic were still substantial, we were ready to spend extra hours facing our screen. We knew it was not what we had been hoping for, but the best compromise given the sanitary conditions. And definitely, better than no meeting at all.

Now, it has become an online three-day meeting on 27th, 28th and 29th August 2020. In addition, the 26th of August is devoted to presenting Quantum Crystallography to a broader audience. The goal is to give the basics to the newcomers so that they can enjoy the three following days of state-of-the-art science.

This new opus, QCrOM2020 as we now call it, was initiated under the auspices of the IUCr Quantum Crystallography commission. Nonetheless, the meeting would not exist without the outstanding work conducted by four undergraduate students from CentraleSupelec: Antoine Marras, Sara Delahaie, Nizar Melk and Hugo Julien. They are responsible for the very welcoming website with its original design (Antoine takes the honours as the webmaster) which is our virtual venue with its poster presentation rooms, the conference hall, the interactive schedule, and many more features. They collected (almost in time) about 40 abstracts and edited this book. I hope that this will endure as a trace of what we have been through, how science managed to find its way and how the exchange of ideas continued to fuel our research.

I hope that when the pandemic is over, we will still remember this Quantum Crystallography Online Meeting 2020 as a fruitful experience, with plenty of exchanges, new research paths, connections and collaborations. All that with less harm to our planet.
Have a wonderful meeting and enjoy your next ten years.

Jean-Michel Gillet, chairman of the IUCr Quantum Crystallography commission

Acknowledgments

CentraleSupélec

CentraleSupélec (CS) is a French institute of research and higher education in engineering and science. It was established on 1 January 2015 as a result of a strategic merger between two leading grandes écoles in France, École Centrale Paris and Supélec. It is a key founding member of the popeEurope) network and also the CESAER association of European engineering schools.

Université Paris-Saclay

Université Paris-Saclay is a French institution composed of universities, grandes écoles and research institutes. Its members include for instance CentraleSupélec, ENS Paris-Saclay and Université Paris-Sud. Its cluster model tends to make it a real centre of innovation and cutting-edge research. Ranked first in the world in mathematics and first in Europe in physics in the Shanghai rankings, Université Paris-Saclay stands out as a major international player in higher education

ViaRézo

ViaRézo is CentraleSupélec's student network and computer science association. It provides Internet on the Paris-Saclay campus as well as all kinds of computer services, such as an internal social network, a site of annals and revision sheets, and mailing lists. We also offer hosting of servers and web sites.

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Day 1

Quantitative Tools for Noncovalent Bonds in Crystals

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Keywords: Electron density, PEAM, three-center four-electron halogen bonds

The recent progress in synthesis of chalcogenazoles has spurred widespread research in the area of potential applications of these compounds in materials science. The understanding of the nature of noncovalent bonds in molecular crystals provides our influence on the properties of novel materials. Thione-iodonium three-center four-electron halogen bonds [S-I$^+$-S] and the other electrostatically driven noncovalent interactions in dithiazolium salts with polyiodide motifs are in the focus of our study.
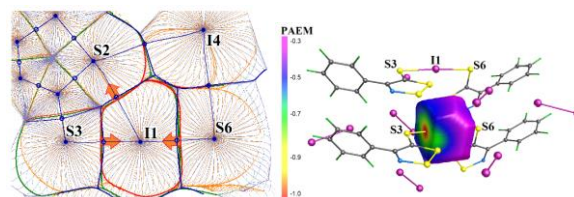
Figure 1 a) Superposition of gradient fields for PAEM, electrostatic potential and electron density with nuclei and bond critical points; b) PAEM (a.u.) mapped on the surface of iodonium atomic basin for three-center halogen bond [S-I+-S] in 1,2,3-dithiazole-5-thione polyiodide crystal1.

As a powerful tool for identifying and quantitative characterization of bond properties in molecular crystals, we suggested using the potential acting on an electron in a molecule (PAEM). Superposition of the boundaries of atomic basins in PAEM, electron density and electrostatic potential allows us to understand the features of strong and weak halogen or chalcogen bonds, and their synergistic effects in organic crystals. Calculations have been performed in WinXPRO 3.4.11 and 3DPlot programs[2].

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UBDB+EPMM method as a tool for calculating electrostatic interactions in protein-RNA complexes

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Keywords: interaction electrostatic energy, UBDB databank

My current project is focused on IFITs proteins (Interferon-induced proteins with tetratricopeptide repeats) which are expressed in cells infected by viruses. By binding foreign RNA they prevent synthesis of viral proteins in human host cell. IFIT1, IFIT2 and IFIT5 bind different forms of RNA: with triphosphate group or cap at 5' end of RNA. I calculated electrostatic interactions in selected complexes of IFIT1 and IFIT5 proteins with RNA and compared the results with experimental values of binding affinity.

One of the more advanced methods to calculate electrostatic energy is University at Buffalo Pseudoatom DataBank[1] (UBDB) together with Exact Potential Multipole Method[2] (EPMM). UBDB enables reconstruction of charge density for macromolecules in quantitative manner. By UBDB+EPMM approach, which takes also charge penetration effects into account, it is possible to compute electrostatic energies with similar accuracy as with quantum chemistry methods, but much faster. Energy calculation are based on the structures deposited in PDB: IFIT5 proteins with pppRNA[3] and IFIT1 proteins with different 5' end of RNA[4]. I want to discuss the hypothesis of the lack of influence of RNA sequence on interaction energy in IFIT-RNA complexes. Moreover I will examine how modifications at 5' end of RNA alter interaction strength.

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High pressure computational search of trivalent di-nitrides

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Keywords: high pressure, nitrides, computational chemistry

Nitrides are much less studied than the corresponding oxides but have been shown to give rise to ultrahard and superconducting materials that can find application in modern technologies as field effect transistors, p-n junctions and energy storage devices.

In this work we focus on binary nitrides with a formally trivalent cation, such as a rare-earth ion.

These class of compounds are mainly studied in their mononitrate form, which exhibit metallic properties. On the other hand, the corresponding nitrogen-rich pernitrides, that can be synthetized under high pressure, exhibit more intriguing properties compared to the mononitrides. In fact, besides the excellent mechanical properties that arise, when $M-N_x$ compounds are synthesized under pressure, they tend to form fairly long chains of nitrogen atoms. The consequent formation of high energy, single N-N bonds is an effective way to store chemical energy. This is not surprising as nitrogen itself is known to polymerize at 110~GPa and 2000~K, forming the so called cubic gauche structure. Moreover, it is known that the alloying of nitrogen with alkali or with transition metal ions, is an effective way to reduce the polymerization pressure. For these kind of materials, several valence configuration have been proposed to try to explain the nature of the nitrogen bonding. Depending on the valence of the cation, in fact, one can find the pernitride structure, with an oxidation state configuration of $M^{4+}N_2^{4-}$ and an N-N bond length of 1.42~Å (single bond), or a dinitride structure, with an oxidation state configuration of $M^{2+}N_2^{2-}$ and a bond length of 1.23~Å (double bond). The case of a trivalent cation does not seem to fit any of the two definitions, and understanding the nature of nitrogen bonding in this case is not so intuitive. Inspired by a recent work on lanthanum [3]pernitrides, we focused on yttrium dinitride (YN_2) and its formation under pressure. In this work we applied an ab-initio Crystal Structure Prediction method ([2]USPEX) to seek for the most stable YN_2 polymorphs up to 100 GPa of pressure. Then we computed the thermodynamic stability of the obtained structures down to ambient pressure using [1]QuantumEspresso. To understand the nature of the N-N bonding and the oxidation state of these materials, we then compare the obtained results with a set of existing compounds. Besides the observations on the nature of N_2 moieties in the three most stable structures we obtained, we also verified structural and dynamical stability by the means of electronic and phonon DOS.

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Invoking QTAIM to interpret the different emissive properties of Cu and Ag coordination polymers

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Keywords: Room temperature phosphorescence, metal-ligand interaction

The photoluminescence properties of 1D and 3D Ag coordination polymers (CPs) based on the cyclic triimidazole ligand (L), i.e. $[AgIL]_n$ and $[AgClL]_n$ respectively, have been determined and compared with those of the isostructural Cu compounds (see Figure 1)[1].
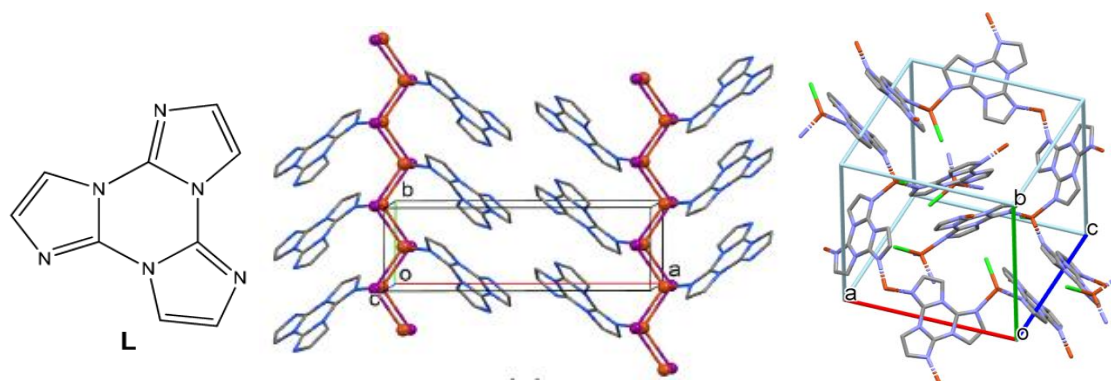
Figure 1 Cyclic triimidazole (L, left) and crystal packing of $[CuIL]_n$ (center) and $[CuClL]_n$ (right)[1]

Powders of Ag CPs display fluorescence and two long-lived emissions at RT, one originated by the ligand itself and the other by the supramolecular H-aggregation of the ligand as observed in both the CPs crystal structures. On the other hand, the spectra of the corresponding Cu CPs are dominated by a broad XMLCT (halogen- and metal-to-ligand charge transfer) band, though proper excitation wavelength can selectively activate the ligand centred transitions. The different behaviour of the Ag and Cu CPs is interpreted also on the basis of QTAIM analysis on Ag and Cu discrete models of the compounds, evidencing in particular a greater covalent character for the Cu–N bond with respect to the Ag–N one.

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Python interface for Crystal14 users

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Keywords: Crystal14, Python

Do you need some help writing Crystal14 input files and visualizing output data? Then you might be interested in the Python interface. Our work consists in a Python-Tkinter program which enables the user to handle Crystal14 input and output files more smoothly. The key features of the program are: 1) write input files, 2) relabel atoms in the primitive lattice, 3) plot data from the Crystal14 output files, 4) Export the plots, 5) Calculations supported: ECHG (Electronic density), XFAC (X-Ray structure factors), CP (Compton profiles) and DENSMAT (density matrix) 6) Add Gaussian noise to data.
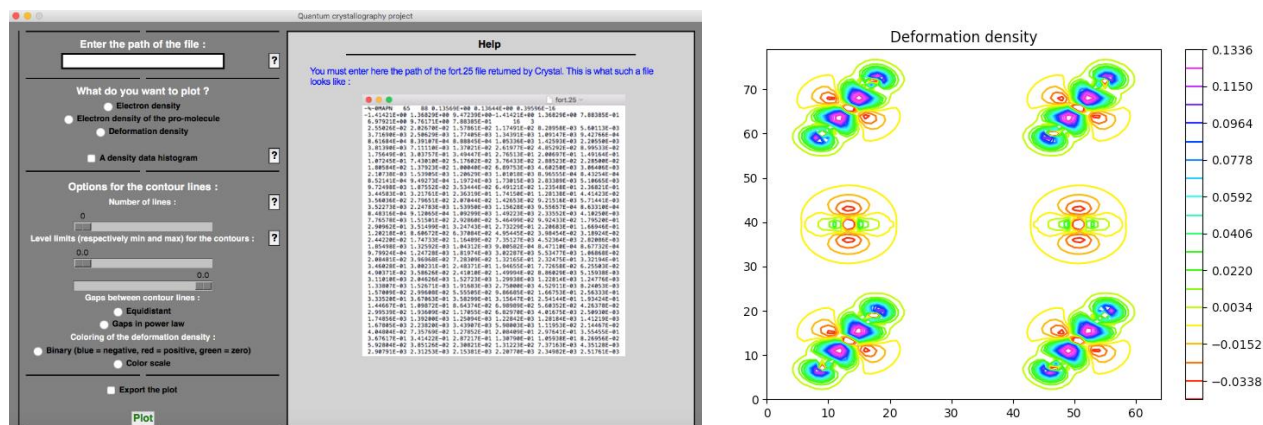
Figure 1: Interface page and deformation density plot

This is the very first version of the program. We will then be glad if you have some suggestions of improvements, or if other functionalities must be added to the interface.

Electronic current density in Covalent Organic Frameworks

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Keywords: COF, QTAIM, DFT, current density

The 2D single layer structure of covalent organic frameworks (COFs) is composed of repeated nanorings made up of smaller rings which are mostly aromatic, i.e. benzene, cyclopentadiene etc.[1] This type of structure opens up the possibility of having a fully conjugated ring network throughout the whole 2D layer, similar to how fullerene possesses 3D conjugation in all of its surface.[2]

To test this we have performed calculations of single nanorings for real COF structures that have semiconducting properties, as well as theoretical fully sp2 conjugated COFs. Using QTAIM at PBE0 density-functional theory level, magnetically induced current densities were studied, as well as delocalization indexes of each nanoring. For an aromatic benchmark the same calculation was performed for a single benzene ring.

For the existing COFs, single nano rings were modeled of CS-COF, BDT-COF,[3] PPY-COF,[4] TP- COF[5] and DA-COF,[6] however the current density results in all structures were always ten times lower than that of benzene's. On the other hand of the _ve theoretical COFs studied, two rendered promising results having current densities three to four times higher that the benchmark benzene's.

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Refinement of electron diffraction data in MoPro: A quest for improved structure model

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Keywords: TAAM, MoPro

The most conclusive and elucidating component of any small or macromolecular study is the proper structure determination. The two most commonly used tool for structure determination are being nuclear magnetic resonance spectroscopy (NMR) and X-ray diffraction. While both these techniques are extremely popular, they have certain limitations. A new technique Cryo-Electron diffraction (ED) data collection for getting near to atomic resolution structures has taken a leap in last few years. In this method, once the three dimensional reciprocal lattice is constructed, the structures are obtained from the ED data using similar tools as used for X-ray diffraction structure solution such as SHE~~XL~~X, OLEX2 etc. In general Independent atom model (IAM) is used for solving and refining the structures, where a precomputed model of electrostatic potential is built using scattering factors from isolated, spherically averaged atoms or ions.[1] In reality the atoms in a molecule are not isolated and spherical. Moreover the usage of improper electron scattering factors in refinement may lead to physically unrealistic values. To overcome this, an aspherical TAAM refinement have been applied both for X-ray and ED refinement which largely improved the physical representation and refinement statistics of the structure.[2] We have chosen a model molecule β-glycine for this study for which ED data is already available.[3] Spherical and Aspherical TAAM refinement is now possible in MoPro with the inclusion of electron scattering factors. Aspherical electron scattering TAAM will be constructed using ELMAM2 and MATTS databanks and refinements will be performed using MoPro. A comparison will be shown between reported data and spherical and aspherical TAAM refinements using MoPro.

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N-Representable one-electron reduced density matrices reconstruction at non-zero temperatures.

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Keywords: 1-RDM, Crystals, Temperature

The 1 electron-Reduced Density Matrix (1-RDM), whose terms are closely related to experimental observables such as X-ray Compton profiles and structure factors, is today the simplest way to access quantum properties without recourse to a full N-electron wavefunction. As temperature is a key parameter for experimental resolution, most scattering experiments on crystals are conducted with the lowest possible temperature conditions. However, since 0K conditions are not achievable, 1-RDM theoretical models need to move forward and include temperature effects, at least to some extent.
We build on both the method proposed by P. Azavant et al [1] to reconstruct "ab-initio dynamic structure factors" from non-zero Kelvin X-ray experiments and B. De Bruyne [2] semi-definite positive least-square approach to 1-RDM reconstruction, to propose an extension of our density matrix model which better accounts for atomic motion in the Born-Oppenheimer approximation.
The ultimate purpose of our study is thus to assess the quality of molecular and crystalline reconstructed 1-RDMs with N-representability conditions from non-zero temperature structure factors and Compton profiles. Our latest results on tests cases will be presented based on non-zero temperature pseudo-experimental data with adjustable resolution conditions.

Measuring Structure Factors in Hard-to-Reach Places.

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Keywords: nanostructures, quantitative convergent-beam electron diffraction, accurate charge densities, materials properties.

At nanometre and sub-nanometre scales, even many irregular interfaces can be approximated as locally planar. From an electron scattering point of view, such an approximation opens the possibility of modelling dynamical scattering of an electron probe passing through such interfaces, using the multislice theory[1].

Quantitative convergent-beam electron diffraction (QCBED) is a well-established technique for measuring structure factors with high accuracy and precision[2]. It involves nanometre or smaller focused electron probes which can be routinely positioned on nanostructures embedded in materials with sub-nanometre spatial precision. By adopting a multislice electron scattering formalism, the requirement of structural periodicity along the direction of incidence of the electron beam is removed. Given the approximation of local planarity, introduced above, and as long as the probed structure is periodic laterally to the incident beam direction within the confines of the probe, it should be possible to measure structure factors in and around nanostructures embedded in a host material.

This work presents early results exploring the application of QCBED to the measurement of structure factors in "hard-to-reach" places, i.e. above, below and around nanostructures, with the eventual aim of making such measurements within them. We can use such measurements to infer highly localised properties that can vary from location to location at the nanoscale, and we can also start to think of the nucleation and growth of other phases within a host material in terms of electronic structure domains and their evolution.

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Accurate Determination of Chemical Bond Strength in Crystalline Structures: Development of Local Vibrational Mode Theory for Periodic Systems

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Keywords: bond strength, vibrational spectroscopy, local vibrational mode theory

"How strong is a chemical bond?" —might be one of the most frequently asked questions by chemists. The conventional way to quantify the strength of a chemical bond in a molecule is to elongate this bond by separating two bonding atoms, and then corresponding bond dissociation energy and bond dissociation enthalpy can be calculated theoretically and measured via calorimetry experimentally, respectively. However, this approach does not work for crystals as the dissociation of a chemical bond will drastically change the lattice structure in crystals and there are simply no available tools to measure bond strength in crystals. In this work, we extended Konkoli and Cremer's local vibrational mode theory from molecules to crystals. By calculating the local stretching force constants, the accurate determination of bond strength in crystals has been enabled for the first time. As showcase examples, polyacetylenes, graphene, diamond, acetone crystals and a series of X-I···O halogen bonds in molecular cocrystals are presented.

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ELF characterization of I-I/S-I bonds in polyiodides

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Keywords: Polyiodide, ELF

The range of iodine-iodine and sulphur-iodine chemical bonds in polyiodides with organic compounds are the subjects of researcher`s interest both from theoretical and experimental crystal engineering. Discrete, chain, net polyiodides, iodonium derivatives with S-I$^+$-S fragment and molecular complexes with strongly bound diiodine S…I-I are considered within the framework of ELF distribution in crystals and validated by the experimental and calculated Raman data.[1] The features of ELF redistribution in the region within polyiodide anions were found. ELF values in bond critical points of electron density for I-I/I…I bonds are more reliable in characterization of bound I_2 inside polyiodide anions than analysis of bond lengths. Consistent usage of experimental and theoretical methods can reveal the bound iodine inside polyiodide anions of complex structure and predict characteristic features of such crystals, such as low thermal stability and iodine loss under heating[2].
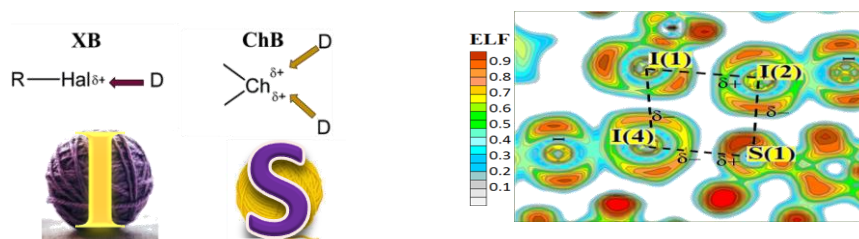

Figure 1 The net of halogen and chalcogen I...I and I...S interactions in ELF representation of benzoxazolothiazinium triiodide

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Towards accurate positions of hydrogen atoms bonded to heavy metals

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Interactions of transition metals (TMs) with hydrogen atoms are crucial in chemistry, however they are very difficult to study with X-ray diffraction due to screening of the weak diffraction signal from the H atom by the strong signal from the TM and since it is difficult to collect high-quality data for such structures. However, a recent study[1] proved that application of aspherical model of electron density such as the one used by Hirshfeld Atom Refinement (HAR) significantly improved positions of H atoms bonded to light elements. The same study also presented the first refinement of 4 X-ray data sets with H atoms bonded to TMs, for only one of which neutron data were available as a benchmark.

This study shows the results of refinement of 11 X-ray data sets containing hydrogen atoms bonded to chemical elements from period 4 (Fe, Ni), 5 (Nb, Ru, Rh, Sb) and 6 (Os). To perform the refinements based on Hirshfeld atomic scattering factors, the DiSCaMB library[2] integrated with Olex2 was used. Molecular wave functions were calculated at the DFT/B3LYP level of theory, using cc-pVDZ, cc-pVTZ-DK or jorge-DZP basis set. The procedure of least squares refinement was adjusted individually for each structure to achieve optimal results. For 4 structures, anisotropic refinement of hydrogen thermal motions was possible. For all the structures but one, free refinement of positions of H atoms bonded to light elements was performed and resulted in considerable elongation of bonds compared to IAM. For 4 of the structures the DiSCaMB-HAR refinement procedure brings the TM-H bond lengths significantly closer to the neutron value, compared to IAM. The most prominent example of successful refinement of such a compound is the structure of a metalloorganic complex containing an Ru-H bond (REFCODE: NOBBOX, Figure 1), which can be refined anisotropically to obtain the Ru-H distance in very high agreement with the one in the neutron structure (neutron: 1.598(3) Å, IAM: 1.56(2) Å, new HAR: 1.593(11) Å).

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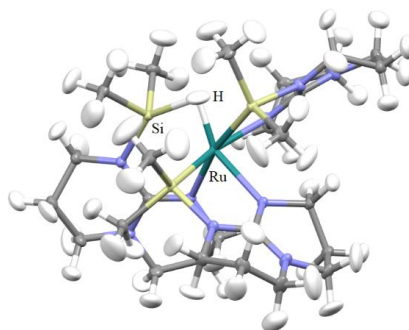
Figure 1 The X-ray structure of NOBBOX obtained with the DiSCaMB-HAR anisotropic refinement

Day 2

Quantum refinement indicates that the bidentate ligand in vanadium nitrogenase is carbonate

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Keywords: Quantum refinement, protein crystallography, nitrogenase

Nitrogenases are the only proteins that catalyse the reduction of dinitrogen gas to ammonium, to make nitrogen bioavailable. This reaction takes place at a complex heterometallic cofactor but the detailed mechanism is still unknown. There are three variants of the enzyme and in vanadium nitrogenase, the FeV cofactor (FeVco) is a $[VFe_7S_8C]$ cluster with a homocitrate ligand to vanadium. Compared to the more common molybdenum nitrogenase, with a catalytic $[MoFe_7S_9C]$ cofactor, one sulfide ligand is replaced by a four-atomic bidentate ligand. It has been suggested to be carbonate or nitrate[1] [1].
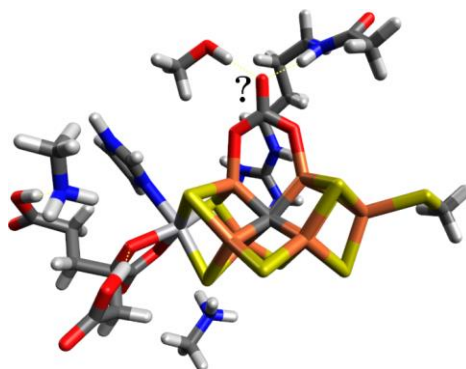
Figure 1 The FeV cofactor (FeVco) of vanadium nitrogenase

At moderate resolution in X-ray crystallography it is difficult do distinguish between isoelectronic species. Therefore, it is not possible with standard crystallography to settle whether the ligand in vanadium nitrogenase (PDB code: 5N6Y) is carbonate or nitrate, although this may significantly influence the reaction mechanism, owing to the differing net charge. It is also possible that the ligand is protonated.

Quantum refinement is standard crystallographic refinement supplemented by quantum mechanical (QM) calculations for a small but interesting part of the protein. Owing to the limited resolution that is usually obtained for bio-molecules it is necessary to supplement the experimental data with additional

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information, in the form of empirical restraints, which in terms of computational chemistry is a molecular-mechanics force field. Unfortunately, force fields are usually rather inaccurate for unusual ligands and metal sites. Therefore, we employ instead more accurate QM calculations for the site of interest in quantum refinement, giving the energy function

$$E_{cqx} = w_A E_{X-ray} + E_{MM12} + w_{QM} E_{QM1} - E_{MM1}$$

where E_{X-ray} is a penalty function that describes how well the model agrees with the experimental data, E_{MM12} is the MM energy function for the whole system, E_{QM1} is the QM energy of the part of interest and E_{MM1} the MM energy of the same part to avoid double counting[1] [2]. Thus, quantum refinement gives a structure that is an ideal compromise between the crystallographic raw data and the QM calculations. By refining structures with different interpretations, we can use standard crystallographic measures, like the electron-density difference maps or real-space Z scores, to decide which ligand fits the experimental data best. Using this approach, we have shown that carbonate fits the crystal structure better than bicarbonate or nitrate.

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Hypoxanthine nitrate hydrate – an interplay between energy, geometry and temperature

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Keywords: TAAM, periodic DFT, NTE, electrostatic energy, dimer energy, MATTS pseudoatom databank

Structures of hypoxanthinium nitrate monohydrate crystals were determined at fifteen different temperatures ranging from 20 to 285 K. Crystals undergo a phase transition from twinned, low temperature (LT) phase of $P2_1/n$ symmetry into high temperature (HT) $Pmnb$ phase. Sets of X-ray diffraction data acquired at each temperature were subjected to two types of refinement - TAAM refinement done with the MATTS pseudoatom databank[3] and periodic DFT geometry optimization done with Crystal17 package[1][2].

Figure1: Interplay between electrostatic potential and thermal expansion along crystallographic axes a, b and c (crystallographic axes are the same for each subfigure). a) electrostatic potential of a surface, b) thermal expansion for LT phase; c) thermal expansion for HT phase. Thermal

We found that as the temperature increases, the layers of hypoxanthinium nitrate monohydrate shift against each other, leading to the negative thermal expansion (NTE) in one direction, and positive (PTE) one perpendicular to it (Figure 1). The β angle diminishes, the layers of molecules slide gradually until the 90° angle is reached, phase transition occurs and structure changes space group from $P2_1/n$ to $Pmnb$. The HT phase has no NTE and the layers cease any sliding. The thermal expansion coefficient is then the highest along a axis, which corresponds to the layers of molecules moving away from each other.

In our work we discuss how the strengths and shortcomings of different methods (in our case TAAM and pDFT) may influence the final values of obtained electrostatic and total energies of interacting dimers. We discuss how interpretation of geometries and energies obtained at distinct temperatures can help in understanding causes for the unique effect of negative thermal expansion and twinning of the crystal structure.

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Evaluation of the reliability of electron density based index, in the study of π-π interactions

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Keywords: electron, density, intermolecular, DFT, MP2, QTAIM.

In the last years, DFT methods have focused on an accurate energy description of the systems while leaving behind the electron density. In this work we evaluate the accuracy of electron density obtained using DFT methods in a system with π-π intermolecular interactions. The objective is to come closer to a reliable method of study of intermolecular interactions in solids, using the electron density. In order to do that, we calculated the electron density for a Naphtalene and Octofluoronaphtalene system, using various DFT methods and comparing them to MP2, using Gaussian16, as well as CCSD(T), using ORCA.

The methods used in DFT were chosen considering which ones have empirical dispersion or long-range correction, in order to get an effective description of the electron density in the intermolecular interaction areas. Once we obtain the electron density, we use tools from the Quantum Theory of Atoms in Molecules to study it. Using the reduced density gradient, we map an isosurface of the interaction, in which we can integrate different properties in order to get an idea of the nature of the interaction. We found a significant difference in the values of the integrated density between MP2 and DFT methods, despite having shown very similar energy values.
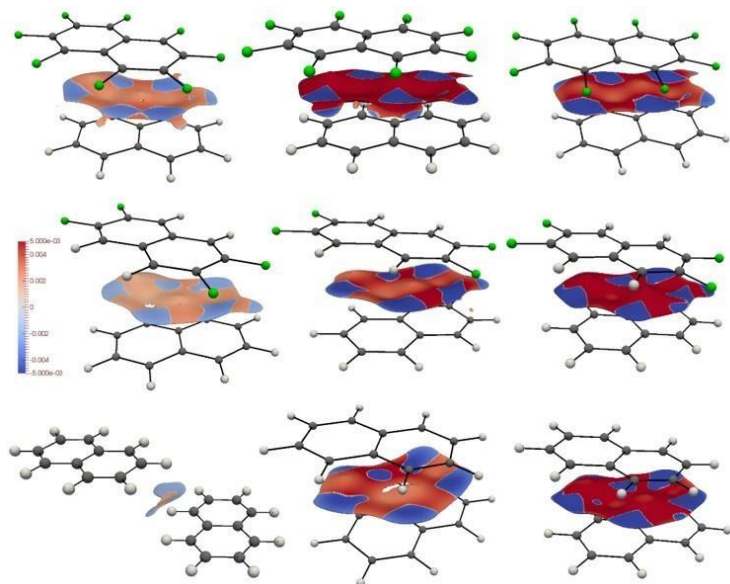
We found that the best DFT methods were M06 with GD3 Empirical Dispersion, and APFD. In order to validate our methodology, we repeated the study using these two methods but this time considering a series of pairs of molecules with π-π intermolecular interactions, in which the area of interaction varies.

Theoretical Charge Density Analysis of Cation···Cation Hydrogen Bonds in Synephrine Salts

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Keywords: Quantum Theory of Atoms in Molecules, Potential Energy Surface Scans, RDG surfaces,

Interaction between the same charged species is not much explored. These hydrogen bonds were sometimes termed as destabilizing or anti-electrostatic in nature. Some researchers have also suggested these interactions to be a result of columbic compression caused by counterions. Such analysis totally neglects the importance of hydrogen bonds present between these same charge species. We have recently studied the nature and stability of O–H···O, N–H···O and C–H···O hydrogen bonded cationic dimers found in dicarboxylic acid salts of p-(↰)-synephrine with the help of theoretical charge density analysis. [1]
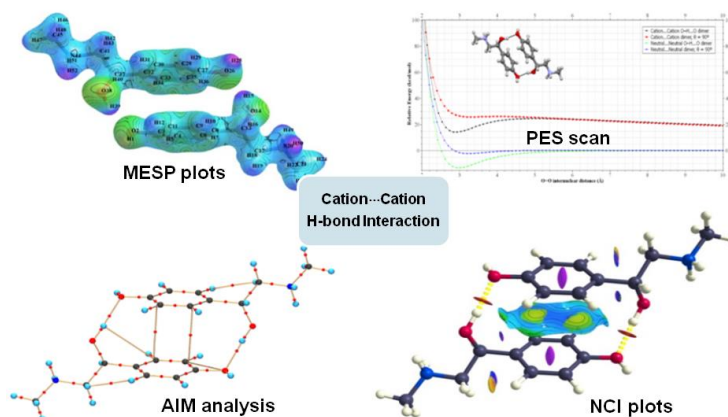
MESP plots

PES scan

Cation···Cation
H-bond Interaction

AIM analysis

NCI plots

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Lead structure(s) prediction for library screening using molecular docking and quantum crystallography

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Keywords: Library Screening, Quantum Crystallography, Molecular Docking

Optimization of lead structure is crucial for drug discovery studies. Although molecular docking and scoring functions are often used for this purpose, none of the scoring functions can be labelled as 'reliable',[1] because their accuracy of prediction can be anywhere between 0-93%.[2] Introducing a reference ligand (lead structure) can increase the accuracy by many folds for these scoring functions.[3] The quantum crystallographic technique *Kernel Energy Method* (*KEM*), is a computationally inexpensive fragment-based approach that accurately calculate the interaction energies (IE) of macromolecules using their crystallographic coordinates.[4,5] In this study, we demonstrate how accurately the lead structure(s) can be predicted using scoring function (*GoldScore*) and counterpoise corrected *KEM* (*KEM-CP*). For this, we have considered the protein complex structures of human aldose reductase (hAR, 0.66 Å), cyclin dependent kinase 2 (CDK2, 2.0 Å) and estrogen receptor β (ERB, 2.7 Å), with active site environment ranging from highly hydrophilic to highly hydrophobic. The known ligands of these proteins were selected from the literature[6-8] and were docked into the respective protein active sites using *GoldScore*. IE of the docked poses having different binding orientations with the active site residues are calculated using *KEM-CP*. Based on the *GoldScore* fitting and the IE of the poses we predicted the lead structure(s) for hAR, CDK2 and ERB and validated the results by comparing the RMSD of predicted lead structure with the crystal geometry of the ligand. The use of *KEM-CP* alongside the *GoldScore* resulted superior prediction than the *GoldScore* alone. Accordingly, it is tempting to conclude that our novel *KEM-CP* approach along with docking studies would help identifying accurate lead structure(s), which in turn may ease the process of virtual screening of potent ligands.

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Accurate refinement of hydrogen atoms positions through a quantum mechanical embedding scheme based on extremely localized molecular orbitals

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Keywords: Hirshfeld atom refinement, extremely localized molecular orbitals, embedding methods

Several physico-chemical properties crucially depend on the spacial disposition of the hydrogen atoms in the crystals. Determining the position of these atoms as precisely as possible is then of utmost importance in many research fields to retrieve accurate and reliable results.

The most widely used approach, the independent atom model (IAM), reconstructs the total electron density as a sum of spherical atomic densities centered on the nuclei. This approximation evidently fails when applied to hydrogen atoms because the only electron is delocalized along the bond. As a result, bonds lengths involving hydrogen atoms are generally too short and not completely reliable.

Within the field of quantum crystallography, the Hirshfeld atom refinement (HAR) is one of the most promising strategies[1]. HAR exploits fully quantum mechanical calculations to obtain tailor-made *ab initio* electron densities, which are partitioned into aspherical atomic contributions to fit experimental structure factors without further approximations. The resulting X-H bond distances are in very good agreement with those obtained from neutron diffraction experiments[1-3]. Moreover, the introduction of crystal environment effects is crucial when strong intermolecular interactions are present. This is usually done adding atomic charges and dipole moments at symmetry-related atomic positions around the selected reference crystal unit[2-3].

In this contribution, we introduce an improvement to the description of crystal field effects in the HAR strategy exploiting the recently developed quantum mechanics/extremely localized molecular orbitals (QM/ELMO) technique[4-5]. In our new modified version of HAR, the reference crystal unit is treated variationally at quantum mechanical level, while the symmetry-related crystal units are described using pre-computed frozen ELMOs.

Other than discussing the theoretical framework, we will present test refinements performed on systems characterized by strong hydrogen bonds (urea and xylitol). Preliminary results show that the new ELMO-embedded HAR approach gives bond lengths involving hydrogen atoms in optimal agreement with neutron results, outperforming both the traditional HAR and the charge/dipole-embedded HAR technique in most of the cases[6]. The very good preliminary results prompt us to envisage the extensive

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application of the new ELMO-embedded HAR technique to refine structures of crystals with strong intermolecular interactions. However, further test-bed refinements will be necessary to draw final conclusions.

Crystals Compressibility and Quantum Electronic Pressure

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Keywords: elastic moduli, quantum electronic pressure

We defined the relationships between quantum electronic pressure[1] (QEP) and spatial dependences of crystal compressibility on the examples of MgB_2 and C_6Hal_6. Crystal compressibility of two types was considered: under uniaxial stress (Young's modulus) and hydrostatic stress (linear compressibility). The crystal stiffness tensors for calculation of elastic moduli were obtained by DFT method with periodic boundary conditions using CRYSTAL17 software. Calculations of QEP were performed using WinXPRO 3.4.29 and 3DPlot programs[2]. The decreasing anisotropy of compressibility under external pressure is correctly matched with the QEP changes along bond paths and in other regions of crystal structures.
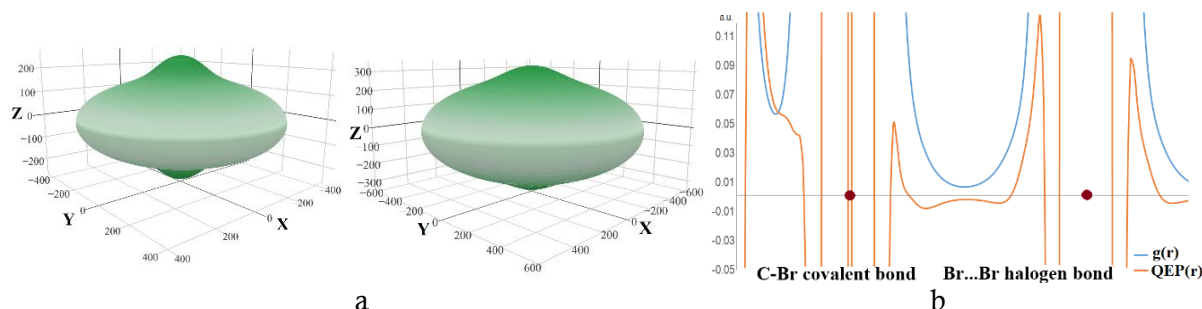
Figure 1 a) Young's modulus of MgB2 under external pressure 0 and 20 GPa; b) QEP and density of kinetic electron energy g(r) for Br...Br halogen bond in C_6Br_6 crystal

In a crystal, the regions of negative QEP indicate that the quantum contribution to the local internal energy of electrons is ready to compensate the stress growing under external pressure. Along these regions arrangement, the maximal crystal compressibility is observed, namely along the stacks in C_6Hal_6 crystals and orthogonally to the B atom and Mg atom layers in MgB_2 crystals. The regions of positive QEP show the largest resistance to external stresses and exhibit the least geometric changes under external pressure, like B–B bonds in MgB_2. The halogen bonds forming Hal_3-synthons in C_6Hal_6 determine the decreasing crystal compressibility in the directions parallel to these bonds in the series Cl > Br > I, which is clearly related with the decreasing negative QEP in the regions of halogen bonds.

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Intrinsic Strength of Hydrogen Bonds in Ice Structures

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Keywords: Hydrogen bonding, Local vibrational mode theory, Chemical bond strength, Ice

Ice comes in many forms and shapes. So far, 17 3D ice structures with square and hexagonal (bilayer) 2D ice structures have been experimentally resolved under different conditions[1]. Accurate lattice energy data exists for these structures which accounts for the cumulative strength of the hydrogen bond network.
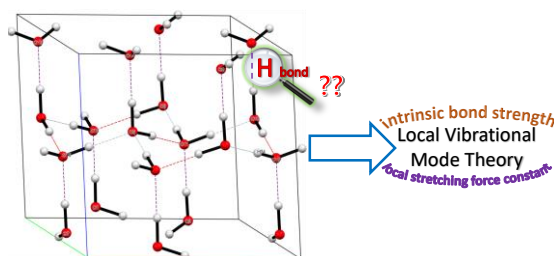
However, the individual hydrogen bond strength within the lattice has not been investigated so far, which could provide valuable information for identifying different hydrogen bonds, their varying bond strength and their influence on physicochemical and structural properties of ice. In this work we studied several experimentally resolved 2D and 3D ice polymorphs to assess the donor and acceptor hydrogen bond interaction strength, utilizing our periodic local vibrational mode analysis to probe their intrinsic bond strength[2,3]. Based on the new insights gained in this work the credibility of several predicted ice polymorphs obtained by various computational approaches is assessed, guiding future experimental studies.

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A Topological Approach to Electronegativity

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Keywords : Electronegativity, quantum chemical topology

Ever since Pauling's work, electronegativity has proven a helpful tool in rationalizing electronic structure, and in particular trends in charge transfer, bond polarity, bond strength, and reactivity.[1] Electronegativity can be quantified in many different ways, for example as an average electron energy, $\bar{\chi}$, a quantity that can be both quantum mechanically calculated or experimentally estimated.[2,3] In our approach, electronegativity is a part of an energy decomposition equation:[4,5]

$$E = n\bar{\chi} + V_{NN} - E_{ee}, \qquad (1)$$

where E is the total energy, n is the total number of electrons, $\bar{\chi}$ is the average electron energy (or electronegativity), V_{NN} is the nuclear-nuclear repulsion, and where E_{ee} equals all electron-electron repulsions.

Here we present our most recent work on the topic of electronegativity and explore the analysis of $\bar{\chi}$ resolved in three-dimensions. Figure 1 shows how topological analysis can be used to partition carbon monoxide into atomic basins, each of which can be attributed to an electronegativity and a charge. Here we will discuss the underlying theoretical framework, and present application of the methodology on well-known molecular examples.
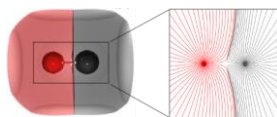
Figure 1. Carbon monoxide subdivided into atomic basins (left) defined from the gradient field of the electron density $\rho(r)$ multiplied by the electronegativity field $\bar{\chi}(r)$ (right).

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Substitution of S by Se. Supramolecular Insight.

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Keywords: Substitution of S by Se; Supramolecular structure

The study includes the crystallographic analysis of interactions of S and Se from Cys, Met, Sec and Mse side chains, based on crystal structures from the Cambridge Structural Database (CSD), and quantum-chemical insight in the strength of their individual interactions.

CSD statistical analyses have shown a similar tendency of sulfur and selenium atoms towards the specified types of interactions. The most numerous are C−H···Se (for Se fragments) and C−H···S (for S fragments) interactions (~80%), while the second group in numerosity are structures with Se···Se and S···S interactions (~5%). The results of quantum-chemical calculations have revealed that C−H···S and C−H···Se interactions (about −0.8 kcal/mol) are weaker than the most stable parallel Se/Se interaction (about −3.3 kcal/mol) and electrostatic Se/Se interaction of σ/π type (around −2.6 kcal/mol). The numerosity of C−H···S and C−H···Se interactions was explained by an abundance of CH groups compared to the numbers of Se and S atoms in the analyzed crystal structures. The substituents bonded to Se or S atom sterically reduce the possibilities of Se and S atoms to interact with species from the environment. The numerosity of crystal structures explains the lower values of O−H···Se (around −4.4 kcal/mol) and N−H···Se interactions (around −2.2 kcal/mol).

Analysis of electron density properties of atom types in Multipolar Atom Types from Theory and Statistical clustering (MATTS) databank using numerical and hierarchical methods

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Keywords: multipole model, electron density, pseudoatoms databank

Independent Atom Model, most widely used in crystal structure refinement, assumes spherical symmetry of the atomic density, ignoring the charge redistribution due to chemical bonding. However, more accurate models of electron density are available, such as the Multipole Model. It presents an aspherical approach describing the surroundings of a nucleus far more accurately using the Hansen-Coppens formalism[1]. In this model, the electron density parameters of pseudoatoms, which are the sum of spherical harmonics for each atom, are almost identical for atoms of one element located in similar chemical environment. For that reason, banks of transferable aspherical atoms with universal parameters were created. MATTS (Multipolar Atom Types from Theory and Statistical Clustering) databank is one of them and supersedes previously used UBDB (University at Buffalo DataBank)[2]. It contains over 300 different atom types categorized by central element type and chemical surroundings. It includes various information about electron density distribution, structure and neighbourhood. The main idea behind the project was to determine relationships between the electron density distribution of different atom types and to organize the databank into reasonable groups, combining clustering based either on density or on topology. The topology clustering takes into account information about number and type of atoms' neighbours, symmetry and planarity. In that case, the databank was visualised by a series of trees where atom types were grouped by those values. For density, we used DBSCAN to do multidimensional clustering of all parameters to get the full image of electron density for whole databank and compared it with results from topology clustering, searching for common features. Such analysis compares and captures similarities in the spatial distribution of electron density of atom types, checks for errors and also makes it possible to distinguish between general and specific atom types. The knowledge about atom types from this perspective contributes to the future development of the databank, facilitating decisions about divergence or convergence of atom types.

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Formate-mediated Magnetic Superexchange in the Model Hybrid Perovskite [(CH₃)₂NH₂]Cu(HCOO)₃

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Keywords: hybrid perovskites, superexchange mechanism

We have investigated the magnetic, electronic, and orbital structures of crystalline [(CH₃)₂NH₂]Cu(HCOO)₃; a model compound that belongs to a wide class of hybrid organic-inorganic perovskites. We present the results of a combined experimental approach, where neutron diffraction and magnetisation measurements were used to solve the ground state magnetic structure (Figure 1a), while the electron charge density distribution was determined by high-resolution x-ray diffraction. The latter enabled a microscopic analysis of the chemical bonding, from which we established a detailed correlation between the structural, electronic, and magnetic properties of [(CH₃)₂NH₂]Cu(HCOO)₃. Our results elucidate the simulated spin density distribution in these systems (Figure 1b), as well as, the mechanism of magnetic exchange mediated by formate anions, from which we examine the applicability of foundational theories of purely inorganic perovskites.
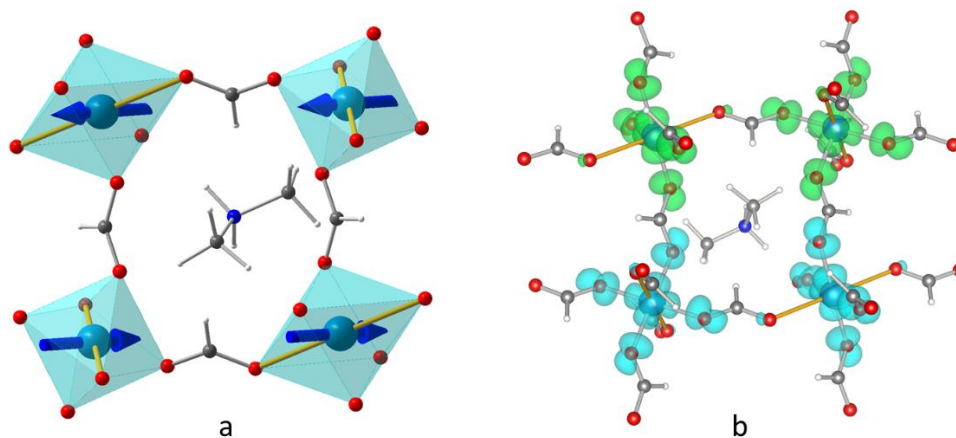
Figure 1. (a) Experimental crystal and magnetic structure of [(CH3)2NH2]Cu(HCOO)3 and (b) calculated spin density distribution represented at an isodensity value of 0.002 au. Green and cyan surfaces represent α and β spin densities. Yellow sticks show Jahn-Teller elongated bonds.

Charge density study of valence shell distortion of sulfur atoms induced by hydrogen bonds

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Keywords: Charge density, Lone pair, H-bond, Methimazole, Thiamazole

In this work, we report an unusual distortion of the valence shell of sulfur atoms likely induced by the H-bonds. Two symmetrically independent thiamazole molecules in crystals of its α_0 polymorph are bonded to each other into the non-planar dimer by a pair of moderate N–H···S hydrogen bonds. The spatial orientation of Laplacian critical points (3, +3) found inside the sulfur atoms' basins is somewhat skewed from the sp^2 geometry[1]. Another type of distortion of the valence shell of the heteroatom was reported for a urea molecule by Pinkerton et al.[2], where a slight change in angle between the Laplacian CPs (3, +3) (CP–O–CP) from the ideal value of 120° was observed. In order to test if the turn of Laplacian CPs (3, +3) around the formally double C=S bonds found by accurate XRD is in fact a real physical phenomenon, solid-state theoretical calculations were performed. Different functionals, e.g., CAM-B3LYP and ωB97X, with pob-TZVP-rev2 basis set were used. Theoretical findings allowed for the observation of incomparably small but reliable deflection of one of two CPs toward the corresponding H-bond for each S-atom. The critical points oriented toward the hydrogen bonds exhibit higher absolute values of both electron density and its Laplacian. The eigenvalues of the Hessian matrix of Laplacian at CPs (3, +3) suggest a higher degree of local density concentration at the H-bond oriented non-bonding VSCCs. Additional deflection of the other CPs (3, +3) especially for the one at S(1b) is not supported by any directional intermolecular interaction and could be attributed to the absence of strongly localized Laplacian minimum inside the toroidal density distribution. In conclusion, considering the obtained data, we assume that the observed distortion of the valence shell of sulfur atoms is most probably the result of polarization occurring due to the hydrogen bonding.

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WinXPRO, 3DPlot and TrajPlot: Computer Software for Orbital-free Quantum Crystallography

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Keywords: chemical bond, computer software, orbital-free quantum crystallography

This report announces the new release of the computer software WinXPRO and 3DPlot (A. Stash, V. Tsirelson, J. Appl. Cryst. 2002, *35*, 371; 2014, *47,* 2086) which provides the derivation of orbital-free bonding information from experimental electron density. The latter is described by parameters of the Hansen-Coppens multipole model derived from accurate X-ray diffraction experiment. The current version of software allows additionally calculating the following novel properties and descriptors:

- The Pauli, von Weizsäcker and Kohn-Sham potentials;
- 2D and 3D gradient fields of different local functions and potentials;
- Critical points in electronic density, electrostatic potential, Laplacian of the electron density, local electronic energies and different potentials;
- Inner-crystal quantum pressure in electron continuum;
- Indicator of quantum pressure focusing (IQPF);
- Local temperature of electron continuum, Parr entropy and Fisher information of the Wigner phase coordinate-momentum distribution function;
- Determination of zero-flux atomic basin in the field of electron density as well as in the any positively-defined scalar field;
- Integration of any scalar field within atomic ZFS volumes as well as over ZFS;
- Determination of zero-flux atomic surface in the electron density between pairs of atoms linked by the bond path followed by the integration of a chosen property over this surface.

Fluorination as a Driving Force in Crystal Structures

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Keywords: Fluorination, Fluorine⋯Fluorine Interactions, Crystal Structures

The results of the crystallographic analysis in combination with quantum chemical calculations have shown that fluorination of organic compounds causes an increase in the proton-donating ability and a decrease in the proton-accepting capacity of the groups in their neighbourhood[1]. The establishment of F⋯F interactions causes the electron density to shift towards the area of F⋯F contact, thus creating a new region with a higher negative potential and the more pronounced accepting ability. This new region has a larger surface area and it is able to form simultaneous interactions with species from the crystal environment. This compensates the reduction of the accepting capacity of the groups in the neigbourhood of the interacting F atoms. Taking into account the formation of this new region, not only the abundance of F⋯F interactions in the crystal structures (the second largest group of interactions), but also a large number of structures with F⋯O interactions (third largest group of interactions) can be explained. Only the C–H⋯F interactions are more numerous than F⋯F interactions, indicating an increased affinity of fluorinated compounds for non-polar groups.

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Electronic structure, electron density and charge density of a Ruthenium-Nitrosyl complex with two Fe(III) Centers

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Keywords: quantum crystallography, Ruthenium-nitrosyl complex, charge density

The present study describes the geometry, electronic structure, energetics and bonding properties at the Ruthenium-nitrosyl complex (Figure 1) which contains two Fe_{III} centers. The geometry optimization calculations were performed in various spin and redox states at the DFT level of theory using the B3LYP functionals along with the def2-SVP basis set and with the utilization of the def2-SVP pseudo-potential for Ru atom in the Gaussian16 program package[1]. The Quantum Theory of Atoms in Molecules (QTAIM)[2], Mulliken population analysis and localized orbitals (LOC) have been applied to analyze the electronic structure. Restricted (closed shell) and unrestricted high spin as well as broken symmetry (BS) approaches

were used to study the different spin state energetics. There have been found the broken symmetry (BS) singlet state to be energetically preferred but the high spin state is being very close in energy. The B3LYP/def2-SVP optimization shows to the fact that all reduced species have a bent structure with Ru-N1-O1 angle around 145° due the Ru-(NO) character of the HOMO. QTAIM Laplacian of electron density and deformation densities have been used to compare experimental and theoretical results.
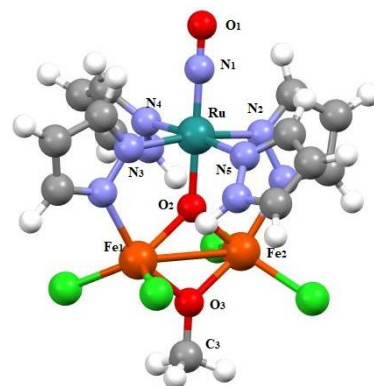
Figure 1 The studied complex[11]$[Ru]^0$

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Day 3

Spin density topology

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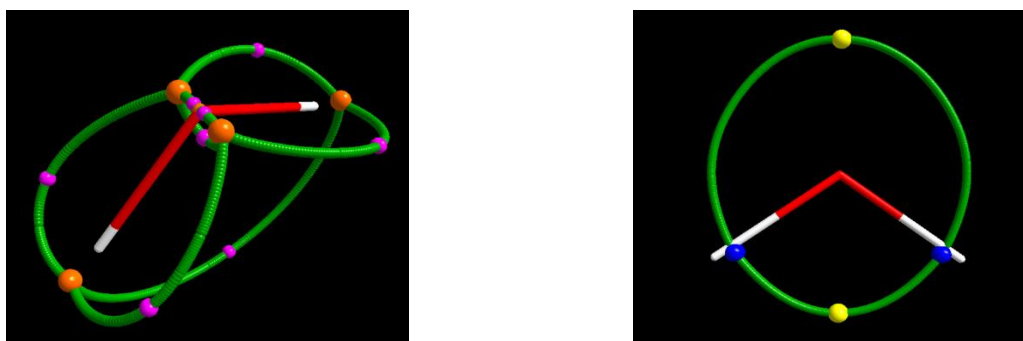
Keywords: spin density, topology

Figure 1: $^3B_1$ H_2O CASSCF(8,8) spin maxima interaction lines for the positive spin density (s($\mathbf{r}$)+, left) and for the negative spin density (s($\mathbf{r}$)-,right), represented as thick green wires. The s($\mathbf{r}$) critical points are portrayed as balls [(3,-3) s+ maxima, orange; (3,-1) s+ saddles, violet; (3,+1) saddles, s+ ring or -s saddles, yellow; (3,+3) s+ minima or -s maxima, blue]. For comparison, also the electron density bond paths are shown in both images (from H nucleus to the bond critical point (bcp) in white and from the bcp to the O nucleus in red).

Despite its role in Spin Density Functional theory and its being the basic observable for describing and understanding magnetic phenomena, few studies have appeared on the electron spin density subtleties thus far. In particular, a systematic full topological analysis of this function seems to be lacking. Our study is aimed at unveiling that kind of information hidden in the spin density distribution which only its topology is able to disclose. The physical significance of the spin density critical points, the different 18 ways by which they physically realize and the peculiar topological constraints on their number and kind, arising from the presence of positive and negative spin density regions, is addressed. The notion of molecular spin graphs, spin maxima (minima) interaction lines, spin basins and of their valence is introduced. We show that to a spin polarized molecule are associated two kinds of structures, the usual one defined through the electron density gradient and the magnetic structure, defined through the spin density gradient and composed in general by at least two independent spin graphs, related to spin density maxima and minima. Several descriptors, like the spin polarization index, are introduced to characterize the properties of spin density critical points and basins. The study on the general features of the spin density topology is followed by the specific example of the water triplet molecule topology, using spin density distributions of increasing accuracy.

Revealing Molecular Interactions through the Laplacian of the Hamiltonian Kinetic Energy Density

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Keywords: Chemical interactions, kinetic energy density, laplacian

Over the last decades, the role of the kinetic energy in chemical interactions has been the subject of a debate between two opposite schools. One school holds that a lowering of the kinetic energy associated with electron delocalization is the key stabilization mechanism of covalent bonding. The opposite school sustains that a chemical bond is formed by a decrease in the potential energy due to a concentration of electron density within the binding region. In this work, we present a topographic analysis of the Hamiltonian Kinetic Energy Density (KED) and its laplacian with the objective of gaining more insight into the role of the kinetic energy in chemical interactions. Atoms, diatomic and organic molecules as well as weakly interacting dimers were considered in our study. We show that the laplacian of the Hamiltonian KED exhibits a shell structure in atoms. Moreover, their outermost shell merge when a molecule is formed. A covalent bond is characterized by a concentration of kinetic energy as well as potential energy and electron densities along the internuclear axis. As for the weakly interacting systems, the external shell of the molecules merge into each other resulting in an intermolecular surface comparable to that obtained by the Non-covalent interaction (NCI) analysis.

Spin density of YTiO3 and SrRuO$_3$ using DFT+U, ACBN0 and hybrid functionals

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Keywords: Spin density, perovskites, DFT, Hubbard correction

We present a comparison between the experimental[1] and theoretical spin density map of two perovskites, YTiO$_3$ and SrRuO$_3$.

YTiO$_3$ is a prototypical ferromagnetic Mott insulator, while SrRuO$_3$ is a weakly correlated ferromagnetic oxide. The structural properties, such as lattice parameters and octahedral tilting of these materials, both at ambient and high pressure, are well described by standard semilocal GGA functionals, such as the PBESOL functional[2]. However, due to spurious self-interaction of localized *3d* orbitals (and *4d* to a lesser extent), advanced DFT methods, such as DFT+U, DMFT or GW, are required to reproduce the photoemission spectra, hence to describe more accurately their band structures in reciprocal space.

In this work, we calculated the spin density using the standard DFT+U method, where the Hubbard U correction is applied to the Ti and Ru ions. In addition, we fully characterized the electronic structure and spin density using the pseudo-hybrid ACBN0 method, where the Hubbard U parameters are determined self-consistently, and not from empirical inputs. We used both the original ACBN0[3] formalism, and the linear response method recently implemented in Quantum Espresso. We found that the ACBN0 method seems to account properly for the screening effect, whereas the linear response method severely underestimates it. Both methods however, yielded a large value of Hubbard U of the oxygen *2p* orbitals. We also used the screened hybrid HSE03 functional, which is widely used to describe the electronic structure of oxides.

Then we analyzed quantitatively the spin density using the QTAIM theory. We extracted the spin density in the atomic basins and compared with experimental reports as well as previous DFT calculations, where the spin densities were integrated inside small spheres, centered around the atoms.

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Multipolar scattering factors for electron diffraction

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Keywords: aspherical scattering factors, TAAM, electron diffraction, structure refinement

Electron diffraction makes it possible to obtain crystal structures at atomic resolutions, for both small and macro-molecules[1-2]. For this purpose, the same as in case of X-ray diffraction, it is necessary to use scattering factors model. Different aspherical models, already known for X-ray diffraction, can be implemented here. However, it is necessary to investigate their possibilities and limits, to verify correctness of obtained structures.

We present analysis of refinements of TAAM with parameters of multipolar model taken from MATTS databank - successor of UBDB databank[3]. We used electron scattering factors implemented in DiSCaMB library[4] and interfaced with Olex2-1.3[5]. Such solution is available through .tsc files[6] and it requires little effort (Fig.1).
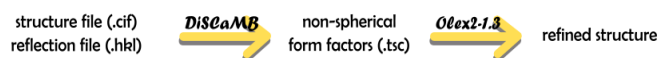

Figure 1. General refinement procedure

We performed numerous refinements against experimental and theoretical electron structure factors so as to find optimum refinement strategy. We discuss, inter alia, possibility of refinement of atomic displacement parameters, both for hydrogen and non-hydrogen atoms or positions of hydrogen atoms. It is interesting how they change e.g. with resolution cut-off. To confirm that our conclusions could be transferred for different organic structures, we made simulations for several pharmaceuticals, such as carbamazepine, paracetamol, 1-methyluracil.

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Polymorphism in Bioactive Molecules: Insights from Quantum Crystallography

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Keywords: Bioactivity, Polymorphism, Binding affinity, Charge density analysis.

Thiazolidinone derivatives are known to exist as potent drug molecules. They play crucial roles in anticancer drug discovery process.[1] Especially, 5-arylidene-2-aminothiazolidinones are found to show antimitotic activities against MCF7 and MDA breast cancer cells.[2] Given their potentiality as anticancer drugs, we have considered a series of thiazolidinone derivatives for the investigation of polymorphism.[3] Here, we present the case of (*Z*)-5-(4-(dimethyl amino) benzylidene)-2-(piperidin-1-yl) thiazol-4(5*H*)-one, for which we discovered three polymorphic forms. Subsequently, we have studied their biological activity - structure - property relationships and correlated these results from quantum crystallography[4] viewpoint. The estimation of energies in terms of interaction energies, lattice energies and *energy frameworks* bring out the energetic stabilities of the three polymorphs. Molecular dynamic simulations on these polymorphic conformations against its putative target gamma enolase resulted distinct binding affinity of the three polymorphs to the enzyme. Further, in order to pin point the differences and similarities among the polymorphs and to correlate their biological properties with structures, we have performed charge density analysis. The topological properties and electrostatic potentials highlighted the differences in electron density distributions among the three polymorphs. The results thus obtained from these quantitative and qualitative analyses are expected to pave the pathway for understanding the role of charge density analysis and polymorphism for drug design.

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Weighting scheme analysis of HAR refinement

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Keywords: HAR refinement, weighing scheme

One outstanding procedure formulated within Quantum Crystallography is the X-ray wavefunction refinement (XWR) developed by Jayatilaka and coworkers,[1] which consists of two steps: a Hirshfeld Atomic Refinement (HAR), followed by an X-ray constrained wavefuntion (XCW) fitting. Having an optimal starting point obtained from HAR before performing the XCW is essential. The key statistical variable in HAR and XCW is the χ^2 function, which is minimized with the aim of attaining the value $\chi^2 = 1$. Achieving this target rests on the assumption that on average the model is within an acceptable error.

In this work we explore the effect of applying different sigma and resolution cutoffs in HAR for three systems: SO_2, urea and carbamazepine. As expected, the weightless residual factor R_1 increases when higher resolutions are employed in the refinement, and decreases as larger sigma cutoffs are applied. Nevertheless, depending on the experimental quality, the χ^2 shows some erratic behavior. For instance, for SO_2 it shows values larger than 15 for low resolution cutoffs, and decreases its value when full data are used in the refinement. We attribute these results to the difference in intensity/sigma relations for low- and high-resolution reflections.

We propose that in order to provide a better estimation of the χ^2 function a change in the weighing scheme of HAR is necessary. Our preliminary results suggest that the application of the SHELX scheme could be a good alternative to obtain χ^2 values closer to unity and, therefore, better starting points for XCW. The importance of this work rests on the possibility of estimating correct fitted wavefunctions that could otherwise reach an artificial minimum (with larger λ) as a consequence of a wrong statistical description.

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Localization of Density Errors in Density Functional Theory

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Keywords: DFT, Electron Density, Quantum Chemistry, Density Errors

Density Functional Approximations (DFAs) are necessary for profiting of the many advantages of Density Functional Theory (DFT). Over the years, significant efforts towards the design and implementation of better DFAs to the exact exchange-correlation functional have been put forward from different scientific communities. Some well-known flaws remain an issue yet versatile solutions have been devised for many of the problems. However, a certain degree of parametrization has been progressively added to DFAs since the inception of the framework.

Some authors have suggested[1] that the development of DFAs that rely on heavy parametrization compromise the quest for the exact functional because the path to the exact functional requires achieving better energies and electron densities simultaneously. On the other hand, assessing the quality of the electron density ($\rho(r)$) and derived scalar fields is non-trivial. Quantum Chemical Topology (QCT) has been developed in order to link the topological features of such fields and chemically meaningful concepts[2].
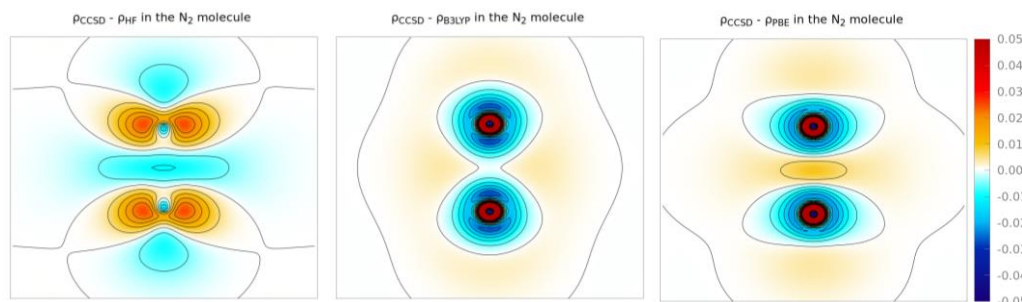

Figure 1. $\rho(r)$ difference maps with respect to CCSD for HF, B3LYP and PBE in the N_2 molecule.

In our work, several simple systems are evaluated using different DFAs in an attempt to understand density errors from a chemical perspective. Density errors might come from very different "chemical regions" of the system. Figure 1 exemplifies how HF and PBE errors with respect to an accurate CCSD electron density arise from either lone pairs or bonding regions respectively. Since errors seem to be related with chemical regions, additional insight can be derived though more sophisticated scalar fields, such as the Electron Localization Function (ELF).

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Quantum Crystallographic Studies of N-H···O=C Hydrogen Bonds and Electrostatic Interaction Energies in High-resolution Secondary Protein Structures:

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Keywords: Library Screening, Quantum Crystallography, Molecular Docking

For the formation of the α-helices and β-sheets in proteins, the main-chain N-H···O=C hydrogen bonds (HBs) play a crucial role. Accurate analysis of such HBs and their energies is essential for studying binding interactions and for improved understanding of the energetics involved in protein folding.[1] For this, we studied 22 high-resolution (0.87 Å to 0.48 Å) secondary protein structures (4.7 kDa to 54.5 kDa) from RCSB PDB and performed topological analyses of 1443 N-H···O=C HBs (750 in α-helices and 693 in β-sheets) using the multipole analysis based experimental electron densities as transferred from the *ELMAM2* database.[2] This is the first study of its kind involving by far the largest number of high-resolution protein structures and HBs from both α-helices and β-sheets.[3] Further, based on the accurate estimation of the electrostatic interaction energies the excellent correlations with various topological parameters have been demonstrated. Thereby, we identified the limiting values of the topological parameters and the electrostatic interaction energies to establish the presence of the true N-H···O=C HBs in protein main-chain *via* quantitative and qualitative analyses of electron densities using quantum crystallographic approaches – Quantum Theory of Atoms in Molecules (QTAIM)[4] and Noncovalent Interaction (NCI) index.[5]

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Relativistic effects from high resolution X-ray diffraction experiments

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Keywords: HAR, heavy elements, charge density, quantum crystallography

Relativistic effects in chemistry manifest themselves in many ways and influence various physical and chemical properties of materials. The most well-known of them are the yellow color of gold or the high voltage of the lead-acid car batteries[1,2]. Therefore, a description of these effects is of great importance for better understanding of the chemistry of heavy atoms.

A perspective method is quantum crystallography that relies on the high-resolution and high-quality XRD data to describe crystal structure in unprecedented details. Intensities of diffracted beam are affected not only by relativistic effects but also by absorption, anharmonic motion, anomalous dispersion[3], and many other effects which highly influence electron density distribution in the crystal and, in consequence, derived properties.

We collected the data sets for the organo-gold(I) compound using both Mo and Ag X-ray radiations at 90K and also performed X-ray diffraction experiment at 80K using synchrotron radiation (at SPring8, Japan). Here, we present the results of Hirshfeld Atom Refinements carried out for different resolution cut-offs. The outcome of DFT-based refinements with the nonrelativistic and quasi-relativistic approaches will be compared, including refinement of anharmonic thermal motion for the gold atom.

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Modelling Anharmonic Motion
of Hydrogen Atoms in α-Glycine

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Keywords: anharmonic motion, H-atoms, neutron radiation, resolution

In our work we check if anharmonic motion for hydrogen atoms can be observed and then described based on neutron diffraction experiment. We have performed single-crystal single-wavelength neutron diffraction experiments for high-quality crystals of α-glycine (P2$_1$/n) at 90 K and 200 K with reflections collected to as high diffraction angle as possible in each setup. For each dataset we have used different resolution limits ranging from full possible down to 0.5 Å^{-1}. Then, for each resolution limit four different models, from the simplest to the most complex, were used for the refinement. Two of them included Gram-Cherlier coefficients up to the third level describing anharmonic motion of H-atoms, the other two did not.

We can see that above certain resolution it is possible to refine anharmonic motion for H-atoms in the crystal structure of α-glycine. What we find the most interesting, is that there is also a dependence of ADPs for all atoms within the glycine molecule on the resolution of the collected data. Such dependences, however, are unique for each model and show monotonic changes as the applied model gets more and more complex. We would like to present a detailed comparison of the results and an interesting relation regarding resolution of collected data, applied model and parameters describing atoms motion.

Applications of quantum crystallography methods for refinements against low resolution X-ray data

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Keywords: CuKα data, charge density

Pseudoatom model of electron density introduced by Hansen and Coppens[1] allows for modelling of deformation of spherical valence electron density. However, application of this model requires an excellent quality of crystals and high resolution XRD data which often is difficult to be fulfilled. Therefore, in the routine X-ray data analysis, mostly, the Independent Atom Model (IAM) of electron density is used and final structures are affected by systematic errors.

The aim of the project is using new methods which have been developed for reconstruction of electron density against low-resolution X-ray data. These methods are Bond-Oriented Deformation Density Model (BODD)[2], Hirshfeld Atom Refinement (HAR)[3] and Transferable Aspherical Atom Model (TAAM)[4]. Structures of three model compounds (tricyclic imide, xylitol and methyluracil) were refined using IAM, BODD, HAR and TAAM methods against low resolution (0.8Å) CuKα and MoKα X-ray diffraction data. The final results were compared to the models obtained by performing neutron diffraction experiments. Although, the final structures refined against low-resolution data are contaminated by systematic errors (geometrical, atomic displacement parameters), the systematic errors of IAM are by far more serious. Therefore, application of quantum crystallography methods improves the final results of refinements against low resolution data.

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NCI-ELMO: towards a more quantitative description of non-covalent interactions in macromolecules

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Keywords: Non-covalent interactions, NCI method, ELMO-libraries, biological macromolecules

Non-covalent interactions uniquely define the structure of macromolecules. Therefore, a thorough analysis of the non-covalent interaction network is crucial to gain insights into functions and dynamics of biological systems.

A strategy that is able to detect non-covalent interactions for a large variety of molecules is the Non-Covalent Interactions (NCI) method[1] a technique simultaneously based on the electron densities and the reduced density gradients of the molecules under exam. Unfortunately, the computation of accurate molecular electron densities through traditional quantum chemistry calculations is often impractical for macromolecules. Therefore, until now, for NCI analyses on large systems one had to resort to the promolecular density approximation, where the electron density of the investigated molecule is described as a sum of independent and spherically averaged atomic densities. These promolecular densities are a drastic approximation. Hence, the analysis of the non-covalent interactions based on the promolecular approach is biased.

To overcome the previous shortcoming, we have coupled the NCI method with the recently constructed database of extremely localized molecular orbitals (ELMOs)[2], giving rise to the novel NCI-ELMO technique[3]. ELMOs are orbitals strictly localized on small molecular units and easily transferable from one molecule to another. The ELMO database currently contains orbitals associated with all the fragments for the twenty natural amino acids and allows rapid and reliable reconstructions of wavefunctions and electron densities of very large biomolecules.

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In this presentation, we will show for a variety of non-covalent interactions in polypeptides and proteins that the new NCI-ELMO method[3] provides results that are very similar to the NCI ones based on electron densities obtained through fully quantum chemical calculations, but definitely better than those resulting from the promolecular approach.

Furthermore, we will illustrate how the new NCI-ELMO technique has been recently further extended in order to successfully quantify non-covalent interactions in systems of biochemical interests. In this context, we will present the results of benchmark calculations on smaller systems (e.g., simple molecular dimers) in order to highlight the differences between the NCI-ELMO and promolecular-NCI approaches also at a quantitative level.

Materials Science Beamline ID11 at the ESRF

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Keywords: Synchrotron, X-ray, Experimental

The ESRF light source has just been upgraded to a new 4th generation lattice and this provides around 20X more high energy X-ray photons for experiments at the Materials Science beamline, ID11. Complementing the source upgrade, the nanofocus station will be equipped with an Eiger2 4M CdTe pixel detector from Dectris. The new detector will offer high frame rates (up to 500 fps), together with the very small X-ray beam sizes (down to ~120 nm) and high X-ray energies (40-70 keV). This facility offers a range of new experimental opportunities for Quantum Crystallographers:

- Very small crystals or small distortions
- Mapping diffuse scattering within a crystal
- Diffraction based tomographic imaging
- Ultra-fine   s
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Speeches and talks

Day 1

Ultrafast time-resolved X-ray experiments at SACLA

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Keywords: X-ray free-electron laser, ultrafast chemistry

X-ray free-electron laser (XFEL) sources have attracted a great amount of attentions with novel light-source properties: an unprecedented peak power, an excellent transverse coherence, and femtoseconds pulse duration. These unique capabilities are useful for researches of nonlinear physics, structural biology, and ultrafast chemistry.

This presentation illustrates the current performance of SACLA[1] and instrumental developments for ultrafast time-resolved X-ray experiments[2-6], which enable to track the nuclear and electronic dynamics during nonadiabatic chemical reactions. This capability is highlighted by our recent study[7] of a prototypical copper(I)-phenanthroline complex, $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline; Fig. 1). In this study, we observed the coherent vibrations and subsequent structural flattening of $[Cu(dmphen)_2]^+$ with time-resolved X-ray absorption near edge structure (TR-XANES), time-resolved X-ray emission spectroscopy (TR-XES), and time-resolved X-ray solution scattering (TR-XSS).
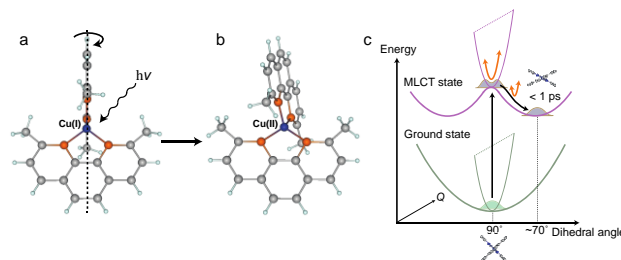

Fig. 1 (a-b) Photoinduced flattening of $[Cu(dmphen)_2]^+$, and (c) potential energy landscape

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Materials Science Beamline ID11 at the ESRF

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Keywords: Synchrotron, X-ray, Experimental

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- Very small crystals or small distortions
- Mapping diffuse scattering within a crystal
- Diffraction based tomographic imaging
- Ultra-fine sliced data collections

A close neighbor to QCr: gas-phase scattering

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Keywords: Spectroscopy, Elastic, Inelastic, and Total X-ray Scattering

Gas-phase scattering opens rich opportunities to explore molecular structure and dynamics. The ultrafast community has, in an effort to interpret new experiments at X-ray Free-Electron Lasers (XFELs), developed tools that have parallel those in the Quantum Crystallography community. It is clear that the two communities can benefit from an exchange of ideas, concepts, and tools.
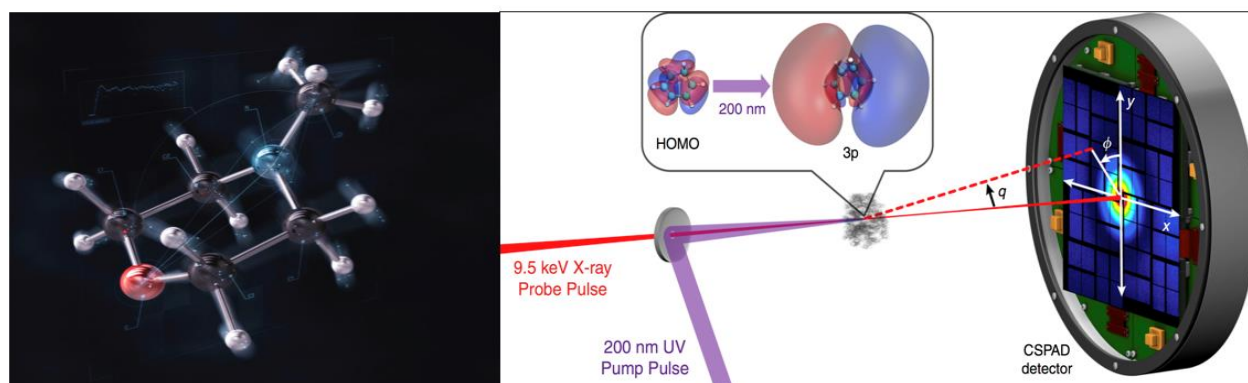

Figure 1 (LEFT) The structure of excited N-methylmorpholine1. (RIGHT) Observation of the transient rearrangement of electrons upon photoexcitation2.

I will briefly review our experimental advances, including a recent measurement of molecular structure in an excited molecule[1] and observation of the electron density associated with an excited electronic state in a molecule[2] (see Figure 1). The focus of my presentation will be on our calculations of elastic[3], inelastic[4], coherent mixed, and total scattering[5] and the physical insights that we can draw from this, with a particular eye on points of possible points of contact with crystallography. I will also show simulations of experiments that track electron transfer and transient electronic coherences in a molecule using X-ray scattering[6].

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[6] M. Simmermacher *Physical Review Letters* 122 073003 2019

Multipolar scattering factors for electron diffraction

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Keywords: aspherical scattering factors, TAAM, electron diffraction, structure refinement

Electron diffraction makes it possible to obtain crystal structures at atomic resolutions, for both small and macro-molecules[1-2]. For this purpose, the same as in case of X-ray diffraction, it is necessary to use scattering factors model. Different aspherical models, already known for X-ray diffraction, can be implemented here. However, it is necessary to investigate their possibilities and limits, to verify correctness of obtained structures.

We present analysis of refinements of TAAM with parameters of multipolar model taken from MATTS databank - successor of UBDB databank[3]. We used electron scattering factors implemented in DiSCaMB library[4] and interfaced with Olex2-1.3[5]. Such solution is available through .tsc files[6] and it requires little effort (Fig.1).

structure file (.cif) → **DiSCaMB** → non-spherical form factors (.tsc) → **Olex2-1.3** → refined structure
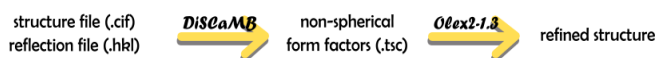
Figure 1. General refinement procedure

We performed numerous refinements against experimental and theoretical electron structure factors so as to find optimum refinement strategy. We discuss, inter alia, possibility of refinement of atomic displacement parameters, both for hydrogen and non-hydrogen atoms or positions of hydrogen atoms. It is interesting how they change e.g. with resolution cut-off. To confirm that our conclusions could be transferred for different organic structures, we made simulations for several pharmaceuticals, such as carbamazepine, paracetamol, 1-methyluracil.

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Day 2

QCBED-DFT – Refinement of DFT Model Parameters by Quantitative Convergent-Beam Electron Diffraction.

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Keywords: density functional theory, quantitative convergent-beam electron diffraction, accurate charge densities, strongly correlated electron systems.

We have fully integrated density functional theory (DFT) into the highly accurate *and* precise method of measuring crystal potentials and charge densitites, quantitative convergent-beam electron diffraction (QCBED). We call this combination *QCBED-DFT*.

The accuracy and precision of QCBED come from the ability to focus electron beams into nanometre or smaller probes, coupled with the ability to position such probes selectively on regions of perfect crystal, with sub-nanometre spatial precision. The highly dynamical nature of electron scattering (because electrons are charged) means that CBED patterns contain extremely complex and detailed intensity distributions as a function of scattering angle. The pattern-matching refinements of QCBED therefore involve thousands of independent intensities *per reflection*, leading to high over-determination of the small number of parameters.

By integrating DFT into QCBED, *QCBED-DFT* dispenses with the conventional use of an independent atom model (IAM) and no longer refines individual structure factors. The fitting of DFT model parameters refines the real space charge density, changing not just a few but all structure factors simultaneously, while the number of refined parameters remains small.

We have applied *QCBED-DFT* to two strongly correlated electron materials, NiO (a Mott insulator) and CeB_6 (a heavy fermion metal). We also demonstrate a way of assessing how well a DFT-modelled charge density agrees with reality and in doing so, show that the uncertainty of individual bonding-sensitive structure factors is reduced to < 0.1%. We expect *QCBED-DFT* to play a role in the future development and testing of new density functionals.

Orbital-free DFT – new approaches to old ideas

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Keywords: orbital-free density functional theory, equilibrium bond length, real space

Although founded fifty years ago in the seminal work of Hohenberg and Kohn, the success of orbital-free density functional theory has been hampered due to the lack of sufficiently accurate approximations for the kinetic energy.

The so-called bifunctional approach with subsequent atomic fragment approximation offers a new strategy for the design of approximate density functionals. The method offers a systematic hierarchy of density functional approximation levels for the kinetic energy, that result in ab-initio, parameter-free implementations of orbital-free density functional theory. So far three subsequent approximation levels [1-3] have been published showing a systematic improvement of equilibrium bond lengths from 25% to 6% relative errors.
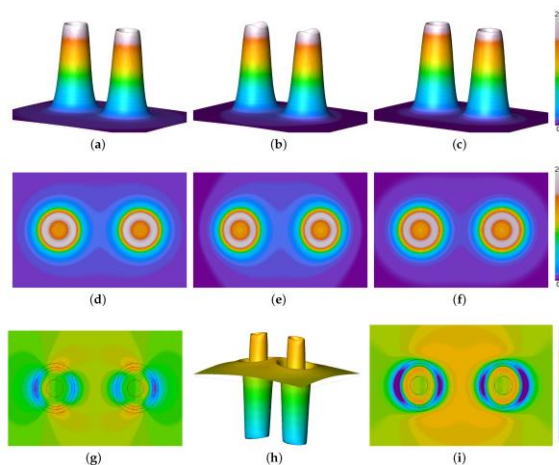

Figure 1 : Pauli potential for dinitrogen from orbital based and orbital-free DFT approaches.

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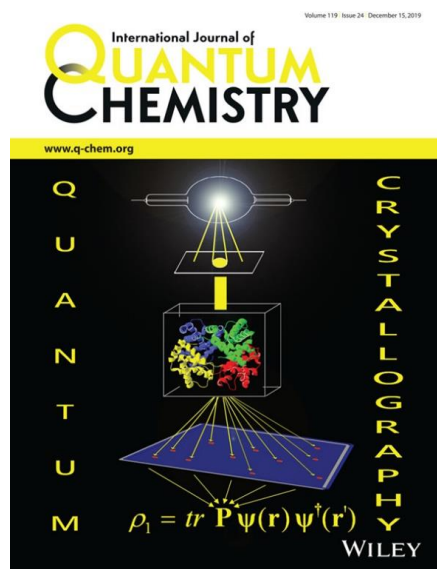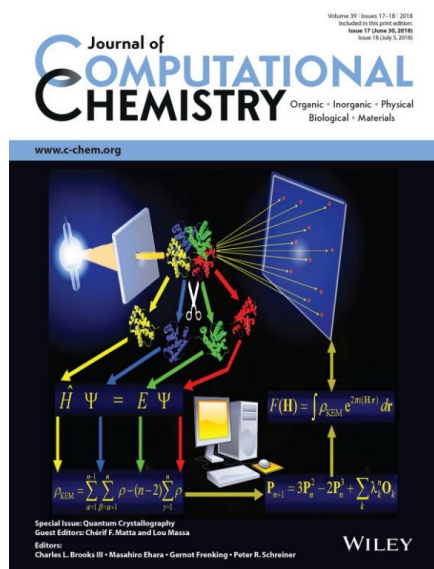
Day 3

Quantum Crystallography:
N-representability Big & Small

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Keywords: Density Matrices, Kernel Energy Method, Born Oppenheimer Approximation.

Classical X-ray crystallography delivers the geometries and electron densities of molecules (and other atomic forms of matter) in the crystalline phase. Total energy, electron momentum density, and information relating to the pair density such as electron delocalization measures—all crucial to chemistry—follow from Quantum Crystallography (QCr), but not from classical crystallography. Quantum crystallography solves the X-ray scattering problem under the mathematical umbrella of quantum mechanics. Density matrices can be extracted from the scattering data, but in reverse may also be injected into a known crystal structure. In both cases, not only geometries and electron densities become experimentally accessible, but also the entire panoply of quantum mechanical properties that are in the output of any quantum chemical software package. Quantum mechanical validity of electron densities and density matrices demand adherence to the fundamental quantum concept of N-representability. How this mathematical condition is imposed upon a crystallographic molecule depends upon its size, whether big or small. In the case of either size, the Clinton equations play a crucial role in imposing N-representability, but differently if the molecule is big or small. When combined with a fragmentation technique, called the "kernel energy method (KEM)", QCr's reach to larger molecules is extended to almost "any size", that is, to systems of up to many hundreds of thousands of atoms.
We look forward here to a new way of simplifying a large density matrix into its kernel components while preserving its original N-representability.

Quantum Crystallographic Bonding Analysis

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Keywords: Hirshfeld Atom Refinement, X-ray Constrained Wavefunction Fitting, X-ray Wavefunction Refinement, Complementary Bonding Analysis, Bonding Correlation

The techniques of quantum crystallography allow us to obtain accurate and precise structures (geometries, ADPs) from single-crystal X-ray diffraction based on non-spherical atomic scattering factors. In combination with modern software, such accurate structure refinements are becoming more and more accessible for normal crystal structure determination experiments, e.g. in terms of Hirshfeld Atom Refinement[1] inside NoSpherA2[2]. Beyond non-spherical structure refinements, the distribution of electrons in crystalline matter is accessible via experimentally fitted wavefunctions, which allows a complementary bonding analysis encompassing orbital, real-space and energy descriptors.[3]

In this contribution, we will show two examples of quantum crystallographic complementary bonding analysis.

1. A series of highly polarized and twisted putative $C=C$ double bonds with varying degree of zwitterionic C^+-C^- resonance contributions will be discussed.[4] We will show that bond distance – bond order relationships are reversed when a conjugated system of $C=C \leftrightarrow C^+$-C^- is highly polarized.

2. A series of pentacoordinated silicon compounds with substituents of varying electron-withdrawing or -donating character will be discussed.[5] We will show how the Bürgi/Dunitz principle of structure correlation can be complemented and enhanced by correlating bonding descriptors against each other.

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