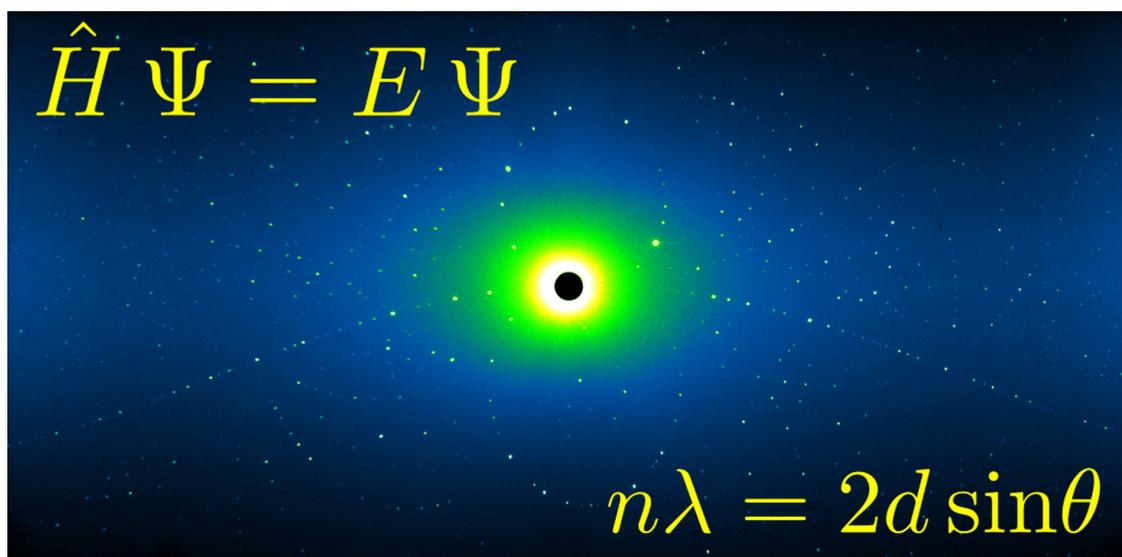
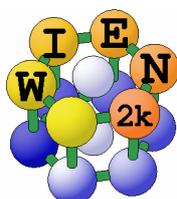


QUANTUM CRYSTALLOGRAPHY: Current Developments and Future Perspectives



Nancy, FRANCE - June 19-20, 2017



FOCUS OF THE DISCUSSION MEETING

The term "Quantum Crystallography" is becoming popular in physical chemistry. For example, in 2018 Quantum Crystallography will be for the first time the main topic of the prestigious Erice International School of Crystallography. But what is exactly Quantum Crystallography? Its meaning has several aspects and its applications can range from materials science over biology to theoretical simulations, involving X-ray, neutron and electron diffraction as well as Compton scattering. Furthermore, and more confusingly, its name is sometimes used as a modern buzzword in funding proposals or research articles.

The term was actually coined in the mid 1990s by Massa, Huang and Karle for methods that exploit "crystallographic information to enhance quantum mechanical calculations and the information derived from them". But there is a second aspect, a converse definition, that was also pointed out by the same authors in 1999: "... quantum mechanics... can greatly enhance the information available from a crystallographic experiment". With many novel methods evolving concerning both aspects of the definition by Massa, Huang and Karle, and with the unclear use of the term "Quantum Crystallography", we believe that it is time to re-initiate and unite the efforts in the community under a well-defined term "Quantum Crystallography".

Such a re-definition and re-initiation of a research field can only happen in a discourse between the developers and users of quantum crystallographic methods as well as the experts of neighboring research domains. During the CECAM Discussion Meeting we will discuss strategies and clarify problems with a representative selection of researchers that work in the fields of Quantum Crystallography, experimental electron density, theoretical chemistry, protein crystallography, materials science, electron diffraction, etc.. Our goals are to start a discourse in our research community as a result of the CECAM meeting, spark discussions in the literature, bundle efforts for future committees, centers or funding initiatives, and communicate the exciting opportunities of Quantum Crystallography to the broader chemical community.

CONFERENCE PROGRAM

CONFERENCE VENUE

The CECAM Discussion Meeting “Quantum Crystallography: Current Developments and Future Perspectives” will take place on the 19th and 20th of June 2017 at the Presidency Building of the University of Lorraine (34 Cours Léopold, 54000 Nancy, FRANCE).

Monday - June 19, 2017

8:30 - 9:00 Registration

Session 1 (Chairs: Alessandro Genoni & Simon Grabowsky)

9:00 - 9:30 Alessandro Genoni & Simon Grabowsky: *Welcome and General Introduction.*

9:30 - 10:00 Louis J. Massa: *Early Days of Quantum Crystallography and Comments on Future Directions from a Personal Point of View.*

10:00 - 10:15 Kenneth M. Merz Jr.: *Using QM Methods to Refine Biological Structures.*

10:15 - 10:30 Carlo Gatti: *What is Quantum Crystallography ?*

10:30 - 11:00 Coffee Break

Session 2 (Chair: Julia Contreras-Garcia)

11:00 - 11:15 Piero Macchi: *Why Refining Wave Functions from Experiments ?*

11:15 - 11:30 Karlheinz Schwarz: *From the Atomic Structure to Properties of Solids Using Wien2k.*

11:30 - 11:45 Philip N. H. Nakashima: *Quantitative Convergent-Beam Electron Diffraction and Quantum Crystallography.*

11:45 - 12:00 Anders Ø. Madsen: *Dynamic Quantum Crystallography.*

12:00 - 12:15 Paolo Giannozzi: *Computational Crystallography with Quantum ESPRESSO (a few years later).*

12:15 - 12:30 Paulina M. Dominiak: *Electron Density, Electrostatic Potential, Electrostatic Interactions in the Context of Intermolecular Interactions.*

12:30 - 14:00 Lunch Break

Session 3 (Chair: Anders Ø. Madsen)

- 14:00 - 14:15 Dylan Jayatilaka: *Quantum Crystallography: Past and Present but mainly the Future.*
- 14:15 - 14:30 Ulf Ryde: *Quantum Refinement of Protein Crystal Structures.*
- 14:30 - 14:45 Marek Sierka: *Turbomole - Fast and Robust Quantum Chemistry.*
- 14:45 - 15:00 Birger Dittrich: *Multi-wavelength Single Crystal X-ray Diffraction Experiments: a Possibility to Study the Limits of the Born-Oppenheimer Approximation?*
- 15:00 - 15:15 Nicolas Claiser: *When Diffraction Experiments Challenge Ab Initio Calculations.*
- 15:15 - 15:30 Chérif F. Matta: *Molecules as Networks.*
- 15:30 - 16:00 Coffee Break

Session 4 (Chair: Birger Dittrich)

- 16:00 - 16:15 Jean-Michel Gillet: *Quantum Crystallography in Spin-Resolved Phase-Space.*
- 16:15 - 16:30 Wolfgang Scherer: *What are the Experimental Prerequisites in Quantum Crystallography?*
- 16:30 - 16:45 Holger Ott: *Accurate Experimental Charge Density Data Collections Using CPAD Technology.*
- 16:45 - 17:00 Enrique Espinosa: *Topological Analyses of the Electron Density, its Laplacian Function and the Electrostatic Potential to Study Molecular Organization in Space.*
- 17:00 - 17:15 Julia Contreras-Garcia: *From Electron Density to Properties?*
- 17:15 - 17:30 Lukas Bučinský: *Relativistic Effects & Quantum Crystallography of Heavy Element Compounds.*

Tuesday - June 20, 2017

- 9:00 - 10:30 **First Round Table Discussion** (Chair: Chérif F. Matta)
Quantum Crystallography: Is a New Definition Necessary?
- 10:30 - 11:00 Coffee Break
- 11:00 - 12:30 **Second Round Table Discussion** (Chair: Piero Macchi)
Strategies for Building a Quantum Crystallography Community.
- 12:30 - 14:00 Lunch Break
- 14:00 -16:00 **Rebuttal Session** (Chair: Paulina M. Dominiak)
Flash 5-minute talks for all the volunteer-speakers.
- 16:00 - 16:30 Coffee Break
- 16:30 - 18:00 **Third Round Table Discussion** (Chair: Carlo Gatti)
Future Perspectives and a Vision for Quantum Crystallography.
- 18:00 - 18:15 Conclusions
- 19:30 - 22:00 Social Dinner at the restaurant “L’arsenal”

ABSTRACTS OF THE TALKS

QUANTUM CRYSTALLOGRAPHY – CURRENT DEVELOPMENTS AND FUTURE PERSPECTIVES

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^b Universität Bremen, Institut für Anorganische Chemie und Kristallographie, Bremen, Germany

The use of the term “quantum crystallography” has become popular in the last decade. Either new crystallographic refinement techniques or quantum mechanical procedures that refer to experimental diffraction or scattering data are referenced. More generally, the term is used as an umbrella term for any accurate measurement based on crystallography, and in that sense it has potential to summarize a new field of accurate crystallography. However, this inherently includes the risk that the meaning and definition of quantum crystallography remain unclear and hidden. If used only as a buzzword, the potential for exciting scientific applications in a collaborative framework of experts will be put at risk. Therefore, we want to discuss the state-of-the-art of quantum crystallography with a panel of experts and formulate directions to strengthen and focus the arising new field simultaneously.

We believe that the definition by Massa, Karle and Huang from the 1990s fully captures the essence of quantum crystallography with its two aspects: (i) crystallographic information can enhance quantum mechanical calculations and the information derived from them;¹ (ii) quantum mechanics can enhance the information available from a crystallographic experiment.² The first application within aspect (i) dates back to 1972 with the seminal paper by Massa and Clinton,³ whereas, concerning aspect (ii), the first applications date back to the 1960s in the field of electron diffraction.⁴ In recent years, a wide variety of methods has been introduced within both aspects, which we reviewed in Ref. 5. In our conference contribution, we will give an overview of past and recent developments in the field according to our view on quantum crystallography. We will furthermore give a short outlook on our own joint efforts within the field, mainly related to the combination of Hirshfeld Atom Refinement and Extremely Localized Molecular Orbitals (HAR-ELMO).

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EARLY DAYS OF QUANTUM CRYSTALLOGRAPHY (QCR) AND COMMENTS ON FUTURE DIRECTIONS FROM A PERSONAL POINT OF VIEW

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It is desirable to have a method for the conversion of X-ray diffraction data into an electron density that reflects the antisymmetry of an N -electron wave function. A formalism for this was developed early on for the determination of a constrained idempotent one-body density matrix \mathbf{P} . The formalism ensures pure-state representability in the single determinant sense. This is accomplished by minimizing the quantity $\text{Tr} (\mathbf{P}^2 - \mathbf{P})^2$ subject to X-ray scattering constraints. The method leads to iterative Clinton matrix equations of the form:

$$\mathbf{P}_{n+1} = 3\mathbf{P}_n^2 - 2\mathbf{P}_n^3 + \sum_k \lambda_k(n) \mathbf{O}_k \quad (1)$$

where $-\lambda_k$ is the k^{th} Lagrangian multiplier pertaining to the constraint $\text{Tr} \mathbf{P} \mathbf{O}_k = \langle \hat{O}_k \rangle$, and $\langle \hat{O}_k \rangle$ is the expectation value of the X-ray scattering observable represented by matrix \mathbf{O}_k . Applications to crystals show that quantum mechanical density matrices can be extracted from X-ray scattering data. Future applications to biological molecules are indicated.

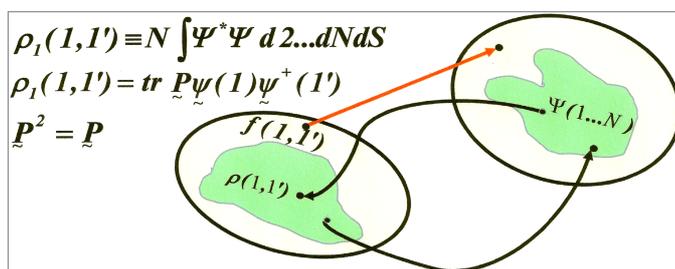


Figure 1. Sketch depicting the mapping problem associated with wave function N -representability of density matrices.

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USING QUANTUM MECHANICAL METHODS TO REFINE BIOLOGICAL STRUCTURES

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^a *Michigan State University, Department of Chemistry & Department of Biochemistry and Molecular Biology, East Lansing, Michigan, USA*

The starting point for structure-based drug design (SBDD) efforts is a high quality structural model obtained using X-ray crystallography or NMR spectroscopic techniques. In most instances classical tools are used as structural surrogates in X-ray and NMR refinement protocols in order to improve the parameter to observation ratio realized from these experimental techniques. While classical approaches are useful structural surrogates, they do suffer from a number of issues that affect their performance including: electrostatic modeling, parameter defects and missing parameters. The way in which these issues can be mitigated is to use more robust structural theories like quantum mechanical (QM) methods, which have had a tremendous impact on our understanding of “small” chemical and biological systems. In this talk we will focus on the application of *ab initio* QM methods to refine protein/ligand complexes for use in SBDD applications using X-ray methods. We will discuss the computational details and describe several uses of QM in structure refinement efforts using X-ray datasets. The strengths and weaknesses of a QM approach in structure refinement will be discussed as well as future prospects of this strategy.

WHAT IS QUANTUM CRYSTALLOGRAPHY?

Carlo Gatti^a

^a CNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, Milano, Italy

The abstract of a recent review by Grabowsky, Genoni and Bürgi¹ on *Quantum Crystallography* (QC) summarises their view about this long-standing, yet increasingly popular subject. While I agree with the authors that “improving approximate wavefunctions by constraining them to reproduce observations derived from diffraction and scattering experiments or, also, that improving *complete* charge density models by supplementing diffraction experiments with quantum chemically calculated, tailor-made electron densities”¹ is of great relevance, I still believe that QC is much broader than that. As in the two papers²⁻³ that coined the term, the territory of QC seems to be restricted by Grabowsky *et al.* to the instrumental goal of *enhancing* quantum mechanical (QM) models or crystallographic information through their suitable combination. Yet, information on a system may in several cases be increased the other way around, i.e. by examining/comparing both crystallographic and QM outcomes, while keeping them as distinct as possible. Analogously to QM calculations, crystallographic data from diffraction/scattering experiments inherently contain QM information, but while the latter contain information on the real system, the former may only refer to a model system. Exploiting such difference, in either directions, provide useful information as I will show for a few representative cases. In particular: A) Many technological materials are only partially ordered and owe their peculiar functionalities to such departures from ideality. A Rietveld/Maximum Entropy Method study revealed the presence of interstitial Zn atoms in Zn₄Sb₃ thermoelectric material. Theoretical calculations on several model systems with variable geometries/compositions inspired from experiment showed that the so discovered Zn interstitials play a fundamental role as electron suppliers and Seebeck coefficient enhancers;⁴ B) Evaluation of faithful Electron Spin Densities (ESD) is a critical issue both from scattering data and from QM models. Proper comparison among the two outcomes, also exploiting the ESD Source Function, is of great value.⁵

QC may thus include all those approaches that are able to enhance the knowledge on a system, by making use of crystallographic measures and/or models/computations, with both being intrinsically tied to quantum effects. Direct combination of “quantum chemistry and diffraction/scattering experiments into a single, integrated tool” is just one, yet very relevant, way to pursue such a goal.

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WHY REFINING WAVE FUNCTIONS FROM EXPERIMENTS?

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^a University of Bern, Department of Chemistry, Bern, Switzerland

The emerging field of Quantum Crystallography¹ is often defined as the improvement of a theoretical wave function using experimental data, obtained from X-ray scattering,^{2,3} or otherwise as the improved interpretation of experimental observations by means of quantum mechanical calculations. The extracted information is often limited to the observable electron density, a quantity available also with other methods, like the multipolar model or the maximum entropy (although the wave function approach may, in principle, provide higher accuracy).

The wave function itself, instead, is not much exploited, despite in “traditional” quantum mechanical studies, the molecular orbitals are often used for a chemical interpretation for example within the framework of the Frontier Molecular Orbital Theory.⁴ The refinement of extremely localized molecular orbital wave functions⁵ has driven the attention to the link with other “traditional” theories, which enable interpretations otherwise not possible with the one-electron density alone. This implies that wave function refinements may provide new (not only more accurate) information compared to electron density only refinements. The energy of a wave function refinement is normally not used. In fact, the most adopted wave function refinement method² links the electronic Hamiltonian and the residual charge calculated in the reciprocal space. However, the structure factors may in principle provide the molecular self-interaction energy in a crystal and the molecular Hamiltonian can be corrected for crystal field effects to obtain a “balanced” operator and a more realistic energy.

In this presentation, some examples are provided, including frontier molecular orbital analysis of electron donor-acceptor interactions, like those occurring in polyiodides (see Figure 1) that eventually become true chemical bonds if for example the crystal is compressed.

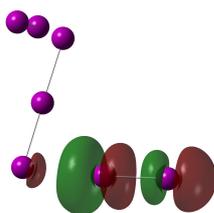


Figure 1. The “HOMO” of a I₂ fragment inside the crystal of I₃(I₂)[N(C₂H₅)].

References

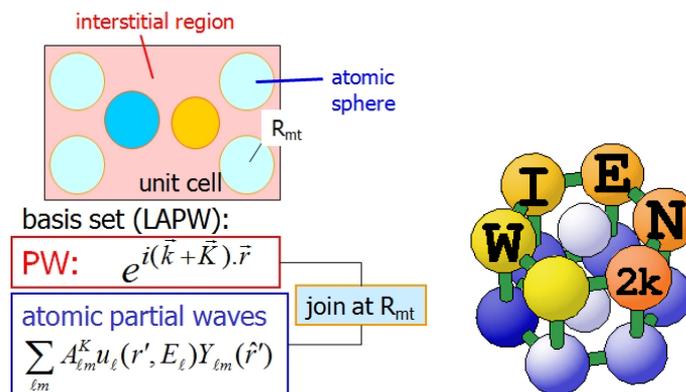
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FROM THE ATOMIC STRUCTURE TO PROPERTIES OF SOLIDS USING Wien2k

Karlheinz Schwarz^a

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A variety of concepts and approximations are needed for modern simulations of materials. Starting with the atomic structure of a solid (assuming periodic boundary conditions) a proper quantum mechanical (QM) treatment is needed for studying the electronic structure, which determines the properties. In our case this is mostly based on density functional theory (DFT). The fundamental idea of DFT is to replace the complete many-electron wave function with the much simpler ground-state electron density as the main variable. One can prove that the total energy E of a system is a functional of the density $\rho(\mathbf{r})$ but since its explicit mathematical form is unknown approximations are needed such as the generalized gradient approximations (GGA) or many others. For the QM solution of the corresponding Kohn-Sham equation we use the linearized augmented plane wave (LAPW) method as implemented in the WIEN2k program (<http://www.wien2k.at>) summarized in a review¹.



In the LAPW method one partitions the unit cell into two types of regions: i) (non-overlapping) atomic spheres centered on the atomic sites and ii) the remaining interstitial region. Inside each atomic sphere, the wave functions have nearly an atomic character and thus can be expressed as a sum of radial functions u_{ℓ} times spherical harmonics $Y_{\ell m}$ labeled with the quantum numbers ℓ and m . In the interstitial region, where the potential varies only slowly, we can expand the wave functions in a set of plane waves (PWs) with the \mathbf{K} vectors defined in reciprocal space. The two types of basis functions are joined at the sphere boundary agreeing in value (and slope). The WIEN2k program has been developed during the last 38 years and is used worldwide by about 2800 groups. It is a highly accurate all-electron code, which allows computing the total energy (for structure optimization or phase stabilities), the band structure, density of states, the charge density (for understanding chemical bonding) and many more quantities (like phonons). For the characterization of solids many experimental results (spectra, electric field gradients, NMR chemical shifts, etc.) require a theoretical simulation for their interpretation providing an understanding of trends by computer experiments.

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QUANTITATIVE CONVERGENT- BEAM ELECTRON DIFFRACTION AND QUANTUM CRYSTALLOGRAPHY

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No matter which approach one takes towards quantum crystallography, highly accurate and highly precise experimental structure factors are indispensable. There have been numerous developments in the area of electron crystallography and quantitative convergent-beam electron diffraction (QCBED) in particular, which are allowing new levels of accuracy and precision to be reached¹⁻³. Some of these developments will be discussed in the context of how they help resolve uncertainty in the determination of bonding charge distribution within a crystal.

By way of example, metals and metallic bonding will constitute the focus of the discussion and act as the conduit for illustrating the importance of improved accuracy and precision in experimental measurements of structure factors. This is because a much smaller fraction of the valence electron density actually engages in bonding than in non-metals⁴, making subtle changes in structure factor magnitudes, due to bonding, very difficult to detect in the absence of very high precision measurements.

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DYNAMIC QUANTUM CRYSTALLOGRAPHY

Anders Ø. Madsen^a, Anna Hoser^b, Ioana Sovago^a, Nanna Wahlberg^a

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^b *University of Warsaw, Department of Chemistry, Warsaw, Poland.*

The use of quantum mechanics in crystallography has a long history, however in most applications the quantum mechanical modeling has focused on the description of the electron density. Much less attention has been devoted to the nuclear motion, although the atoms in the crystal are of course vibrating, even at the lowest temperatures. This is unfortunate. Not only does the atomic and molecular motion define important physico-chemical properties such as the mechanical and thermodynamic stability of the crystal, but the concerted motion of atoms give rise to thermal diffuse scattering which affects the Bragg intensities. In other words, from the point of view of X-ray scattering the electron density and the nuclear density are communicating vessels.

We see great potential in the use of quantum mechanics to construct models of the thermal vibrations in crystals, which can be refined and/or validated against scattering data. Scattering data is here understood in the broadest sense; the traditional methods of X-ray and neutron diffraction should be complemented by other probes, such as ssNMR, Raman and terahertz spectroscopies, as well as inelastic scattering or thermal diffuse scattering, which are all techniques that holds the key to understand the correlated motion of atoms in crystals.

On the computational side, we believe that a similar broad range of techniques should be employed, from simple force-field models to periodic density functional theory calculations. These techniques can be used to construct lattice-dynamical models, or to perform molecular dynamics simulations.

Ultimately, the quantum-mechanical models of electron density distribution and nuclear motion should amalgamate into a common model, which can be compared and refined against the experimental evidence, and which can be used to understand solid state properties at the atomic level.

We will present our recent approach to refine lattice-dynamical models against diffraction data^{1,2}, demonstrate a combined model of normal mode and multipole refinement, and we will also demonstrate how thermal diffuse scattering, when not accounted for, affects the modeling of charge density models against diffraction data, based on models refined against synthetic data.

References

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COMPUTATIONAL CRYSTALLOGRAPHY WITH Quantum ESPRESSO (a few years later)

Paolo Giannozzi^a

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The interplay between crystallography and quantum simulations - i.e. atomistic simulations based on the electronic structure - has a long story. Crystallography provides starting structural data for simulations, while in turn, simulations provide tentative structures and structural data for cases where direct experimental measurements are either not possible or not easy to interpret. One may wonder whether tighter and more fruitful interactions are possible, in which crystallography and quantum simulations complement and improve each other.

The class of first-principle simulations I am considering is based on Density-Functional Theory, pseudopotentials and a plane-wave basis set, as implemented in the Quantum ESPRESSO open-source software¹. The first mention of "computational crystallography" and "Quantum ESPRESSO" in the same title² dates back to 2005. Since then, many theoretical and methodological advances have been introduced and made available in such software of widespread usage. I will briefly describe a few of those advances, notably:

- efforts towards software verification and validation, reproducibility of computations³
- all-electron charge density with Projector-Augmented Waves (PAW)
- hybrid and nonlocal functionals

and their potential relevance in the field of charge density analysis⁴ and quantum crystallography.

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ELECTRON DENSITY, ELECTROSTATIC POTENTIAL, ELECTROSTATIC INTERACTIONS IN THE CONTEXT OF INTERMOLECULAR INTERACTIONS

Paulina Maria Dominiak^a

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Research Centre, Warszawa, Poland*

My research activities oscillate around electron density modelling and intermolecular interaction energy estimations in crystallography and structural biology or chemistry. During the meeting I will present some of my personal views on analysis of intermolecular interactions in crystals and other supramolecular assemblies: proteins, nucleic acids, their complexes, etc.. As a case study I will briefly show our recent results on experimental charge density determinations for nucleobase chloride salts and followed them quantum mechanical calculations. I will touch the following concepts and methods: computing of electrostatic interaction energies from molecular/crystal charge densities, estimation of interaction energies from topological parameters, charge density overlap, and perturbation theory approach to total interaction energy decomposition. At the end I will shortly comment on single particle electron cryo-microscopy and related with it electrostatic potential.

QUANTUM CRYSTALLOGRAPHY: PAST AND PRESENT BUT MAINLY THE FUTURE

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The wavefunction is, strictly, an invalid concept. The Schrödinger equation is wrong. It is only a stepping-stone on the way to the *density matrices* of quantum statistical mechanics, the more general second-quantized *fields*, and our current accepted theory, the *Standard Model*. The wavefunction is therefore only a model, just as classical mechanics was before it. Yet modern Quantum Chemistry demonstrates that the wavefunction is *incredibly useful*. So it makes sense to model the wavefunction by any means possible.

With this preparation, I want to define Quantum Crystallography (QCr) as follows: *it is the field by which we derive some of the parameters in a model wavefunction or density matrix of a subsystem, by using experimental scattering information, for the purposes of making predictions for properties which are more reliable than from other types of calculations or experiments.*

The QCr field has been nicely reviewed by Grabowsky and Bürgi, recently; and we will hear from others at this meeting, more qualified than I, speaking about its history. I only want to highlight the work of Parr and coworkers, who developed an algorithm for a somewhat systematic search for improved density functionals, a really significant idea. In my own work, with my colleagues, I only tried to extend their wavefunction fitting method to use experimental X-ray diffraction data.

Now to the present.

The old IUCr commission for Charge, Spin and Momentum Densities, the home for what we would call QCr, is experiencing difficulties. I want to speak a bit about what the source of these problems are. I want to speak about the name QCr and why it is in many ways an unsuitable name; yet it presents a fantastic opportunity for the future. I want to speak about developments on the experimental front, which are necessitating a re-examination of all aspects of high resolution crystallography. And what about the crystal in QCr? Why spend so little time on it except for a few weeks before synchrotron time? What should be the mission and vision of QCr? How can it compete with, and differentiate from, single molecule diffraction, electron crystallography, crystal engineering, or <whatever>? Who will do the work? How can we excite others? I want to consider these and questions, taking what I have seen from other successful disciplines.

After this analysis, and with some trepidation, I want to present my plan for the future, and discuss it with you, because it depends on all of us.

QUANTUM REFINEMENT OF PROTEIN CRYSTAL STRUCTURES

Ulf Ryde^a

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We have developed methods to replace the empirical (molecular mechanics, MM) potential employed in standard X-ray crystallography by more accurate quantum-mechanical (QM) calculations for a small, but interesting part of the protein¹. We typically employ density-functional theory (DFT) for the QM calculations. We have shown that this approach allows us to locally improve the crystal structures². Moreover, we can determine the protonation state of metal-bound ligands³, the oxidation state of the metal⁴ and detect photoreduction of the structure^{4,5}. This quantum-refinement method has been employed for many proteins of interest, e.g. ferrochelatase¹, myoglobin⁶, cytochrome C₅₅₃,² peroxidase⁷, [NiFe] hydrogenase⁵, Mn superoxide dismutase⁴, nitrogenase⁸ and particulate methane monooxygenase⁹. The method has been extended to use neutron-crystallographic data¹⁰, as well as NMR structure refinement¹¹ or EXAFS spectroscopy¹².

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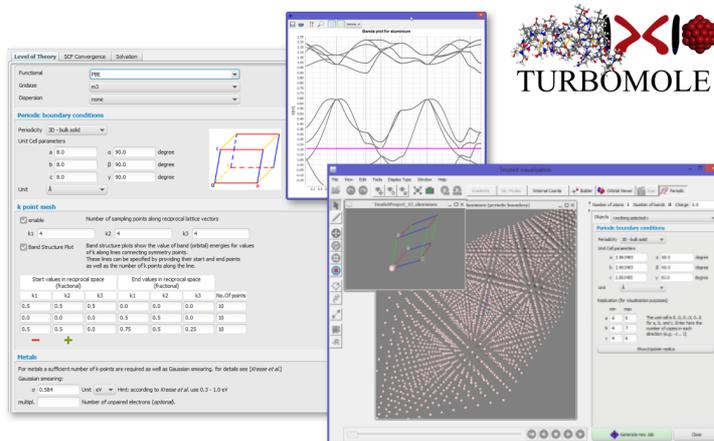
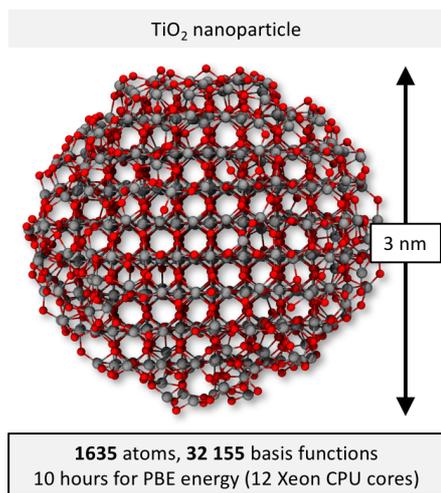
TURBOMOLE – FAST AND ROBUST QUANTUM CHEMISTRY

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An overview of the algorithm and capabilities of Turbomole is given in relation to the topic of the meeting - Quantum Crystallography. Turbomole is a highly optimized software package for large-scale quantum chemical simulations of molecules, clusters, and extended systems under periodic boundary conditions¹. It uses Gaussian basis sets and specializes on predictive electronic structure methods with excellent cost to performance characteristics, such as (time-dependent) density functional theory (TDDFT), second-order Møller–Plesset theory, and explicitly correlated coupled cluster (CC) methods. These methods are combined with ultraefficient and numerically stable algorithms such as integral-direct and Laplace transform methods, resolution-of-the-identity, fast multipole, and low-order scaling techniques. Apart from energies and structures, a variety of optical, electric, and magnetic properties are accessible from analytical energy derivatives for electronic ground and excited states. Recent additions include post-Kohn–Sham calculations within the random phase approximation, DFT calculations under periodic boundary conditions, spin-orbit couplings, explicitly correlated CCSD(T) methods, and nonadiabatic molecular dynamics simulations using TDDFT. In addition, TmoleX is available as a dedicated graphical user interface allowing the user to perform the entire workflow of a quantum chemical investigation ranging from building of an initial structure to the interpretation of the results².



TmoleX is the free graphical user interface for TURBOMOLE that can be used to prepare input files, run jobs and to visualize results

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MULTI-WAVELENGTH SINGLE CRYSTAL X-RAY DIFFRACTION EXPERIMENTS: A POSSIBILITY TO STUDY THE LIMITS OF THE BORN-OPPENHEIMER APPROXIMATION?

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During the elastic scattering process in single-crystal X-ray diffraction (XRD) electrons of a molecule of an irradiated crystal become oscillating emitters of radiation with the same wavelength than the incoming radiation. The scattering process is instantaneous, in a time span as fast as attoseconds. During scattering a fraction of core electrons get excited, which leads to a phase change of the respective scattered radiation ("anomalous dispersion", AD). In crystallography AD is taken into account by a complex contribution to atomic scattering factors in crystal structure modeling and refinement. The correction factors directly correspond to the number of electrons affected. They are small for light elements, but can be considerable for metals. Corrections are energy dependent and have been tabulated for wavelengths commonly used. In quantum chemistry the Born Oppenheimer approximation assumes that the electrons directly follow the motion of the slower nuclei, so that electronic and nuclear motion can be treated separately. When synchrotron radiation is used for an XRD scattering experiment the photon energy used can be chosen to an accuracy of approximately one or a few eV. It is thus possible to choose a wavelength at and below values, where AD is strong for a chosen element. This way only some of the electrons of an atom in a crystal structure contribute to AD. This is exploited for phasing non-centrosymmetric macromolecular structures. Studying AD provides other so far unexplored opportunities. Crystal structures of metal complexes with only one heavier element provide the opportunity to selectively investigate instantaneous core-electron excitation. We have carried out single-crystal diffraction experiments on a nickel compound in the laboratory and compounds with zirconium and molybdenum with tunable wavelengths at the SLS or PETRA III synchrotrons for this purpose. The energy close to the absorption edge of these metals corresponds to wavelengths that permit measuring diffraction data to a resolution of 0.83 in $\sin \Theta/\lambda$ in each case, a resolution high enough to provide a detailed map of the electron density distribution. An important detail in subsequent data analysis is that only accurate structural models (i.e. phases) do allow detailed analysis¹. The first results of our experiments are conceptually simple difference electron-density maps. Differences are calculated from residual electron density remaining after aspherical-atom analysis above and below the absorption edge of a structure under investigation.

What I would like to discuss on the meeting is the role of theory in understanding our experiments. Comparison of the experimental results to those of theoretical computations would be helpful, but theoretical modeling of the experimental results is currently challenging at best.

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WHEN DIFFRACTION EXPERIENCES CHALLENGE AB INITIO CALCULATIONS

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Thanks to user's friendly - black boxes - software, DFT calculations are nowadays almost routine for modelling the electronic structure of molecules and materials and calculating physical properties. On the other hand accurate X-ray and polarized neutron experiments diffraction allow accurate charge and spin density modeling. Experimental electron density modeling also becomes routine among crystallographers who are able to use also user's friendly – black boxes- software (Mopro, XD) and many experimental results are compared to DFT calculations. Quantum crystallography relies on these two approaches and therefore questions about the precision and accuracy of both approaches must be addressed.

If both experimental and theoretical electron densities agree then one can calculate realistic electron density derived properties. At this stage one question is addressed: how should we compare experiment with theory in direct space? In reciprocal space? Using or not a common model like the multipole model? What about thermal motion? The first part of the talk will try to clarify this difficult question.

If DFT calculations disagree with experiments, either the experimental accuracy and/or precision are not good enough or the theoretical model is inadequate or too primitive. This will be discussed in the second part of the talk on two examples:

- charge transfer in a donor acceptor complex as estimated from DFT and accurate X-ray diffraction;
- charge and spin density modeling of an organic radical comparing DFT and CASSCF with a model refined against joint X-ray and polarized neutron diffraction data.

Acknowledgments. This work is a collaborative work between four research teams, CRM2/IJB (Bolivar Voufack, Nicolas Claiser, Mohamed Souhassou, Pilar Garcia, Janos Angyan, Slimane Dahaoui), SRSMC/IJB (Alessandro Genoni and Marco Marazzi), Ecole Centrale de Paris (Zeyin Yan and Jean Michel Gillet), Laboratoire Leon Brillouin (Beatrice Gillon). We thank ANR (Agence Nationale de la Recherche) for partly sponsoring this project.

MOLECULES AS NETWORKS

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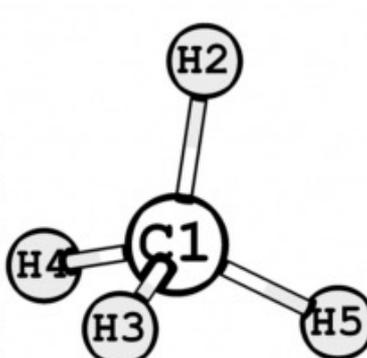
Chemical graph theory (CGT) represent the molecular graph using connectivity matrices followed by the extraction of matrix invariants to be used as molecular descriptors in QSAR/QSPR studies. Using similar techniques, matrices built from the complete set of QTAIM localization and delocalization indices (LIs and DIs) represent molecules as a “fuzzy, complete” networks of interacting atoms. In a molecular network, an edge exists between any pair of atoms weighted by the DI between them. This fuzzy and complete matrix representation of a molecule is termed the (electron) “localization-delocalization matrix (LDM)”. LDMs are powerful QSAR/QSPR modeling tool with applications ranging from predicting physicochemical properties of homologous series of molecules, corrosion protective abilities (and identifying active protective species), ribotoxicity, pKa's, aromaticity, and more. LDMs of large molecules can be reconstructed from kernel fragments (within the KEM scheme) if a geometry is available whether from a computational optimization or from an X-ray diffraction experiment.

$$\text{LDM} \equiv \begin{bmatrix} \Lambda(\Omega_1) & \delta(\Omega_1, \Omega_2)/2 & \cdots & \delta(\Omega_1, \Omega_n)/2 \\ \delta(\Omega_2, \Omega_1)/2 & \Lambda(\Omega_2) & \cdots & \delta(\Omega_2, \Omega_n)/2 \\ \vdots & \vdots & \ddots & \vdots \\ \delta(\Omega_n, \Omega_1)/2 & \delta(\Omega_n, \Omega_2)/2 & \cdots & \Lambda(\Omega_n) \end{bmatrix}_{n \times n}$$

$\left. \begin{array}{l} \sum_{\text{row}} = N(\Omega_1) \\ = N(\Omega_2) \\ \vdots \\ = N(\Omega_n) \end{array} \right\} \sum_{i=1}^n N(\Omega_i) = N$

$\underbrace{\sum_{\text{column}} = N(\Omega_1) \quad = N(\Omega_2) \quad = N(\Omega_n)}_{\sum_{i=1}^n N(\Omega_i) = N} \quad \text{tr}(\zeta) = N_{\text{loc}}$

| | C1 | H2 | H3 | H4 | H5 | Σ |
|----------|-------|-------|-------|-------|-------|----------|
| C1 | 4.040 | 0.492 | 0.492 | 0.492 | 0.492 | 6.007 |
| H2 | 0.492 | 0.444 | 0.021 | 0.021 | 0.021 | 0.998 |
| H3 | 0.492 | 0.021 | 0.444 | 0.021 | 0.021 | 0.998 |
| H4 | 0.492 | 0.021 | 0.021 | 0.444 | 0.021 | 0.998 |
| H4 | 0.492 | 0.021 | 0.021 | 0.021 | 0.444 | 0.998 |
| Σ | 6.007 | 0.998 | 0.998 | 0.998 | 0.998 | 10.000 |



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QUANTUM CRYSTALLOGRAPHY IN SPIN-RESOLVED PHASE-SPACE

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Scattering of X-rays and electrons is essentially done by the entirety of the electron density cloud, while spin-polarized neutrons are diffracted by the limited number of unpaired electrons¹. In the same spirit, it is possible to use circularly polarized X-rays to perform magnetic-state sensitive inelastic scattering experiments and thereby probe the very same unpaired electrons, simply from a different perspective.

Obviously, the quantum state (or mixture of quantum states) of the scrutinized electrons is not conditioned by the chosen experimental techniques (or combination of techniques). It is a major challenge of Quantum Crystallography to exploit this basic fact: all scattering techniques, which are employed in crystallography, probe different aspects of the N -electron wavefunction, or the one-electron reduced density matrix². They thus offer complementary pictures of a wider reality that is only (and imperfectly) accessible by solving Schrödinger's equation. Moreover, these independent experimental results need to be coherent with each other. Therefore, the least possible biased common basis, or connection, ought to be constructed.

While Heisenberg's indetermination prevents any probability distribution of quantum particles in phase-space, this representation still proves useful for re-connecting position and momentum pictures as provided by high-resolution diffraction and Compton scattering data respectively³. In this talk, we will give a subjective view of our attempts at finding the most adequate strategy to enrich our knowledge of electron behavior by modelling a spin-resolved density matrix or, equivalently, a Wigner function with the help of polarized neutron, x-ray, electron diffraction structure factors and magnetic (or regular) directional Compton scattering profiles. We hope to demonstrate that this joint approach of exploiting two experimental techniques which were at the very foundations of quantum physics still holds promise when it comes to providing an ever more accurate description of how electrons actually do behave in crystals.

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WHAT ARE THE EXPERIMENTAL PREREQUISITES IN QUANTUM CRYTALLOGRAPHY?

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In this contribution we outline new experimental and instrumental techniques to derive quasi-static correlated electron density distributions, which are in the ideal case solely biased by the inherent zero-point motion of atoms in solids. These correlated densities provide the necessary starting point to identify and analyze density based control parameters of physical and spectroscopic properties. The talk will also provide some examples to illustrate why the expression “quantum crystallography” should be taken with a grain of salt.

ACCURATE EXPERIMENTAL CHARGE DENSITY DATA COLLECTIONS USING CPAD TECHNOLOGY

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After the introduction of hybrid pixel array detectors for synchrotrons more than ten years ago, the detector development for 4th generation synchrotrons (free electron lasers; FEL) went away from direct photon counting technology¹ because of severe draw-backs in X-ray detection including charge-sharing and count-rate saturation^{2,3}. Due to rapid degradation of the sample, data collections at FELs normally do not allow for collecting high-multiplicity data on one single crystal, and therefore the systematic effects on the intensities from an HPAD cannot be corrected. Consequently, charge integrating pixel array detectors (CPAD) are currently in use/development at the European XFEL, the Swiss FEL and the LCLS (SLAC, Stanford).

A CPAD detector for the home lab (PHOTON II) is available for more than a year now and a series of first experimental charge density results underline the superior CPAD data quality compared to CCD, IP, CMOS APS (PHOTON 100), and HPAD devices.

Results as well as data collection and processing tricks and advice will be presented.

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TOPOLOGICAL ANALYSES OF THE ELECTRON DENSITY, ITS LAPLACIAN FUNCTION AND THE ELECTROSTATIC POTENTIAL TO STUDY MOLECULAR ORGANIZATION IN SPACE

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The electron density distribution $\rho(\mathbf{r})$ is the conceptual bridge between the structure and the energetic properties of molecular systems through the Hellmann-Feynman and Hohenberg-Kohn theorems.¹ Accordingly, $\rho(\mathbf{r})$ codes essential features of molecular organization in space. Important aspects such as molecular recognition, intensity, nature and directionality of intermolecular interactions are at the origin of this organization in supramolecular structures with important applications in Crystal Engineering, Supramolecular Chemistry and Material Science. These aspects are not only implicitly coded on $\rho(\mathbf{r})$ but also in its derived properties, as in the laplacian function $\nabla^2\rho(\mathbf{r})$ and the electrostatic potential $\varphi(\mathbf{r})$. Hence, to extract the information of the intermolecular interactions that are driving the molecular organization in space, the analyses of $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$ and $\varphi(\mathbf{r})$ are main issues. In this context, the topological analysis of any scalar function, which is the analysis of its derivatives, provides richer information than appears from the direct observation of the scalar function itself. It should be however noted that the topological features of $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$ and $\varphi(\mathbf{r})$ need to be specifically interpreted, because each function bears different information with respect to the others on the properties of the molecular system. In our work, topological developments on these scalar functions have permitted the analysis of (i) the intensity² and the nature³ of intermolecular interactions, (ii) the molecular orientation⁴ and (iii) the influence zones of molecular electrophilic and nucleophilic sites that are at the origin of molecular assembling, in particular with anionic or cationic complexes.⁵

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FROM ELECTRON DENSITY TO PROPERTIES?

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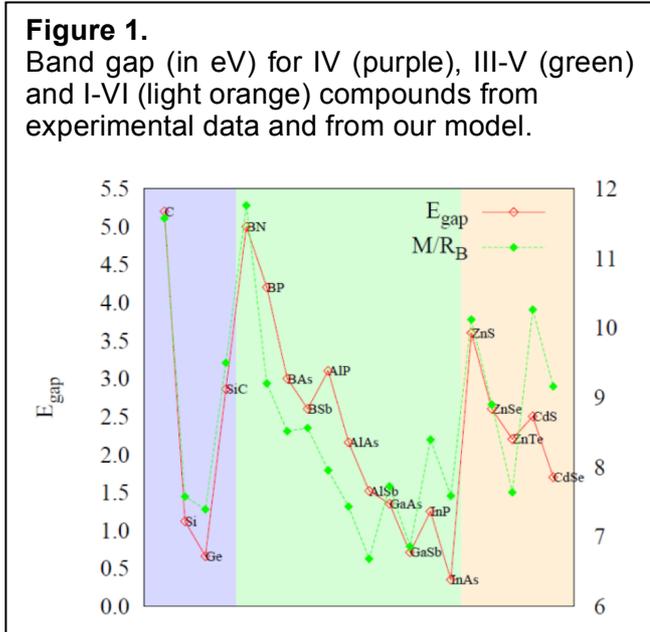
Topology has been a great source of insight in the understanding of crystalline organization. However it lacks a fundamental characteristic: it is barely predictive. This is so due to the lack of a direct (known) link between electron density topology and energetics.

One way to approach this gap is to build energy models relying on topology. We have explored using a potential energy surface that includes chemical quantities explicitly, so that properties provided are directly related to the inherent

organization of electrons within the regions provided by topological analysis.

As a start, we have resorted to a very simple model, the Bond Charge Model by Parr (BCM)¹, to describe the energetics of electron pairs. Coupling this to conceptual DFT, the band gap of solids can be univocally defined². Applied to zinc-blende solids as a model case, trends in band gap can be predicted in terms of bond properties (length, charge, crystalline structure- Figure 1). However, this is just a first step towards the understanding of the electron density-

macroscopic properties link which we thoroughly believe needs to be intensively explored. But how? I propose we discuss this topic, basic to electron density studies, crystallography and quantum chemistry in general.



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RELATIVISTIC EFFECTS & QUANTUM CRYSTALLOGRAPHY OF HEAVY ELEMENT COMPOUNDS

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In this lecture, we will focus on formal and practical issues of Quantum Crystallography methods related to heavy element compounds¹. Compounds of mercury will be considered in particular. The quasi-relativistic Infinite order two component (IOTC)² version of the Dirac Hamiltonian will be employed.

- Robustness of relativistic Hirschfeld atoms refinement (HAR)³ will be considered.
- X-ray constrained wavefunction (XCW) fitting⁴ will be explored, with respect to information extraction power of the XCW method. Electron density, structure factors and electronic properties will be examined. The XCW fitting of relativistic and electron correlation effects⁵ will be compared.
- Side effects of the IOTC methods for properties evaluation will be critically examined, i.e. picture change error (PCE) of the IOTC wavefunction for high angle structure factors (atomic scattering factors).

The study will be performed on a theoretical level. Currently the structures suffer under severe radiation damage. Apart of that, side effects such as absorption is a serious challenge in the proper treatment of experimental data of heavy element compounds (the quantum treatment of core electron excitations seems worth the effort to take into account that the scattering wave function does not ought to be predominantly in the grounds state).

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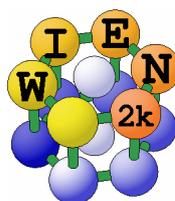
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- Wien2k (<http://susi.theochem.tuwien.ac.at/>)



TOURISTIC ATTRACTIONS IN NANCY

(Selected from <http://travel.michelin.com>)

If you need detailed information visit also the "Office de Tourisme" in "Place Stanislas". For a rapid tour of the main touristic attractions you can also consider the that leaves every 45 minutes form "Place de la Carrière" (see <http://petit-train-nancy.fr/en/>)

- **Place Stanislas** (UNESCO World Heritage Site; Place Stanislas)

The square's main point of interest is the marvelous gold-plated wrought iron gates made by Jean Lamour that adorn the four cut-off corners and entrance to Rue Stanislas and Rue Sainte-Catherine. The northern gates surround the fountains of Neptune and Amphitrite, by Nime artist Guibal. Five raised and two-ground floor pavilions complete the startling harmony of this square, which is crowned with a statue of Stanislas Leszczynski.

- **Place de la Carrière** (UNESCO World Heritage Site; Place de la Carrière)

This long square used to be for horse training and dates back to the ducal period, but was redesigned by Héré. It is surrounded by lovely private mansions and each corner is adorned with a fountain. At each end there are gates by Jean Lamour with lantern brackets.

- **Parc de la Pépinière**

Designed for Stanislas Leszczynski, this 23 ha promenade includes a terrace, an English garden, a rose garden and a zoo. It contains a statue of the painter Claude Gellée, called "le Lorrain" by Rodin

- **Porte de la Craffe** (Grande Rue)

At the end of the "Grande Rue", this majestic gate, built in the 14th century, is the oldest in the city. It was used as a prison and is now an annex of the Lorraine Historical Museum. It is decorated with the Nancy thistle and the Lorraine cross.

- **Palais Ducal** (64 Grande Rue)

Built in the 13th century, The Ducal Palace was rebuilt after the victory of René II over the Foolhardy. Today the palace houses the Lorraine Historical Museum.

- **Marché Central de Nancy** (Place Charles III)

The Nancy Central Market is a permanent market building which is open from Tuesday to Saturday from 7 am to 7 pm. Because of the quality and variety of products sold by more than 110 artisans, this is one of the most important markets of Lorraine gastronomy.

- **Basilique Saint-Epvre** (Place Saint-Epvre)

Built during the 19th century in the gothic style and preceded by a monumental staircase offered by the Emperor of Austria.

- **Eglise Saint-Sébastien** (Place Charles III)

The church has a spectacular concave facade decorated with four large bas-reliefs and is masterpiece of architect Jenesson. It was consecrated in 1732. Inside, the three hall-style naves are topped with a strange flat vault. The lateral altars are by a member of the school of Nancy (Eugène Vallin).

- **Musée des Beaux-Arts** (3 Place Stanislas)

The Fine Arts museum is housed in one of the pavilions in Place Stanislas. It displays its collections from the 14th to the 20th century works with subtle use of light and sometimes unexpected combinations. Some of the most interesting collections include the 787 engravings by Jacques Callot, 1,400 drawings by Grandville, glass and crystal work by Daum, pieces from Caravaggio, Delacroix, Bonanrd, Utrillo and Matisse, sculptures by Duchamp-Villon and Zadkine, to name but a few.

- **Musée de l'Ecole de Nancy** (36-38 Rue du Sergent Blandan)

An overview of the rebirth in decorative arts in Nancy from 1855. Inlaid wood furniture by Gallé, Louis Majorelle, Eugène Vallin and Jacques Gruber, posters and drawings by Pouvère, Martin and Collin, glasswork by Gallé and the Daum brothers, stained-glass windows by Gruber... A lovely dining room by Vallin (ceiling and mural leather by Prouvé), a stunning bathroom in ceramic by Chaplet, a lovely study... A perfect introduction to your discoveries of "Art Nouveau" in the city!

- **Art Nouveau Tour**

A tour showing you the houses built by the members of the "Art Nouveau" school of Nancy. 86 Rue Stanislas (Eugène Vallin, 1896), Est Républicain (5 Avenue Foch), the BNP branch (9 Rue Chanzy) with ironwork by Majorelle, the shop at 2 Rue Bénit with its metallic structure and stained-glass windows by Gruber, the building at 42-44 Rue Saint Dizier by Biet and Vallin, the Crédit Lyonnais at 7bis Rue Saint Georges with glasswork by Gruber, and the houses on Quais Claude-Le-Lorraine by Emilie André.

- **Musée Lorrain** (64 Grande Rue)

The Lorraine Historical Museum contains documentation of exceptional quality and depth about the Lorraine region, from prehistory to World War I. Souvenirs of the destiny of the dukes of Lorraine, tapestries, paintings by Georges de La Tour, prehistorical archaeology, paintings and documents, miniatures and earthenware, and sculptures by Clodion. Twenty centuries of Lorraine history passes in front of your eyes.

- **Muséum-Aquarium de Nancy** (34 Rue Sainte Catherine)

The Museum-Aquarium houses a tropical aquarium where fishes from the Red Sea, Indian Ocean and Amazon Basin can be found in a selection of 70 different tanks. On the first floor, there is a collection of 10,000 stuffed animals.

Restaurants in Nancy

Several restaurants for lunch and dinner can be found in Nancy, going from fast food to fine dining. Other than central "Place Stanislas, streets with many restaurants are the "Grande Rue", "Rue de Maréchaux" and Rue Stanislas, all of them at walking distance from the conference site and from the "Hôtel de Guise".

