



Commission on Quantum Crystallography

A CENTURY AFTER THE BRAGGS AND VON LAUE – QUANTUM CRYSTALLOGRAPHY

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Abstract

This is a summary of different views on Quantum Crystallography (QC). This term was introduced in the 1990s by Massa, Huang and Karle who defined Quantum Crystallography as a collection of: (1) techniques for which crystallographic information enhances quantum mechanical calculations and (2) methods in which quantum mechanics enhances the information available from a crystallographic experiments. Within years this original definition of QC seems to be too narrow. This summary presents my personal point of view on a definition of the area and the most important milestones of this field of quantum crystallography.

Introduction

More than century ago Max von Laue, William Henry Bragg and William Lawrence Bragg originated the field of structural applications using X-ray diffraction. Since then, the X-ray diffraction methods have been used to establish crystal and molecular structures of more than 1.5 million compounds - among them many of pharmaceutical, biological and medical importance. However, it is a great paradox that more than 99 % of all these structures have been refined by applying the simplest possible model of electron density which is the Independent Atom Model (IAM). Even now the overwhelming majority of all newly established structures are obtained with the IAM which was introduced by W. H. Bragg in 1914. However, modern crystallographic methods go far beyond just routine crystal structure analysis based on approaches that are theoretically and methodologically stricter than IAM which are now undergoing a rapid development. This is often termed Quantum Crystallography(QC) to stress its relation to quantum mechanics. A strength of theory is in the fact that model systems can be simulated irrespective of their existence in nature, allowing the investigation of effects associated with different modifications on system properties. Theoretical approaches are also based on numerous approximations and assumptions. On the other hand, experimental techniques often introduce severe experimental errors and simplifications. Combining the two is a real challenge.

There have been plenty of interesting papers published within this emerging field – some selected ones are mentioned as references. However, I want to stress in particular

a very interesting conceptual Chem. A Eur. J. viewpoint paper by Genoni and co-workers [1] resulting from a small conference devoted to this field. This paper was initiated at the Discussion Meeting “Quantum Crystallography: Current Developments and Future Perspectives” (Nancy, France, 19–20 June 2017) under the umbrella of the European Centre for Atomic and Molecular Calculation (CECAM). The meeting was devoted to definition and perspectives of quantum crystallography and gathered most of the researchers active in this field (although definitely not all of them). This paper [1] defines a modern understanding of QC. As I am to represent our community and present the main ideas of the whole field, I will use the above review paper as an excellent overview of the field, so this account is a kind of an extended summary of this viewpoint review publication. Although in this contribution, I will also try to present also my personal point of view on a definition of the area and the most important milestones of this field of quantum crystallography. I would say that I share and support the most of the ideas presented in QC literature and particularly in the reference [1]. However, at some points my opinion differs from those presented in QC literature.

Discussion

Quantum crystallography is an active (I would even say volcanic) area now, full of discussions and new developments. Even the definition of the field is subject to a great debate. Historically, the term Quantum Crystallography was introduced in the 1990s by Massa, Huang and Karle (the 1985 Nobel Prize in chemistry laureate for the development of direct methods for solving crystal structures) [2, 3]. They defined Quantum Crystallography as a collection of: (1) techniques for which crystallographic information enhances quantum mechanical calculations and (2) methods in which quantum mechanics enhances the information available from a crystallographic experiments. However, within years this definition began to appear to be too limited to characterise the whole broader and broader field.

It is worth to note that since the very first crystal structure investigations, crystallography and quantum mechanics have been quite strongly connected. An excellent example of this complex coupling is that refinement of a model of a crystal structure against X-ray diffraction data as atomic scattering factors of electron density of the atomic ground state are calculated with quantum mechanical methods. The sum of spherical ground state electron densities of the isolated atoms defines the crystal electron density. This is the definition of IAM. In routine refinements, IAM is complemented by thermal factors usually in the form of independent vibrations of atoms (ADPs) under the harmonic approximation. So the aim of routine X-ray

structure investigations is to obtain as reliable as possible atomic position data (thereby the geometry of molecule and interatomic contacts) and atomic displacement parameters.

However already in 1915, Debye raised a hypothesis that on the base of X-ray data it should be possible to establish special arrangement of electrons inside an atom. It took ca. 50 years to accomplish quantitative distributions of electron density from X-ray data. This was possible thanks to the use of maximum entropy methods and development of multipole refinement methods. The multipole refinement of experimental electron density is based on a finite spherical harmonic expansion of the electronic part of the charge distribution about each atomic center. Such an atomic expansion is called a pseudoatom and the molecular electron distribution at any point in a crystal is the sum of pseudoatomic densities. Historically, there were different variants of multipole refinements as, for example, the ones proposed by Hirshfeld [4], Stewart [5]. In the most commonly used formalism now of Hansen and Coppens, [6] the pseudoatom electron density is defined by:

$$\rho(\mathbf{r}) = \rho_c(r) + P_v \kappa^3 \rho_v(\kappa r) + \sum_{l=0}^{l_{\max}} \kappa^{l^3} R_l(\kappa' r) \sum_{m=0}^l P_{lm\pm} d_{lm\pm}(\theta, \varphi)$$

where $\rho_c(r)$ and $\rho_v(r)$ are spherical core and valence densities, respectively. The third term contains the sum of the angular functions $d_{lm\pm}(\theta, \varphi)$ to take into account aspherical deformations. The angular functions $d_{lm\pm}(\theta, \varphi)$ are real spherical harmonic functions. The coefficients P_v and $P_{lm\pm}$ are populations for the valence and deformation density multipoles, respectively. The κ and κ' are scaling parameters introduced to make valence and deformation densities expand or contract. In the Hansen-Coppens formalism the P_v , $P_{lm\pm}$, κ and κ' are refineable parameters together with the atomic coordinates and thermal coefficients. Recently [7], the corresponding

parameters of core densities were allowed to change as well. The least-squares refinements are performed against the measured intensities $F^2(hkl)$ of reflections obtained by single crystal X-ray diffraction. This requires resolution of data up to 0.40-0.45 Å and data completeness around 99 %.

Starting atomic coordinates and anisotropic displacement parameters are taken from the ordinary spherical refinement stage and freely refined. The C-H bond distances and thermal motions of H-atoms are usually taken from neutron diffraction studies or fixed (when neutron data are not available) at the averaged neutron distances for similar groups. Each atom is assigned core and spherical-valence scattering factors derived from Clementi and Roetti (or a few others) wavefunctions [8]. A single- ζ Slater type radial function multiplied by density-normalized spherical harmonics are used to describe the valence deformation terms. The multipole expansion usually is truncated at the hexadecapole level for the non-hydrogen atoms. Usually, only bond-oriented dipole components for H atoms are applied. The radial fit of the valence density is optimized by refinement of the expansion-contraction parameter κ for all non-hydrogen atoms. The valence-deformation radial fits are optimized by refinement of the κ' parameters. The validity of all κ and κ' values are checked against the values obtained from multipole refinement based on theoretical structure factors for a series of model compounds. [9] The adequacy of proper deconvolution of the thermal motion from the bonding density for each model is tested with the Hirshfeld rigid-bond test [10,11].

Once such an aspherical atomic electron density $\rho(r)$ is defined, then it can be used to obtain aspherical atomic form factors and aspherical structural factors for a given crystal. The squares of such aspherical structural factors corrected for numerous experimental effects such as thermal motions, extinction, absorption, TDS when present, *etc.* are proportional to the measured intensities of the reflections.

The radial decay of the pseudo-atoms and the core and valence scattering factors in multipole models are directly calculated from wavefunctions and hence the analytical shape of the refined electron density is significantly shaped by quantum chemistry. In fact the multipolar orbitals can be related to hybridization states [12] and even to some individual orbital occupancies of d-orbitals in transition metals, [13] and of f-orbitals in lanthanides [14]. Additionally, the multipole model of charge density can be extended to include spin-density information.

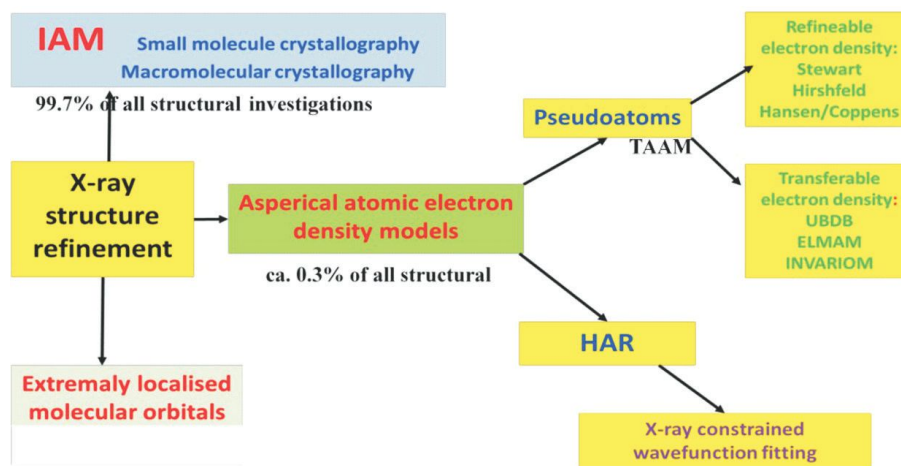


Figure 1. The most common approaches used in modern crystallography to obtain structural and electronic information.



As electronic parameters for the same type of atoms in identical topological environments appear to be grouped close to their average values, the idea of constructing databanks of pseudoatoms emerged [15]. Pseudoatoms are the smallest transferable atomic fragments of electron density, from which the full electron density distribution can be reconstructed. There are three major pseudoatom databanks: UBDB [16-19], Invariom [20-22] and ELMAM [23-24]. ELMAM is based on purely experimental charge densities resulting from multipole refinement against high resolution X-ray diffraction data, whereas the other two databases are based on theoretical results. The above pseudo atom databanks are extremely useful in reconstruction of electron density of macromolecules (proteins and their complexes with drug molecules in particular). This allows investigations of interactions between protein receptors and drug molecules at the level of energy of interactions.

TAAM. When the total electron density in a given molecule or macromolecule is reconstructed on the basis of pseudoatoms taken from one of the available databanks, which is referred to as the Transferrable Aspherical Atom Model (TAAM) and refinement against X-ray data will be referred to as TAAM refinement [17, 23]. A careful comparison of all databases has been discussed by Pichon-Pesme *et al.* in ref. [25], Volkov and Koritsanszky in [16] and Bąk *et al.* in ref. [26]. With all these databases, it is possible to model electron density (ED) apparently better than by using IAM, and more accurately deconvolute thermal motion within the TAAM refinement [17, 23]. In TAAM refinement, pseudoatom parameters for each species are transferred from a chosen database and only atomic coordinates and ADPs are refined. This refinement is more efficient than routine crystallographic refinements and can be used to improve the quality of structural information gathered in CSD, ICSD or PDB databanks.

Another group of QC methods are those based on a direct fitting of the shapes of orbitals and wavefunctions to the measured intensities of the scattered X-ray radiation. These methods originated from discussions at the 1964 Sagamore conference [2, 27, 28] and a few years later Clinton and Massa published their paper on the first QC methods [29]. Nowadays, this field has been further developed by D. Jayatilaka who introduced the X-ray constrained wavefunction (XCW) fitting approach [30–34] and its later developments [35] with a significant contribution also from A. Genoni [36–41] who introduced the “extremely localised molecular orbitals” ELMO approach and others (DFT [34], relativistic Hamiltonians [35-36]). ELMO orbitals also goes with the name “non-orthogonal localised molecular orbitals” (NOLMOs). This group of methods aim at determining wavefunctions that are used to minimize the energy, while reproducing, within the limit of experimental errors, experimental X-ray structure factor amplitudes. It appears that XCW fitting allows for obtaining reliable charge density distributions and determining physical properties of materials [42–46] such as, for example; non-linear optical properties, and also to capture electron correlation [47], polarization and crystal field effects. Other studies also focus on capturing relativistic effects [35, 36] and determination of experimental spin densities [48]. Future challenges for the technique are its extensions

to periodic systems and to multi-determinant wavefunction approaches, although the recent X-ray Constrained ELMO-Valence Bond (XC-ELMO-VB) method [39, 40] can be already considered as an attempt to move in the latter direction [1].

Development of HAR and XCW clearly shows the importance of the availability of a proper code which could then be easily used by a broader group of users. There is also an alternative approach, joint refinement methods for the complete reconstruction of N-representable one-electron density matrices based on X-ray diffraction and inelastic Compton scattering data.[49–53]

The second point of the original definition of QC covers methods in which quantum mechanics enhances the information available from crystallographic experiments. Within this part of QC, the first developments are associated with Quantitative Convergent- Beam Electron Diffraction (QCBED) [54–57], for which the knowledge of the wavefunction describing the high-energy electron passing through the crystal is essential for solving the dynamical electron scattering equations [1]. The solutions to these equations give scattered intensities in calculated diffraction patterns that can be compared to experimental ones in QCBED refinements. Maybe less visible are QC applications in macromolecular crystallography [58, 59], where theoretically derived restraints are used to supplement the limited resolution and amount of diffraction data compared to the number of parameters needed to model atomic positions and displacements in large systems. However, Hirshfeld Atom Refinement (HAR) gives the most spectacular representation of this part of QC. In HAR, Hartree–Fock (HF) or DFT computations are used to derive fragment electron densities for very accurate and precise refinements of structural results currently possible on the base of X-ray data. In HAR, molecular electron densities are taken from theoretical calculations and are partitioned using Hirshfeld’s stockholder partitioning method [60, 61]. This enables a least-squares refinement of atomic positions and thermal parameters using quantum atoms. These preserve all the information from the parent wavefunction (or electron density) from which they have been partitioned. The HAR procedure is iteratively repeated until convergence is reached. HAR currently provides the most accurate and precise structural results from X-ray data, even for the positions of hydrogen atoms [62-64] even in the proximity of heavy atoms. A future challenge for HAR is an extension to large molecules (e.g., proteins) and to heavy-metal systems (e.g., coordination compounds) [1]. XCW fitting and HAR coupled together are termed X-ray Wavefunction Refinement [65]. This is a new approach for both structure and charge density determination from experiment [66]. A summary of different the most common approaches in QC is presented in Figure 1.

Dynamic QC. Many important bulk solid-state properties depend on crystal vibrational properties. The atomic and molecular motions determine the vibrational entropy of crystals, and are crucial for understanding stabilities and phase transitions. Also mechanical properties, such as the elastic moduli of the crystal, are dependent on the crystal lattice dynamics. Information on the correlation of atomic motion is lost in the standard elastic scattering experiment.

However, as the atomic motion reduces the diffraction intensities, this effect is accounted for by introducing the Debye–Waller factors. In consequence the atomic fluctuations—mean square displacements—can be retrieved from a diffraction measurement, and combined with lattice-dynamical models derived from periodic DFT calculations [67, 68]. In this approach, the amplitudes of the acoustic and lowest-frequency optical phonons are refined against the diffraction intensities. In the simplest model, these phonon modes are approximated by the motion at the Gamma point of the Brillouin zone. These Normal Mode Refinements (NoMoRe) take into account essential information about the crystal dynamics from the experiment [68, 69] as has been proved by studies of heat capacity of naphthalene (excellent agreement between results of NoMoRe refinement and experimental heat capacities). The atomic mean square displacements obtained by fitting the normal modes against the diffraction intensities compare well with the displacements obtained from standard crystallographic models. Additionally, the hydrogen atom anisotropic displacements compare well with independent information from neutron diffraction experiments. More detailed studies [70] clearly show that the border between structure, electron density and dynamical properties will be a fertile area of research with the most obvious step being inclusion of Thermal Diffuse Scattering (TDS) in quantum crystallographic studies of the dynamics of crystals.

Topological analysis of electron density. One of the most characteristic landmarks of QC are quantum topological methods of analysis of electron density. Once electron density is established different methods of electron density partitioning can be used to analyse properties of the studied systems. These are, for example, such methods as stockholder [61], pseudoatom partitioning or, the more popular, Atoms-In-Molecules theory [71] (AIM) proposed by R. Bader. These methods are the abbreviated Quantum Theory of Atoms in Molecules (QTAIM) [72]. The AIM theory [72] offers a self-consistent way of partitioning any molecular system into its atomic fragments, deduced from the first principles of Quantum Mechanics and Schwinger's principle of stationary action [73]. In AIM theory, the many electron system is separated into subsystems (atomic basins) by zero-flux surfaces (ZFSs) that satisfy the following condition for every point on the surface: $n\nabla\rho(r) = 0$, where $\nabla\rho(r)$ is the gradient vector field of the molecular electron density, r is a point on the zero-flux surface that separates two fragments, and n is the vector normal to the surface at that point. Further analysis of the gradient vector field of electron density results in localization of extrema of the electron density by finding points named critical points (CP) at which following equation applies: $\nabla\rho(\mathbf{r}_{CP}) = 0$. Particularly useful are bond critical points – the weakest points in bonds which determine their properties. Integrating properties over atomic basins is one of the cornerstones of AIM theory because it yields valuable information such as the energy of an atom, its electronic population and its higher multiple moments [74], its polarizability [75], etc. Localization and delocalization (sharing) of indices have also been defined within QTAIM by integrals of the Fermi hole density (or exchange-correlation hole density in correlated calculations). A certain extension of this concept is

the Localization-Delocalization Matrix (LDM) [76]. This approach has found practical applications in Quantitative Structure–Activity Relationship (QSAR) predictions of molecular properties [76, 77].

A complete population analysis including localization and delocalization information can be derived from the Laplacian of the electron density [1], an experimentally accessible quantity, from the Bader-Gatti Source Function (SF) [78, 80]. Also the electrostatic potential is very useful in the interpretation of properties of the system. Due to their delocalized nature, special f functions have been designed to visualize non-covalent interactions. As an example, the reduced density gradient [81] has been designed to detect weak interactions such as halogen bonds or non-covalent interactions from the electron density (for example, weak interactions in benzene crystals, the delocalized nature of $\text{CH}\dots\pi$ vs. $\text{CH}\dots\text{C}$ interactions). Another important set of the f -functions are those used in analysis of electron pairing, such as the electron density Laplacian [82], the Electron Localization Function (ELF) [83] and the Electron Localizability Indicator (ELI) [84]. This family of functions identifies localized electrons, such as those in covalent bonds and lone pairs [85].

I personally would add two other important area to the QC field which have an auxiliary character. A very important part of QC procedures is based on fitting different models of electron density. This requires sophisticated analysis of errors, and advanced fit indicators which go well beyond routine statistical tools commonly applied in crystallography. The calculated intensities are expected to be close to the observed intensities for good agreement of the model with the true structure. The difference between the observed and the calculated intensity divided by the standard uncertainty of the observed intensity is called the *residual* (ζ). The comparison between observed and calculated intensities is performed by adapting the parameters of the model in order to minimize the sum of residuals (the least-squares minimization in a model refinement). In such a way, the model parameters are fitted to the observed data. The better the fit the better the model. The best model distinguishes itself from other models with the same number of model parameters by showing the smallest residual sum in this class of models. The agreement between observed intensities and model derived intensities as well as the GoF play a central role in the evaluation of a model. A very large number of new fit quality indicators were developed recently by J. Henn [86-90]. Further tools are the alternative GoF, the alternative agreement factors, the Bayesian conditional probability plots and associated χ^2 values, which are well suited to give a more detailed overview over the fit data quality. These are many different diagnostic plots with associated χ^2 values for the joint probability distribution of the residuals and a property X : plots (ζ, X) and plots (ζ, X^2). X could be one of the following properties: intensity, standard uncertainty, resolution, significance or other properties. All these tools allow for careful checking of the quality of fit and verification of whether a given model uses all the information present in the measured intensities of reflections and detect possible systematic errors which in practice means that will have a good estimation of accuracy of the results.



Another auxiliary subarea is crystal structure prediction (CSP). CSP is a global optimization problem since the stable structure is associated with the lowest minimum of the free energy surface [91]. Given a chemical formula, CSP stands for finding the corresponding stable crystal structure at a given pressure (and temperature) or all stable stoichiometries and structures for a set of composing elements. [ref] Recent methodological theoretical developments [91] have led to many successes and impressive discoveries associated with CSP [92–95]. Without a doubt that success in CSP is associated with progress in periodic electronic structure calculations, force fields used, DFT approaches, more reliable estimation of thermodynamic properties, progress in reliability of phase diagrams, etc. Exploring the details of potential energy surfaces, often leads to the discovery of new structures with unusual properties and bonding situations [92–97].

So for me, the most important property of QC methods is their quantitative character and in consequence exceptional predictive power. I would personally draw the border line between routine and quantum methods somewhere between IAM and multipole refinement and would include all crystallographic quantitative methods going beyond IAM into QC. No doubt that QC methods are ideally suited to study all aspects of molecular interactions such as molecular recognition, molecular assembling and molecular organization in crystals, crystal growth, crystal engineering, supramolecular chemistry and materials science, studies of polymorphism and phase transitions, etc. QC methods are being more rigorously defined and more quantitative and supply more accurate and precise information than older methods. This high quality scientific information forms a good base for the acceleration of progress in science and new discoveries in all fields of crystallography, medicine, pharmacy, physics, chemistry, materials science, crystal engineering, etc. The authors of the viewpoint Chem. A Eur. J. review [1], stress, however, that the term “quantum” does not only refer to computational approaches. Experiments themselves can have a quantum nature for example superconductivity or tunnelling effects or scattering of X-rays by electrons and electrons by electrostatic potential. Additionally, crystallography is not only associated with scattering techniques but also quantum chemical models that are widely used to interpret the results of measurements. Crystallography also consists of direct applications of first-principle quantum mechanical methods with periodic boundary conditions. The definition of quantum crystallography has to be broader and more general. At the end of the Chem. A Eur. J. review [1], they propose four different possibilities: (1) preserving the original meaning of QC. In this option, the purpose of QC is making predictions of crystal features and properties more reliably than from pure first-principle calculations or experimentally derived models; (2) Outcome-based definitions. In this approach experiments validate and stimulate theoretical predictions and vice versa. However, crystallographic experimental results contain information on real imperfections, whereas QM calculations refer to a model system. In this view, QC would be the branch of science studying the quantum mechanical functions (and properties derived from them) in crystals. This includes the investiga-

tion, in position or in momentum space, of charge and spin density, wavefunctions, density matrices, based on experiments, on theoretical calculations or on a combination of them; (3) Crystals as quantum objects. According to this approach, QC is the study of those properties and phenomena which occur in crystalline matter and can be explained only by quantum mechanics. The experimental methods include scattering and spectroscopic techniques, with observations that enable the refinement of quantum mechanical models that reveal structural or functional features. Specific goals of QC are the determination of quantum related functions and quantities (such as wavefunctions, charge and spin densities, density matrices, electric or magnetic moments, etc.), the evaluation of the properties of materials and the analysis of the bonding features between the atoms and molecules that constitute a crystal. This open definition means that QC is the field that bridges structure and functions through the distribution and dynamics of electrons in space; (4) Quantum crystallography as a multidisciplinary field. This covers all quantum mechanics-based problems in crystallography [1]. This is the broadest approach including all possible applications in all possible fields of science. This concept of QC is not limited to solid-state science, but also includes surface science as well as studies of nanoscale materials, for example, femtosecond X-ray protein nanocrystallography [98–100] or via electron diffraction in thin films and monolayers [101], scattering and imaging of isolated (macro-)molecules or single objects such as cells [102], which is nowadays feasible with new X-ray lasing or intense electron sources [103–107]. This broadest perspectives seems to create a really broad interdisciplinary field of science bringing different communities together and I personally support such an interpretation of QC.

So except for the main general micro symposium devoted to the newest developments of QC (Quantum Crystallography Challenges and Newest Accomplishments), we propose a set of micro symposia focused on more specialised topics such as: Quantum Biocrystallography, Electronic and Magnetic Phenomena by Quantum Crystallography Methods, Quantum Crystallographic Studies at Extreme Conditions, Computational and Experimental Quantum Crystallography, Quantum Crystallography in Materials Science, Large Scale Facilities for Quantum Crystallography Research, Dynamic Phenomena in Quantum Crystallography and Teaching Quantum Crystallography. Together with the keynote lecture(s) on Quantum Crystallography, the above micro symposia will give us a proper coverage of the whole field.

I want to stress that development of QC methods are strongly coupled with the increasing quality of collected X-ray data. In this context, the availability of rotating anode sources, high-brilliance microfocus sealed tubes, development of a new type multi array X-ray tubes, improved multilayer optics, sources with short wavelengths (Ag/In – significant extension of resolution of data), development of hybrid pixel array detectors and charge integrating pixel array detectors based on CMOS technology, large scale facilities (synchrotrons of latest generations and XFELs) and recently desk-top large scale facilities have been increasing the quality of X-ray data to such an extent that makes QC

applications feasible. As charge density investigations are the driving force of progress on this border with quantum mechanics, it is really surprising that so few beam lines are dedicated to experimental charge densities and sophisticated experiments leading to really high quality charge density data which could be useful for more sophisticated QC applications.

No doubt that the combination of different methods of quantum mechanics (Hartree-Fock(HF) and post HF leading to more accurate wavefunctions (configuration interaction and coupled cluster methods) and the broad field of different DFT methods with numerous energy functionals, and crystallographic experiments within QC is one of the most promising challenges which should lead to progress in crystallography and in science in general. A kind of hybrid approach that is accelerated by availability of useful computer programs for molecular and solid state quantum mechanical simulations, for example, CRYSTAL [108], Quantum ESPRESSO [109], Turbomole [110], and WIEN2k [111, 112], VASP [113-116], etc. These programs use different approaches: plane waves and pseudo-potentials, Gaussian basis-sets, all-electron augmented plane waves and significantly strengthen different aspects of crystallographic research.

No doubt that only strict collaboration between researchers, developers of new QC methods, hardware and software providers as well as those who develop methods of data analysis will facilitate progress in QC and in science in general.

Instead of conclusions

Quantum Crystallography is now one of the most excited areas of scientific research. Due to synergy between crystallography and quantum mechanics, accurate distributions of electron density can be obtained from diffraction and scattering experiments. It can be broadly understood as research on the solid, crystalline materials applying full set of methods which are offered by quantum mechanics. This includes all research utilising wavefunctions, electron charge and spin densities, density matrices and related quantities such as electrostatic potential, electric and magnetic moments, magnetic susceptibilities, etc. The Quantum Crystallography methods rely on experimental measurements mainly elastic and inelastic scattering of X-rays, even γ -rays or particle radiations (neutrons, electrons), also spectroscopic methods. The experimental models used in QC include atomic multipolar expansions, maximum likelihood methods, reduced density matrices refinements and constrained wavefunctions fitting. QC practitioners also intensively use theoretical calculations based on periodic/cluster quantum chemical approaches mainly using DFT methods.

QC is undergoing now an immense progress resulting from the technological progress in X-ray production and detection, a kind of revolution in electron microscopy and diffraction, progress in analysis of quantum mechanical functions and a certain increase of cooperation between researchers in the field of crystallography and quantum mechanics. Even classic multipolar model undergoes significant improvements such as refinement of electron density in the cores of atoms or joint refinement of charge

and spin density distributions (utilising X-ray and polarised neutron data).

Dynamical QC keeps also progressing utilising frequencies associated with normal modes calculated by periodic ab-initio calculations and then refined against X-ray or neutron data.

HAR, starting from ab-initio molecular electron densities and utilising new partitions of electron density into atomic contributions for the refinement against diffraction data supplies the most accurate and precise structural results for light atoms including hydrogens.

Converged Beam Electron Diffraction (CBED) leads to very accurate electron density distributions for model systems. Electron diffraction allows to study even nanocrystals for a wide class of materials supplying diffraction data with a very high spatial distributions. Modelling this data with dynamical scattering supplies positions of hydrogen atoms in organic and inorganic crystals. Another technique, atomic force microscopy allows for mapping of electron density distribution on surfaces by using semi-empirical modelling. When these new advances will improve methodologies and methods of analysis, potential of QC methods seems to be really enormous. It is impossible to foresee the limits and borders of Quantum Crystallography.

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Commission on Mathematical and Theoretical Crystallography

THE IUCr-MATHCRYST

was founded to promote and achieve the following aims:

- To strengthen links and interactions among crystallographers, mathematicians and theoretical physicists and chemists, and to promote a common language in these fields.
- To promote the presence at IUCr meetings of scientists working in the fields of mathematics, such as geometry, topology or functional analysis.
- To strengthen the recognition of crystallography as an interdisciplinary science in those fields where nowadays it is considered only to be a technique.
- To promote the publication of mathematical and theoretical papers in the journals of the Union.
- To encourage the development and dissemination of mathematical and theoretical methods, software and databases to solve crystallographic problems.
- To promote and organize symposia of interest to mathematical and theoretical crystallographers during IUCr congresses and meetings of regional associates, or in other scientific conferences possibly in cooperation with other Commissions of the Union
- To promote and organize meetings, workshops and schools possibly in collaboration with other Commissions particularly targeting post-graduate students and young scientists needing and willing to complete their education in crystallography.

Motivation

Far from having exhausted its research potential, Mathematical and Theoretical Crystallography (**MaThCryst**) face new challenges, not only in the very classical field of group theory (magnetic groups, chromatic groups, N-dimensional groups) and its applications (phase transitions, polymorphism and polytypism, twinning, bicrystallography, ferroic crystals), but also in several directions that previously were less strongly perceived as being directly related to crystallographic and crystal-chemical problems, such as graph theory, combinatorics, topology, number

theory, discrete geometry, functional analysis, etc. The development of mathematical and theoretical crystallography will strengthen the interaction between crystallographers, mathematicians and materials scientists and will definitely contribute to the recognition of crystallography as an interdisciplinary science.

The outstanding success of applied crystallography in recent years has transformed common structural investigation into a routine task, often performed by researchers with no specific background in crystallography. Moreover, the success of automated structure solutions, whose results are persistently accepted without sufficient criticism, has contributed to the spread of the pernicious impression that a specific education in crystallography is no longer necessary in order to perform crystallographic tasks on a daily basis. The result is that nowadays crystallography is increasingly perceived as a technique, if not just as a tool, rather than an interdisciplinary science strongly interacting with fundamental and applied disciplines like mathematics, chemistry, physics, material science, geosciences and biosciences. As a consequence, the time devoted to crystallographic education in secondary, undergraduate and graduate courses is continuously shrinking, and the requirement of a solid background in crystallography is disappearing from the requirements of many positions that involve a considerable amount of crystallographic work.

The IUCr-MaThCryst commission was started on September 2002 as an informal working group from a nucleus of researchers who felt the necessity of trying to reverse the current trend towards “crystallography as a black-box tool”. From the didactic viewpoint, the commission aims at an activity which will hopefully cover the gap now existing between the “user” and the “specialist”. To achieve this, the commission regularly organizes summer schools and workshops and provides printed and printable (downloadable) material (do not hesitate to visit the commission’s website <http://www.crystallography.fr/mathcryst/>).