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Exploiting the Full Quantum Crystallography*

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* This paper is dedicated to the faculty of the Department of Chemistry of Dalhousie University, past and present, on the occasion of the 200th anniversary of the founding of Dalhousie University.

Abstract

Quantum crystallography (QCr) is a branch of crystallography aimed at obtaining the complete quantum mechanics of a crystal given its X-ray scattering data. The fundamental value of obtaining an electron density matrix that is N -representable is that it ensures consistency with an underlying properly antisymmetrized wavefunction, a requirement of quantum mechanical validity. But mostly X-ray crystallography has progressed in an impressive way for decades based only upon the electron density obtained from the X-ray scattering data without the imposition of the mathematical structure of quantum mechanics. Therefore, one may perhaps ask regarding N -representability “why bother?” It is the purpose of this article to answer such a question by succinctly describing the advantage that is opened by quantum crystallography.

Résumé français

La cristallographie quantique (QCr) est une branche de la cristallographie visant à obtenir la description quantique complète d'un cristal compte tenu de ses facteurs de structure obtenus à partir de la diffraction des rayons X. La valeur fondamentale de l'obtention d'une matrice de densité électronique qui est N -représentable est l'assurance de sa cohérence avec une fonction d'onde sous-jacente correctement anti-symétrisée comme l'exige la mécanique quantique. Mais la cristallographie aux rayons X a, pour la plupart, progressé de façon impressionnante pendant des décennies en se basant uniquement sur la densité électronique obtenue à partir des facteurs de structure expérimentaux sans l'imposition de la structure mathématique de la mécanique quantique. Par conséquent, on peut peut-être se demander à propos de la N -représentabilité «pourquoi s'en soucier?» Le but de cet article est d'adresser cette question en décrivant brièvement l'avantage que présente la cristallographie quantique.

KEYWORDS: Momentum density; Density matrices; Clinton equations; N -representability; Bader's quantum theory of atoms in molecules (QTAIM); Interacting quantum atoms (IQAs)

1. Introduction

Quantum Crystallography (QCr)¹ is a branch of crystallography bringing crystal experiments within the purview of quantum mechanics. X-ray scattering data analyzed with a strictly quantum mechanical formalism closely related to the Schrödinger equation is just one example of problems addressed within QCr.

Quite recently there has been a renewed and heightened interest in Quantum Crystallography (QCr).¹⁻⁸ A meeting was held in Nancy (France), in 2017, sponsored by the *Centre Européen de Calcul Atomique et Moléculaire* (CECAM), for the expressed purpose of discussing the present state of Quantum Crystallography and planning how best to utilize the results which one may foresee as obtainable within the field. Soon after the CECAM meeting, at the 2017 triennial conference and general assembly of the *International Union of Crystallography* (IUCr) held in Hyderabad (India), the IUCr adapted “Quantum Crystallography” as the title of one of its standing Commissions. The Commission on Quantum Crystallography is a continuation (and therefore an extension) of the previous IUCr “Charge, Spin and Momentum Density (CSMD)”.

The purpose of the *IUCr Commission on Quantum Crystallography* parallels the goals which came out of the CECAM meeting. There are at least two IUCr meetings devoted to Quantum Crystallography scheduled to occur in 2018: The *First Erice International School on Quantum Crystallography* (in Erice, Italy), and the *Sagamore XIX - 2018 Conference on Quantum Crystallography* (Halifax, Canada). There is, thus, a scientific ferment rising in the subject that is much to be welcomed because the outcome surely will enhance the usefulness of crystallography. This paper tries to anticipate the advantage that quantum mechanics may bring to the interpretation of crystallographic experimental data.

The present state of quantum crystallography was of course preceded by a mature and highly developed field of X-ray diffraction crystallography. The independent atom model (IAM) of refinement is still prevalent after many years.⁹⁻¹¹ In this model each atom is represented by a spherical electron density obtained from a Hartree-Fock (HF) calculation centered on its nuclear position. The density of the molecule or the unit cell under study, ρ_{IAM} , becomes that of a sum of the spherical atomic densities:

$$\rho_{\text{IAM}} = \sum_{i=1}^n \rho_i^{\text{spherical}} \quad (1)$$

where $\rho_i^{\text{spherical}}$ are the spherical atomic densities and n is the number of atoms in the molecule or unit cell. In the past, these spherical atomic densities were obtained from the HF calculations. Nowadays, for most atoms the spherically-averaged electron densities are obtained from Dirac-Fock multiconfigurational calculations.¹² The relativistic effects are incorporated to account for the contraction of the cores of heavy atoms brought about by the relativistic change in the mass of fast moving electrons.¹³⁻¹⁸ Functions designed specifically for charge density studies that include relativistic effects have been constructed as linear combinations of Slater-type functions.^{19,20}

The experimental parameters fixed by the diffraction data are the atomic positions and the Debye-Waller factors that describe the atomic displacements due to atomic vibrations. This spherical atom model is more than adequate to obtain the basic crystal structure. By definition, the IAM is inherently incapable of representing the non-spherical aspects of the molecular density. But these aspects are important, since they are responsible, for example, for chemical bonding.

Once X-ray data became sufficiently accurate to discern the presence of non-spherical electron density around nuclear positions a formalism was created to reflect that reality. The spherical atomic density was replaced by non-spherical multipole representations of the density.²¹⁻²⁷ Within the popular Hansen-Coppens model, the multipole definitions of the density is of the following form (in standard notation):^{24,25}

$$\rho_{\text{atom}} = P_{\text{core}} \rho_{\text{core}} + P_{\text{valence}} \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=0}^{l_{\text{max}}} \kappa^{l+3} R_l(\kappa r) \sum_{m=-l}^l P_{lm\pm} Y_{lm\pm}(\theta, \varphi) \quad (2)$$

where P are population coefficients that satisfy the condition $P_{\text{core}} + P_{\text{valence}} + \sum_{m=0}^l P_{lm\pm} = N$ (the total number of electrons of the atom or ion), ρ_{core} and ρ_{valence} are the normalized Hartree-Fock densities of the free atom or ion, and R_l are exponential radial functions. The first two terms model the core and valence densities spherically while the third is a valence density deformation term.

Given Eq. (2) as a model for the aspherical atomic electron density, the structure

factor expression becomes:^{24, 25, 28}

$$F(\mathbf{H}) = \sum_j \left[P_{j,\text{core}} f_{j,\text{core}}(\mathbf{H}) + P_{j,\text{valence}} f_{j,\text{valence}}(\mathbf{H}, \kappa) + 4\pi \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l P_{lm\pm} i^l \langle j_l \rangle Y_{lm\pm}(\beta, \gamma) \right] \exp[2\pi i \mathbf{H} \cdot \mathbf{r}] T_j(\mathbf{H}) \quad (3)$$

where $f_{j,\text{core}}$ and $f_{j,\text{valence}}$ are the Fourier transforms of $\rho_{j,\text{core}}$ and $\rho_{j,\text{valence}}$ respectively, $\langle j_l \rangle$ is the l^{th} Fourier-Bessel transform of the radial part of the multipole functions R_l , Y_{lm} are spherical harmonics in reciprocal space polar coordinates, and $T_j(\mathbf{H})$ are the temperature factors. In the refinement, $P_{j,\text{valence}}$, P_{lm} , κ , and κ' are optimized in addition to the nuclear coordinates and the temperature factors (T_j). The use of good quality crystals and low temperatures in conjunction with this model yields high resolution electron densities that reflect chemical bonding.²⁸⁻³⁴

The crystallographic spin density of a molecular magnet has also been determined by means of a modified multipolar model.³⁵ Such spin-resolved electron density distribution can be obtained experimentally by combining X-ray and polarized neutron diffraction using a “spin-split” pseudo-atoms model.³⁶

Bader’s quantum theory of atoms in molecules (QTAIM) analysis of molecular densities, whether obtained from theory³⁷⁻³⁹ or from experimentally-obtained electron densities refined with a multipolar model,^{25, 26, 28} reveals various topological and topographic features of physical importance. These include for example bond paths, critical points, and the laplacian of the electron density whether at the critical points or in the whole space.

QTAIM also analyzes properties, such as the kinetic energy densities, the potential energy density $V(\mathbf{r})$, and the electron localization and delocalization indices, that require more than simply the electron density for their evaluation. There is no general method to obtain energy information from the experimental X-ray diffraction data presently. However, there are approximations that can apply under certain circumstances.

For instance, Abramov has proposed to use the following approximate expression to estimate the kinetic energy density $G(\mathbf{r})$ at regions of low electron density and where

the laplacian of the electron density is small:⁴⁰

$$G(\mathbf{r}) = \left(\frac{3}{10}\right) (3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3} + \left(\frac{1}{72}\right) \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} + \left(\frac{1}{6}\right) \nabla^2 \rho(\mathbf{r}), \quad (4)$$

(in atomic units (a.u.)), an approximation usually valid within *ca.* 0.5 - 2.1 Å from an atomic nucleus.

With $G(\mathbf{r})$, one can invoke the local virial theorem, written again in a.u.:⁴¹

$$\frac{1}{4} \nabla^2 \rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r}), \quad (5)$$

to obtain $V(\mathbf{r})$ and thus also the total energy density $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$.

Espinosa, Molins, and Lecomte,⁴² have shown that hydrogen bond dissociation energy (D_e) in dimers exhibit a strong statistical correlation with the potential energy density obtained from Eqs. (4) and (5) with the startling result (often called the EML expression) that:⁴²

$$E = -D_e = \frac{1}{2} V(\mathbf{r}_{\text{BCP}}), \quad (6)$$

a relation that has been revisited by Spackman.⁴³

Given the importance of the energy densities, it is desirable to have a method that delivers them exactly and anywhere in the molecular or crystallographic direct space. Such a method is part of the quantum crystallography programme.

There exist today hundreds of crystal structures, including many protein structures, that have highly accurate multipole density representations of their electronic structure.^{29-34, 44-53} This is truly a great accomplishment allowing insight into chemical bonding, the chemical influence of multiple bonds, substituent effects, the nature of dipole moments, and in general the prediction of molecular properties which are dependent upon quantum operators that are multiplicative such as any powers of the electron density.

The density alone however is not sufficient to satisfy the calculation of all quantum operators. Properties, for example, that are represented by derivatives within the usual rules of quantum mechanics cannot be derived using only the density. That is to say, the usual rules for expectation values require that they be evaluated according to the

expression

$$\langle \hat{O} \rangle = \int \Psi^* \hat{O} \Psi d\tau \quad (7)$$

where $d\tau$ is a generalized volume element of integration.

Only for operators that are multiplicative can one evaluate the above expectation value (Eq. (7)) using only the density. In contrast, those properties represented by derivative operators *require* the wave function or density matrices that are N -representable by a wave function. The exploitation of the full quantum crystallography referenced in the title is to extract from the X-ray scattering factors the density matrices allowing the calculation of all quantum operator properties, not just those obtainable from the electron density.

There are two aspects to obtaining the quantum mechanical density matrices needed for the general expectation values representing systems in a complete way. These two aspects are the mathematical problems of first ensuring N -representability and secondly the practical calculations of extracting the density matrices from the X-ray scattering data. These two practicalities are discussed in the following two sections of this paper.

2. N -Representability, What Is It?

N -representability of a density matrix is the mathematical guarantee that it can be mapped bijectively to an antisymmetric N -body wave function.⁵⁴ This mathematical mapping is illustrated in Fig. 1. N -representability is a requirement for consistency with quantum mechanics.

$$\rho_1(\mathbf{l}, \mathbf{l}') \equiv N \int \Psi^* \Psi d2 \dots dN dS$$

$$\rho_1(\mathbf{l}, \mathbf{l}') = \text{tr } \mathbf{P} \psi(\mathbf{l}) \psi^\dagger(\mathbf{l}')$$

$$\mathbf{P}^2 = \mathbf{P}$$

Fig. 1 An illustration of the bijective mapping between the space of N -representable density matrices and that of N -body antisymmetric wave functions.⁵⁵ (The single-determinant nature of the wavefunction is implied by the idempotency of \mathbf{P}).

Fig. 1 illustrates a set of antisymmetric wave functions and a set of N -representable one-body density matrices to which they are connected. Integration over a squared wave function results in a quantum mechanically valid density matrix. Note however that in general an arbitrary function $f(\mathbf{l}, \mathbf{l}')$ will not be connected to a valid antisymmetric wave function. Only in the case of an N -representable density matrix it will map back to a wave function, and it is that which allows it to be called N -representable.⁵⁴

The general condition for N -representability of a one-body reduced density matrix (1-RDM) that includes spin is that its eigenvalues must fall in the range $0 \leq W_k \leq 1$, for all k .⁵⁶ Moreover, for single determinant N -representability, the 1-RDM is a projector, *i.e.*, $\mathbf{P}^2 = \mathbf{P}$ (condition of idempotency).⁵⁷

N -representability is important to quantum crystallography. The indistinguishability of electrons is a manifestation of density matrix N -representability. The momentum density matrix may be obtained by a double Fourier transform of the position density matrix. However, for that to be valid in momentum space, when so obtained, it must be from an N -representable position space density matrix.

The projector condition includes both Hartree-Fock (HF) wave functions and those of density functional theory (DFT) orbitals of the Kohn-Sham (KS) equations.

Walter Kohn emphasized that “[t]he only purpose of the KS orbitals is to deliver the exact density”.⁵⁸ Interestingly, the orbitals related to density matrices of the form $\mathbf{P}^2 = \mathbf{P}$ whose elements are constrained by X-ray scattering factors do just that. *That condition defines orbitals which in principle deliver the experimental, and thus the exact density.*

Thus, what are the equations which determine projectors that satisfy experimental X-ray scattering factors? These are the Clinton equations,⁵⁹ which are therefore of such importance to quantum crystallography.

3. The Clinton Equations

The Clinton equations to determine a projector density matrix are of the iterative form,⁵⁹
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$$\mathbf{P}_{n+1} = 3\mathbf{P}_n^2 - 2\mathbf{P}_n^3 + \sum_k \lambda_k^n \mathbf{O}_k. \quad (8)$$

The Lagrangian multipliers λ are obtained by inserting \mathbf{P} into the equations of constraint,

$$\text{tr } \mathbf{P}_{n+1} \mathbf{O}_k = \langle \hat{O}_k \rangle, \quad (9)$$

where the matrix representative of the constraint operator is \mathbf{O}_k and the expectation value is the magnitude $\langle \hat{O}_k \rangle$. The iterative equations are well behaved and converge to projector matrices, $\mathbf{P}^2 = \mathbf{P}$, satisfying equations of constraint such that the λ 's go to zero.

The key points are summarized in a question-and-answer format: (i) What do the Clinton equations pursue in a nutshell? These equations deliver a projector which satisfies X-ray experimental constraints. (ii) In the iterative procedure, what is the initial guess matrix? Experience shows that the initial guess is essentially arbitrary as long as it satisfies the normalization condition. (iii) What are the constraints? Normalization and the experimental X-ray scattering factors.

The Clinton equations are significant in that they deliver single determinant N -representable projectors which satisfy experimental constraints such as normalization and X-ray scattering factors. The importance of these equations to quantum crystallography is demonstrated by a brief outline of simple applications.

4. Some Applications of the Clinton Equations

The Clinton equations have been applied to the Beryllium (Be) crystal⁶¹ using the X-ray scattering data of Larsen and Hanson.⁶² The core is fixed to be the Be free atom $1s$ orbital of Huzinaga.⁶³ The valence orbital of the Be atom is expanded in a linear combination of two basis functions. The mathematical definitions of the basis functions are given in Ref. 61. The valence density matrix is of dimension 2×2 . The Clinton equations are used to obtain the elements of the one-body density matrix using as a constraint minimization of the crystallographic least squares R -factor.

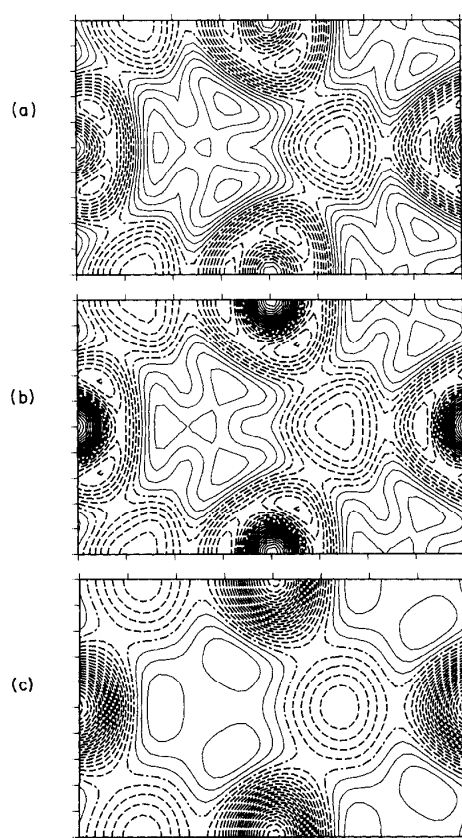


Fig. 2 Valence electron density of beryllium crystal from (a) Dovesi *et al.*,⁶⁴ (b) Massa *et al.*,⁶¹ and (c) Cohen, *et al.*⁶⁵ The steps between contour levels are each $0.01 e/\text{\AA}^3$. Solid/dashed contours are for positive/negative values, respectively. The zero contour (last solid contour) refers to four electrons per unit cell volume. (Experimental data of Larsen and Hansen).⁶² (Reproduced with permission from Ref. 61. © *American Physical Society*).

Illustrated in Fig. 2 are valence-density maps for the $(x, y, 1/4)$ crystal plane. In this figure, two different *ab initio* calculations are shown together with the result of the calculations. One sees here the results of Dovesi *et al.*,⁶⁴ Fig. 2(a), the work of Massa *et al.*,⁶¹ Fig. 2(b), and of Chou *et al.*,⁶⁵ Fig. 2(c). There is close correspondence between the *ab initio* and X-ray projector valence-density features. The map by Massa *et al.* agrees closely with the experimental map of Larsen and Hansen (not shown because of their very close similarity) and falls numerically between the *ab initio* maps of the figure.

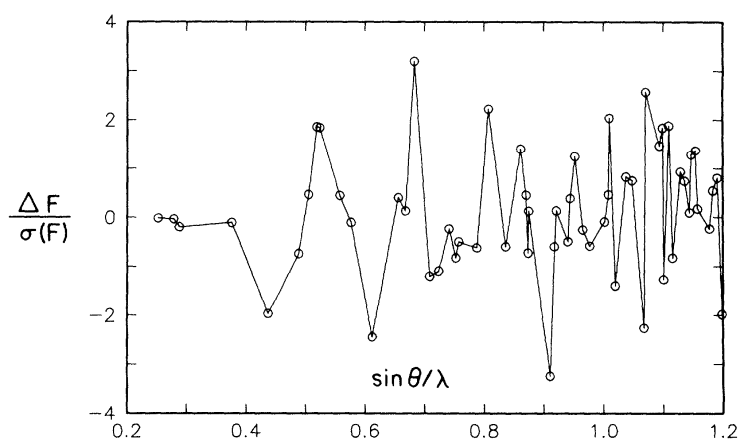


Fig. 3. Error distribution in the structure factors (R -factor = 0.0018) for the beryllium crystal. (Reproduced with permission from Ref. 61. © American Physical Society).

Notice in Fig. 3 that the projector model closely represents the X-ray experimental data. Illustrated there, is the difference between corresponding sets of observed and calculated structure factors ($\{F_{\text{obs.}}\}$ and $\{F_{\text{calc.}}\}$) as a function of scattering angle θ , in units of standard deviation. Clearly, the projector density fits very well the Be data. As with a normal distribution *the errors are randomly distributed out to highest angles*. The R -factor is remarkably small, at 0.0018. In summary, the projector density matrix has extracted from the X-ray scattering experiment a satisfactory quantum mechanical representation of the data. Other important quantum crystallographic studies on Be include Jayatilaka's X-ray constrained wave function analysis⁶⁶ and the maximum entropy study of Iversen.⁶⁷

Hernández-Trujillo and Bader⁶⁸ applied the idea of using projectors to enforce N -

representability in their quest to determine the transferability of atoms in molecules defined within Bader's QTAIM.³⁷⁻³⁹ Their goal is to determine the viability of reconstructing large molecules from transferable QTAIM atoms and functional groups stitched at their zero-flux inter-atomic surfaces, defined as:³⁷

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})=0 \quad \forall \mathbf{r}\in S(\Omega,\mathbf{r}), \quad (10)$$

where $\nabla\rho(\mathbf{r})$ is the gradient of the electron density at the location defined by the position vector \mathbf{r} , $\mathbf{n}(\mathbf{r})$ is the normal vector to the surface $S(\Omega,\mathbf{r})$ of an atom Ω . (In QTAIM, the symbol Ω is often used interchangeably to mean the volume occupied by an atom in a molecule or a crystal or the atom itself).

The inter-atomic surfaces of the pieces that are joined in such piecemeal fashion are then melded together by the use of Clinton equations.⁶⁸ The Clinton equations are used by these workers to ensure N -representability on systems that ranged from ionic to polar.⁶⁸ (See Fig. 4).

Polkosnik and Massa have recently imposed N -representability in the reconstruction of water clusters from smaller fragments.⁶⁹ In contrast to the work of Hernández-Trujillo and Bader,⁶⁸ in the work of Polkosnik and Massa kernels are recombined into an augmented density matrix of the full system rather than extracted at an inter-atomic surface as in the work of Hernández-Trujillo and Bader.

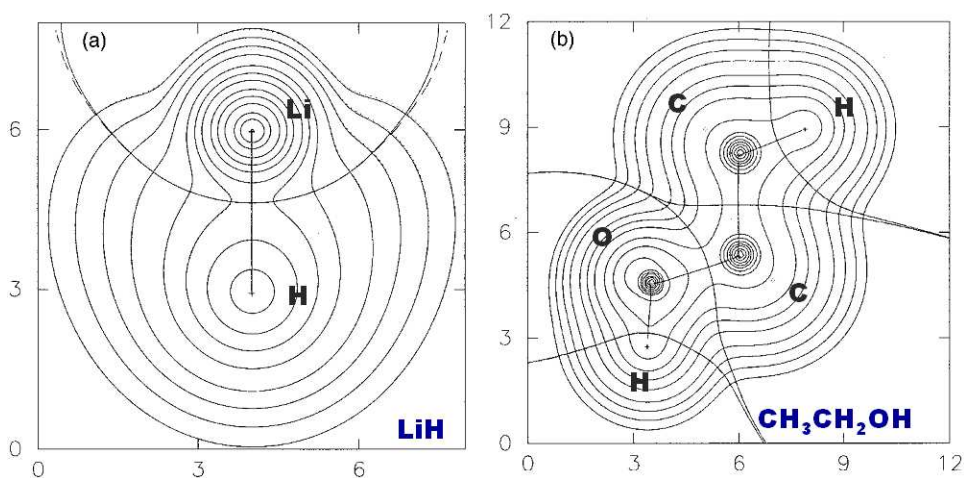


Fig. 4 Comparison of reconstructed idempotent ($\mathbf{P}^2 = \mathbf{P}$) and direct Hartree-Fock electron densities contours and zero-flux inter-atomic surfaces: Reconstructed

densities are represented by solid lines overlaid with the directly calculated contours (dashed). The different contours are almost indistinguishable, inter-atomic surfaces diverge very slightly at low values of the electron density. (Left (a) is for the ground state LiH molecule as an example of an ionic system and right (b) for the ground state of the ethanol as a typical polar organic molecule. All axes are in atomic units (a.u.) – See text). (Adapted with permission from Ref. ⁶⁸, Copyright *American Physical Society*).

5. The Quantum Crystallography Advantage: Select Examples

5.1 Electron Density in Momentum Space

One cannot calculate the momentum density directly from the electron position density. This is yet another example of a property for which the electron density alone is not enough. However the position one-matrix ($\rho_1(\mathbf{r}, \mathbf{r}')$) does allow calculation of the momentum one-matrix ($\rho_1(\mathbf{p}, \mathbf{p}')$). The diagonal elements the one-matrix, in either position or momentum space, will yield the density in either space.

The double Fourier transform of the one-matrix $\rho_1(\mathbf{r}, \mathbf{r}')$ in the variables \mathbf{r} and \mathbf{r}' delivers the one-matrix $\rho_1(\mathbf{p}, \mathbf{p}')$ in the momentum variables \mathbf{p} and \mathbf{p}' . Thus,

$$\rho_1(\mathbf{p}, \mathbf{p}') = \iint \rho_1(\mathbf{r}, \mathbf{r}') e^{i(\mathbf{p}\cdot\mathbf{r} + \mathbf{p}'\cdot\mathbf{r}')} d\mathbf{r} d\mathbf{r}', \quad (11)$$

and,

$$\rho(\mathbf{p}) = \rho_1(\mathbf{p}, \mathbf{p}') \Big|_{\mathbf{p}' \rightarrow \mathbf{p}}. \quad (12)$$

Here too we see that extraction of the density alone, from the X-ray scattering, is insufficient for another important physical property, the momentum density. That is to say, symbolically,

$$\rho(\mathbf{r}) \not\rightarrow \rho(\mathbf{p}), \quad (13)$$

in contrast:

$$\rho_1(\mathbf{r}, \mathbf{r}') \rightarrow \rho_1(\mathbf{p}, \mathbf{p}') \rightarrow \rho(\mathbf{p}). \quad (14)$$

5.2 Total Molecular Electronic Energy

Certainly, one of the most important quantum mechanical properties of a molecular system is its total electronic energy. To obtain this quantity from the X-ray experiment would allow comparison of the energy of analogous molecules, isomers, homologous series, the interaction energies between drug and its receptor, *etcetera*.

Let us consider how to calculate the molecular electronic energy, as in the expectation value,

$$E = \langle \hat{H} \rangle = \int \Psi^* \hat{H} \Psi d\tau \quad (15)$$

where Ψ is the molecular wave function, and \hat{H} is the molecular Hamiltonian operator. The expectation value of the energy operator $\langle \hat{H} \rangle$ can be calculated in terms of density matrices as follows,

$$E = \langle \hat{T} \rho_1 \rangle + \langle \hat{V}_{ext} \rho \rangle + \langle \hat{V}_{ee} \rho_2 \rangle. \quad (16)$$

Eqn. (16) shows that three different density matrices are required to calculate the expectation value of the Hamiltonian. The kinetic energy is represented by a one-body derivative operator that requires the one-body density matrix for its calculation. The external potential is a multiplicative operator evaluated with the density. The electron-electron potential is a non-local two-body operator requiring the two-body density matrix for its calculation. Notice the electron density alone is not sufficient to evaluate the expectation value of the molecular Hamiltonian.

The quantum crystallographic advantage is here evident. By extraction of all three density matrices, ρ , ρ_1 , and ρ_2 from the crystal scattering data one can evaluate all of the usual quantum operators of interest.

5.3 Bader's Atomic Virial Partitioning of Molecular Energy

Bader invented an important quantum mechanical way of defining the space occupied by an atom in a molecule referred to above, *viz.*, the quantum theory of atoms in molecules (QTAIM).³⁷ An atom in a molecule is defined as a bounded region of space where the boundary consists of the union of one or more inter-atomic surfaces of zero-flux in the

gradient vector field of the electron density (Eq. (10)) and possibly an isodensity surface normally taken as the van der Waals surface, $\rho(\mathbf{r}) = 0.001$ a.u., if the atom is a terminal one (see Fig. 4).

The kinetic energy of each atom in a molecule $T(\Omega)$ can be obtained from the following volume integral over the atomic basin Ω (in a.u.):

$$T(\Omega) = -\frac{1}{2} \int_{\Omega} \nabla^2 \rho_1(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}' \rightarrow \mathbf{r}} d\mathbf{r}. \quad (17)$$

Bader proposed⁷⁰ and then demonstrated^{37, 71-73} the existence of an atomic virial theorem that parallels the molecular virial theorem.⁷⁴ For a system at an energy-minimized geometry (where the virial of the forces on the nuclei vanish, in principle), whether a minimum or a transition structure on the potential energy surface, the atomic virial theorem is written:³⁷

$$V(\Omega) = -2 T(\Omega), \quad (18)$$

where $V(\Omega)$ is the potential energy of the atom in a molecule or crystal.

This theorem leads to the definition of the so-called virial energy of an atom in a molecule or crystal at an optimized geometry since atomic energy is given by:

$$E(\Omega) = T(\Omega) + V(\Omega) = -T(\Omega). \quad (19)$$

Such (virial) atomic energies are endowed with the desirable and non-trivial property of additivity, *i.e.*, adding-up to the total molecular energy:

$$E = \sum_{\Omega} E(\Omega). \quad (20)$$

Notice that although the density alone defines the space occupied by each atom, the density alone is *insufficient* to deliver the kinetic energy. For that property the one-body density matrix $\rho_1(\mathbf{r}, \mathbf{r}')$ is required. Armed with $\rho_1(\mathbf{r}, \mathbf{r}')$ and the kinetic energy, one bypasses the calculation of the complicated and expensive $V(\Omega)$ in the calculation of $E(\Omega)$.

5.4 Interacting Quantum Atoms (IQA) Energy Decomposition

Another decomposition of molecular total energy is that pioneered by Martín-Pendás *et*

al.⁷⁵⁻⁷⁷ whereby one- and two-electron energy contributions are integrated over individual QTAIM atomic basins as well as over all possible pairs of basins in the molecule or unit cell. This partitioning is known as the interacting quantum atoms (IQA) energy decomposition, and is exact.

The IQA expresses the total energy as a sum of self- and interaction-terms:⁷⁵⁻⁷⁷

$$E = \sum_A E_{\text{self}}^A + \frac{1}{2} \sum_A \sum_{B \neq A} E_{\text{int}}^{AB}, \quad (21)$$

where the self-energy of atom A is defined as:

$$E_{\text{self}}^A = T^A + V_{en}^{AA} + V_{ee}^{AA}, \quad (22)$$

where T^A stands for its kinetic energy, V_{en}^{AA} is the interaction of its electrons with its nucleus, and where V_{ee}^{AA} is the electron-electron repulsion within its basin. The interaction energy contribution between a pair of atoms A and B , in its turn, is defined as:

$$E_{\text{int}}^{AB} = V_{nn}^{AB} + V_{en}^{AB} + V_{ne}^{AB} + V_{ee}^{AB} \quad (A \neq B), \quad (23)$$

where the superscripts refer to atoms A and B and the subscripts refer to energy interaction types between them. For example, V_{ne}^{AB} is the symbol for the energy of interaction between the nucleus of A and the electrons of B . The total energy is decomposed exactly in this form into a set of self- and interaction-contributions.

The IQA energy components can be combined in such a way as to yield additive atomic energy contributions. These additive energy contributions, which are different from the additive virial energies (Eq. (20)), satisfy the following summation rule:

$$E_{\text{add}}(A_i) = E_{\text{self}}^{A_i} + \frac{1}{2} \sum_{j \neq i} E_{\text{int}}^{A_i A_j}. \quad (24)$$

Thus within IQA, the total energy is viewed as a sum of intra- and inter-atomic contributions (Eq. (24)), which require computing all terms of the type discussed above. That is to say the energy integrals required will invoke all three density matrices ρ , ρ_1 , and ρ_2 . This has proven to be a highly successful extension of Bader's ideas based upon the definition of the QTAIM atomic basins. But again the quantum crystallography advantage shows itself as usual in allowing calculation of properties that go beyond those

obtainable from the density ρ alone.

5.5 *Excited State Electron Densities from X-Rays*

It has been shown by Coppens *et al.* that time-dependent X-ray measurements can reveal the electron density of excited states of molecular crystals.⁷⁸⁻⁸¹ This has been carried out using bright synchrotron X-ray sources in concert with laser pulses to create the excited states in time-resolved pump-probe photocrystallographic experiments. This is still a frontier area of crystallography. Although it has been shown that excited state densities have been observed, what is their best mathematical representation?

It is suggested here that the unoccupied orbital space of the ground state one body density matrix contains the excited state orbitals. Thus the projector density matrix discussed above obtained from the Clinton equations (Eqs. (8) and (9)) can be used to represent both ground and excited state orbitals. The one-body density matrix $\rho_1(\mathbf{r}, \mathbf{r}')$ of the ground state orbitals would be obtained in the usual way for the ground state. In that process there will occur a density matrix corresponding to orbitals unoccupied and orthogonal to those of the ground state.

In a second experiment laser pumping to the excited state will give rise to scattering data for that excited state.⁷⁸ That data can be used to fix the elements of an excited state density matrix projector. The excited state density matrix can then be determined using the Clinton equations. In this case, the imposed constraints are normalization, the X-ray scattering factors of the excited state, and one new constraint. The required new constraint is that *the excited state orbitals must be orthogonal to the ground state orbitals*. In this case the general form of a constraint condition, *viz.*,

$$\text{tr } \mathbf{P}\mathbf{O} = \langle \hat{O} \rangle, \quad (25)$$

becomes

$$\text{tr } \mathbf{P}_{\text{excited}} \mathbf{P}_{\text{ground}} = 0, \quad (26)$$

where the matrix being constrained is that of the excited state $\mathbf{P}_{\text{excited}}$, and the matrix representative of the constraint is the ground state matrix $\mathbf{P}_{\text{ground}}$ which will already be

known from calculations with the scattering data of the ground state, and the constraint expectation value is exactly zero.

Again the formalism suggests that it should be constructed on more than the electron density alone. In this case, one is suggesting a one-body density matrix for the ground state orbitals ($\rho_1^{\text{ground}}(\mathbf{r}, \mathbf{r}')$) and one for the orbitals of the excited state ($\rho_1^{\text{excited}}(\mathbf{r}, \mathbf{r}')$).

6. Conclusions

The concept of quantum crystallography has been the subject of a number of recent discussions by Grabowsky, Genoni, and Burgi,¹ and by Jayatilaka² in a highly relevant book by C. Gatti and P. Macchi.³ In this paper, arguments that the complete quantum mechanics can be extracted from the X-ray data in the form of ρ , ρ_1 , and ρ_2 have been discussed. The point is that the incorporation of a quantum mechanical formalism to describe the scattering data achieves two important goals: (1) It opens the door for the extraction of an *entirely new range of properties* from X-ray diffraction experiments, properties (*e.g.* the momentum density, energies, *etc.*) that are not obtained in the ordinary X-ray analysis, (2) by incorporating the quantum mechanics into the solution of the crystallographic problem, the densities thus obtained have *quantum mechanical validity* not otherwise guaranteed, whether from spherical or aspherical (multipolar) refinement.

In short, more information is available from the X-ray data, over and above just the electron density ρ , no matter how precise it may be in terms of the crystallographic agreement *R*-factor. One certainly recognizes all of the good information and chemical interpretations that have been brought forward by the crystallographic pioneers of non-spherical density. That has been and still remains in present science all to the good. It is simply pointed out here there is a natural quantum mechanical formalism to extract even more useful information from X-ray scattering data.

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