Symmetry and Structure in the Solid State
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Lecture – 59
Quantum Crystallography 1

So, having seen the issues related to powder diffraction and the way we can use powder diffraction data. We will look at another aspect you see we have always been stressing on the fact that the diffraction which we observed in a diffraction experiment is coming solely due to the electron density.

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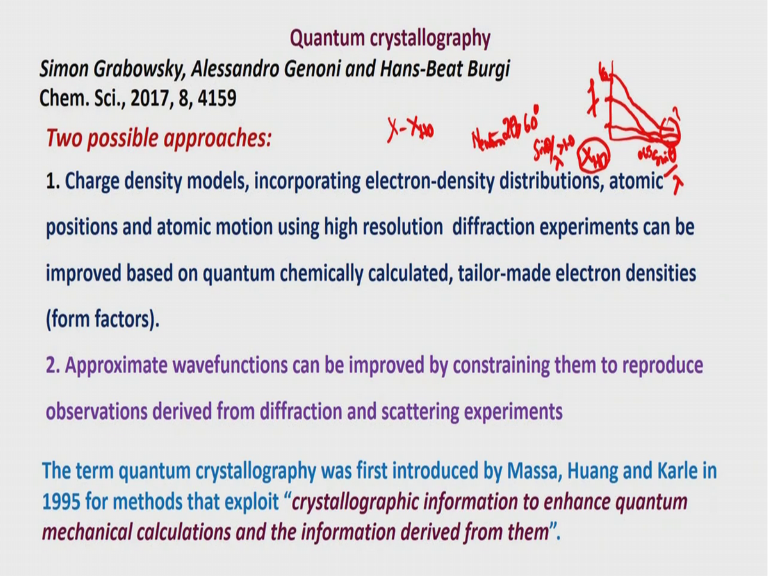

Quantum crystallography

Simon Grabowsky, Alessandro Genoni and Hans-Beat Burgi

Chem. Sci., 2017, 8, 4159

Two possible approaches:

1. Charge density models, incorporating electron-density distributions, atomic positions and atomic motion using high resolution diffraction experiments can be improved based on quantum chemically calculated, tailor-made electron densities (form factors).

2. Approximate wavefunctions can be improved by constraining them to reproduce observations derived from diffraction and scattering experiments

The term quantum crystallography was first introduced by Massa, Huang and Karle in 1995 for methods that exploit "*crystallographic information to enhance quantum mechanical calculations and the information derived from them*".

So, in principle it should be possible to map the electron density, once we solve the structure which is what we do when we plot the Fourier diagrams and then from that derive the positions of the atoms and do the so called R type diagram and so on. So, this heralds the area which has been named as Quantum Crystallography in 2017 in fact, this is the one would think is the youngest member in crystallography regime because it has been christened in 2017 IUCR meeting and this is an area which is now pursued vigorously.

What is very interesting is the very first idea in crystallography, when people like brag and of course, before that form Lauve indicated that the diffraction is a consequence of the electrons electron density around the atoms which are inside the crystals. When once that idea came up it was almost taught in an immediate fashion that one should be able to see electrons in orbits. In fact, that was the ambition, it was predicted also that one can see electrons in orbitals.

And so there were some experiments which were done by physicists at that time to see whether we can actually plot the electron density and see the distribution of electron density associated with where it orbits; because at that time the theory of the orbital's and all that work there means Bohr was there who gave the kl ml m shell concepts. So, people were thinking that maybe it is possible to see the electrons inside the k shell, inside the l shell and so on.

So, they thought this is the ideal experiment which will allow it to happen. So, the idea of mapping the charge densities from those days 1913 onwards has been there. The problem was that as we already know that if we want to see very subtle electron density distributions particularly, the distribution of electron density in bonds and molecules and also in the inter molecular region and so on.

Because of the fact that the amount of electron density that is present is so small that it is necessary to have very high quality experiments performed and that level of experiments could not have been performed in those days, so it has to wait a long time. The other aspect is of course, the fact that we should have very accurate data sets in order to see those very subtle effects of remaining electron density other than the molecule.

And so these things took a long time, so long that the actual electron density ideas that particularly charge density mapping and so on were developed in the early 70s and since 80s. So, early 70s saw the resurgence of this activity in the area to map the electron densities and this originated from the fact that we can have both X ray experiments as well as neutron experiments performed on the same crystal.

If we perform the electric X ray experiment as well as the neutron experiments we have certain advantages. Because the neutron experiment will give us the variation of the there is no variation of sin theta by lambda of the scattering length, on the other hand by X rays give the variation is sin theta by lambda.

Now, we know in what way this is going to help? We will have a quick look at that in I will just draw a small diagram to show how this would have happened. Say for example, if you now see f sin theta by lambda you have sin theta by lambda, the it will fall off asymptotically and go toward 0 at higher angles, If we now separate the core and the valence that is associated with a given atom, so this is let us say carbon and that means, it will starting point is 6 electrons, we will put two core in the core and four in the valence because we know carbon has a valence of valency of four.

So, these four electrons now if we now follow the fall of f with respect to sin theta by lambda it will fall off and in fact, go towards 0 somewhere around 0.65 and the core electrons which are here two of them, they will continue to fall, but then they will sort of have some nonzero value beyond that particular point. In the case of a neutron diffraction of course, we have a straight line which is associated with the scattering length this not cannot be plotted on this diagram obviously. So, it is depends on the scattering length, but that is not varying with respect to sin theta by lambda.

So, suppose we conceived of experiments let us discuss it from the experiments point of view and then bring in the quantum concept a little later. So, if we can conceive of experiments where we can measure this region and that region as you see will have very little contributions from various atoms and therefore, the diffraction is weak. Now, we have to make this region to have better diffraction. How are we going to make this region to have better diffraction? We have to then have two issues one is of course we can collect low temperature data.

So, when we collect the low temperature data it is better to have estimates of higher angles and then we have to measure these reflections at higher angles. In a typical X ray experiment what we do is we collect the data of let us say copper radiation we go to 2 theta up to 60 degrees and that represents, the limit of the limiting sphere or nearly the limit of the limiting sphere. That would mean that we are going to values of sin theta by lambda only around this value of 0.6 or 0.65. So, that would take the contributions coming from the core completely away from the calculation.

So, effectively since we now consider that structure of scattering factor which is starting at a value of 6 and falling off to 0 toward 0, there is inclusion of the core in some sense in the plot which we have done and therefore, we can get the values. But realistically these values are not very strong, so the reflections the reliability with which we can measure the reflections is not very strong.

So, the third process was now to cool the crystal to below nitrogen or towards helium temperatures, in which case some of these measurements probably can be made. Effectively the data which we collect now should go far beyond the 60 degrees; that means we have to look for sin theta by lambda which are going beyond 1 or even 1.2, 1.3 and so on.

So, now we are considering a situation where we are trying to get the maximum data which we can get from a given material which is in the form of a single crystal and that single crystal therefore, has to be an extraordinarily good quality single crystal and in terms of diffraction. And then we collect the low temperature data and the low temperature data effectively brings in the possibility of measuring these what we call as X high order reflections.

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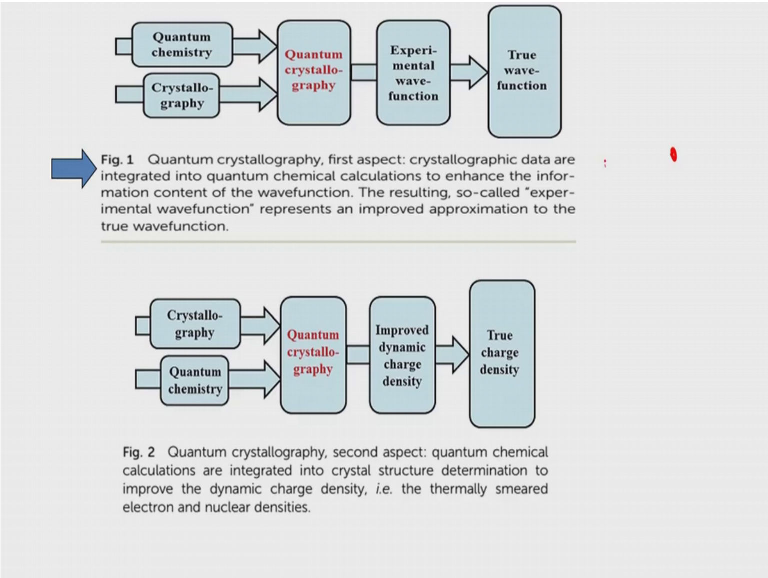

Quantum chemistry

Crystallography

Quantum crystallography

Experimental wavefunction

True wavefunction

Fig. 1 Quantum crystallography, first aspect: crystallographic data are integrated into quantum chemical calculations to enhance the information content of the wavefunction. The resulting, so-called "experimental wavefunction" represents an improved approximation to the true wavefunction.

Crystallography

Quantum chemistry

Quantum crystallography

Improved dynamic charge density

True charge density

Fig. 2 Quantum crystallography, second aspect: quantum chemical calculations are integrated into crystal structure determination to improve the dynamic charge density, *i.e.* the thermally smeared electron and nuclear densities.

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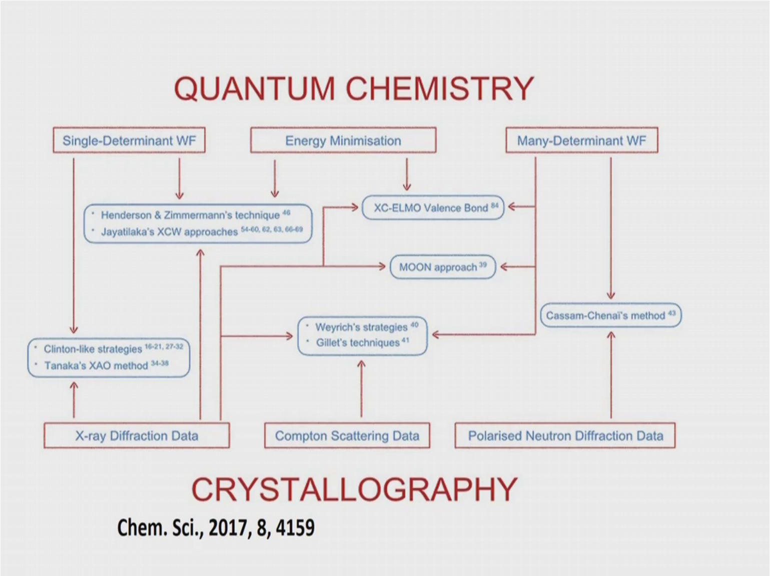

QUANTUM CHEMISTRY

Single-Determinant WF

Energy Minimisation

Many-Determinant WF

- Henderson & Zimmermann's technique [46]
- Jayatilaka's XCW approaches [54-60, 62, 63, 66-69]

XC-ELMO Valence Bond [84]

MOON approach [39]

Cassam-Chenaï's method [43]

- Weyrich's strategies [40]
- Gillet's techniques [41]

- Clinton-like strategies [16-21, 27-32]
- Tanaka's XAO method [34-38]

X-ray Diffraction Data

Compton Scattering Data

Polarised Neutron Diffraction Data

CRYSTALLOGRAPHY

Chem. Sci., 2017, 8, 4159

Now what is the example of the X high order reflection? The advantage of this X high order reflection is that we have now the contribution only coming from the core number 1, and number 2 the contribution is not varying with respect to sin theta by lambda. So, effectively it is like the delta which is coming out from a neutron diffraction, only factor is that we have to consider is that these reflections are beyond, the normal range of data collection which we normally do for single crystal work. So, that is why we call it the high order data.

And using this idea we can actually look at the possibility of measuring the electron density beyond the region where the valence contribution stops and therefore, effectively you are now looking at the inside of the atom. And So if you now do the difference Fourier plot, that difference Fourier plot in principle should give us the electron density which is coming from this high angle region, which is coming essentially from the core region and therefore, in principle we should be able to see the bonding densities.

So, that that was the logic which was used in those experiments and such experiments were initially performed with lot of care and people also used the neutron data on the same crystal that is because with the case of a neutron data we have no variation with respect to sin theta by lambda. So, we could get as much diffraction as possible from the crystal. Again as we mentioned in the morning regarding the powder diffraction the amount of sample that is required.

In case of neutron diffraction also the crystal size should be almost centimeter size because the strength which these moderated neutrons come out they will just pass through the crystal if we want a normal crystal which we use for XRD, the signal crystal X ray diffraction which is 0.3 millimeter cube. So, if we go towards 1 centimeter; that means, we have to grow very; very large crystals and that becomes a rate limiting step.

Instead we use the same X ray diffraction on the same small little crystal, but get the get the high order data augmented we can replace the neutron results from the X high order results and this was known as the X minus X high order analysis and people calculated these maps. Now, what do these maps give when we subtract the overall data from the data which is coming only from the higher angles, the higher angles are essentially representing the core electrons and therefore, we can determine the positions x y z more accurately.

So, if we use the X high order data and calculate the structure factors, those structure factors will be now coming more or less from the core and therefore, they will be very accurate. So, now, we subtract from the observed data, the data which is coming from higher order, then what is left out will be the electron density in the valence region. And since we are now looking at the electron density in the valence region we are able to see the what is the amount of electron density that is there between the bonds and the density which is between molecules inter atomic interactions.

So, that is the logic which was used in the experimental aspect of charge density analysis. And at the same time collecting the data at low temperatures ensures that the thermal vibrations are minimized and as a consequence we do not have to worry about the fact that, the thermal vibrations which also give wrong positions or rather positions of the atoms which are a little removed than what they are where they are you know because of the lattice vibrations that gets reduced.

So, the accuracy with which we can determine the atomic positions increases extensively when we collect the high angle data and use the so called X minus X high order refinement. So, the early days of charge density 70s in fact, 60s, 70s and early part of 80 also you will see large number of literature associated with X; X high order refinements X minus n maps X minus X high order maps and so on where people have tried to look at the bonding densities.

And the success of that is mainly because of the fact that when we used the high angle data, the data is devoid of the fall of f with respect to sin theta by lambda it is more or less a straight line.

At this stage quantum crystal quantum mechanics and quantum chemistry came into prominence over the years and people are became aware of various kinds of ways in which the contributions from atoms can be calculated and so we one could actually calculate wave functions and the square of the wave function if we take we are aware of that aspect we will get the approximation towards the intensity associated with the X rays and we now know that takes the intensities come from the planes in a crystal, so I of h scale will be the source. So, keeping that in mind when the models have to be constructed one of the thoughts which I occurred was we will discuss it when once I once I highlight the basics of quantum crystallography.

So, just like the you know we have the quantum chemistry fundamental laws and rules we have fundamental laws and rules followed by form for quantum crystallography and that you see is formed only very very recently in the year 2017. So, it is a very infant area of a very old thought process, it is a area is infant, but the thought process is very old because it was very beginning people thought that it should be possible to see the electrons in orbits at the time X ray scattering was realized.

So, there are two possible approaches in quantum crystallography as has been formulated and in fact, it is at this moment spearheaded by a group of people several groups around the world are working on it, one of these groups is the consist of three people there is Simon Grabowski, Alessandro Genoni and Hans Beat Burgi. So, these three gentlemen wrote this article which is interaction to the new area of quantum crystallography.

What they discussed was that we can look at this area into two part possibilities; one is we look at models that we can develop for charge densities in crystals and of course, this model will incorporate electron density distributions, atomic positions and atomic motion using high resolution diffraction experiments which we just now discussed can be improved based on quantum chemically calculated, tailor made electron density.

So, what was suggested was in this approach, that we now calculate the electron densities and this calculated electron density is essentially the form factors which is also the scattering factor which we have discussed just now it is also referred to as the form factor. So, the we can we can actually from quantum mechanics calculate these form factors and these form factors which we are going to calculate will include the concept of questions like what happens to an atom when it is put in a which is a part of the molecule and what happens to the molecule when it is put inside the crystal?

So, two fundamental questions get asked what happens to an atom when it becomes a part of a molecule. Obviously, the electron density of atom one and electron density of atom two gets shared, it could be a covalent sharing, it could be an ionic sharing or whatever. So, there is a certain amount of electron density which is going from one atom to the other; that means, the carbon atom will no longer be having six electrons some amount of electrons or either donated or transferred to the region between the two carbon atoms or it is transferred to the next atom which now becomes an electronegative atom. So, that way the propagation of electron density takes place and we form a molecule.

So, sharing of the electron density between atoms in general will allow for sharing to form the molecule and therefore, these molecules now exist in crystal structures and they obey the rules which we have formulated in the entire course the rules of symmetry. So, depending on how the symmetry directs these molecules, these molecules arrange themselves inside the unit cell and there will be a possible interactions between one molecule and the other.

These interactions in fact, lead to the area of crystal engineering where we can actually identify the nature of these interactions and see whether either they are highly directional or whether they are highly attractive or repulsive depending upon the nature of the interaction, which allows for us to understand the concepts of how crystals get engineered through molecules how these molecules arrange themselves inside the crystal lattice. And so the concept of hydrogen bonding, the concept of halogen bonding and other kinds of bonding issues come up.

So, basically the idea is to use the quantum mechanical modeling, one of the early models which we are going to discuss in detail in the next few minutes will be the one which is called the multipolar refinement approach where we develop a multi polar model associated with an atom. Obviously, now atom cannot be a spherical atom in this modeling, it has to be distorted.

The atom should be distorted in such a way that it is now oriented it's itself to the connecting bond a bonds it should be directed towards connecting bonds and then certain amount of electron density should be going out, certain of amount of electron density should be coming in. So, that the overall molecule remains neutral. So, the electron neutrality of the molecule is result and as a consequence there is a redistribution of the electron density and that can be estimated from quantum chemical calculations.

So, the possible approach is that we have the charge density model, the charge density models will be developed, incorporating the electron density distribution, atomic positions and atomic motions using high resolution diffraction experiments. So, this is what we do to get the charge density models and these can now be improved with quantum chemical calculations. This is one way of redefining the behavior of f versus sin theta by lambda. So, it will change accordingly when the atoms bond to each other.

The second approach is we have we can calculate wave functions from quantum mechanics and those wave functions always are approximate, they are not final. We know that apart from hydrogen atom the other atoms quantum chemically quantum mechanically we cannot fully solve for them and therefore, there are approximate wave functions.

These can be improved by constraining them; these can be improved by constraining them to reproduce observations derived from diffraction and scattering experiments. So, we have these experiments done, we have this higher resolution experiment done where we are collected data beyond sin theta by lambda, we have done the Fourier analysis, we have located the atom positions and so on.

So, these are the observations that are already a part of the diffraction experiment and therefore, they represent the chemical structure. So, the chemical structure is available and therefore, these wave functions now can be improved by including this information from the experiment. So, one is the improvement of quantum mechanical observations using the experimental data which are very very accurate, the other one is the use of the models the correction to the models that can be introduced when once we have quantum mechanically calculated electron density.

So, quantum mechanics and crystallography these two get combined and therefore, this area has the name quantum crystallography. In 1995 in fact, it was defined crystallographic information to enhance quantum mechanical calculations and the information derived from them. So, we are using the crystallographic information to enhance the quantum mechanical calculations in a given molecule. So, how best we can use this approach how best we can do this we will see in the coming slide.

So, two approaches as we just now discussed one is the first aspect where the crystallographic data are integrated into quantum mechanical chemical calculations and the information content of the wave function. So, we have quantum chemistry, we have crystallography, they build it together into quantum crystallography which will allow for experimental wave function. See one of the things which we can we have the problem we have when we get the experimental wave function, this will have all kinds of errors that is because we have made the first of all we have made the spherical atom approximation.

Secondly, we have these errors in phases we do not have the actual phases. We estimated the phases the phase problem in crystallography persists and therefore, the experimental wave function which we get has to be going towards the actual true wave function. So, we can use this data and then try to see whether we can take this over to that that is one approach.

And the other approach is now we have the crystallography and quantum chemistry coming together to quantum crystallography. Here what happens is that we end up with improved dynamic charge density, see what we are doing from the charge density experiments is to map the electron density after removing the presence of the atoms which participate in forming a molecule.

So, as I mentioned what happens to an atom when it becomes a part of a molecule, there are certain amount of electron density is shared between the atoms. So, when we do this charge density mapping, we remove the atom contributions and look at only the accumulation of the charge density in the regions between the two atoms the topology of the electron density is what we analyze. And that is subject to again considerable amount of errors because it depends upon what model we are going to use.

So, that with quantum mechanics input will give us the improved charge density. We put here dynamic because that is very crucial to have as let us say the change of if there are some changes which are brought about by shining light onto the crystal, photo crystallography is an area which has developed in recent years. So, we can see the energy changes and then therefore, calculate the dynamic charge density in such systems.

So, effectively this will now go and lead us to the truth charge density in the model this is what is our approach. Experimentalist look for this theoreticians look for that and you see that the marriage between quantum chemistry and crystallography therefore, leads to either of these two successes. So, that is the idea of quantum crystallography and so we see that this is the way it gets defined.

In fact, quantum crystallography and crystal the quantum chemistry and crystallography are not very far from each other, this particular diagram shows how quantum chemistry and crystallography have contributed to various aspects of theory and experiment. So, here you have the X ray diffraction data, Compton scattering data, polarized neutron diffraction data and then you can go up to a the single determinant wave function, energy minimization many determinant wave functions.

So, there are lots of experimental and theoretical calculations which I will develop in between and therefore, this is a very straightforward link which brings in quantum chemistry and crystallography or quantum mechanics and crystallography together right.

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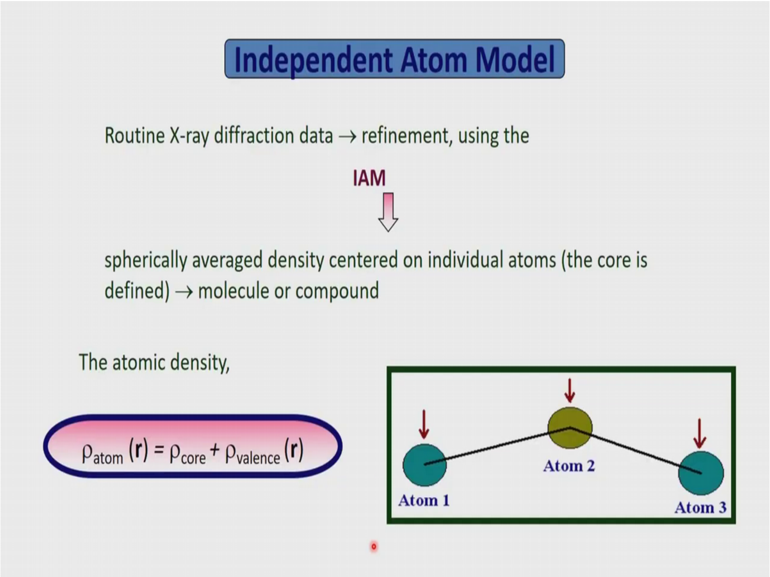

Independent Atom Model

Routine X-ray diffraction data → refinement, using the

IAM

spherically averaged density centered on individual atoms (the core is defined) → molecule or compound

The atomic density,

$$\rho_{atom}(r) = \rho_{core} + \rho_{valence}(r)$$

Having seen that how does this all happen and how are we coming into the picture as crystallographers. What we do is we most of the structure which we determine is based on assumption that atoms are spherical this is what we have done in the structural determination protocol using both the single crystal methodology and the powder diffraction. So, we assume that the atoms are spherical and they keep their asperity even when they are bonded which is a rather not so acceptable concept, but we believe in that.

And then we so therefore, model the electron density as though it is made up of a electron density from the core and electron density from the valence. So, this is a spherically average density and it is referred to as the independent atom model. So, the atoms are all independent of each other this is the routine X ray diffraction.

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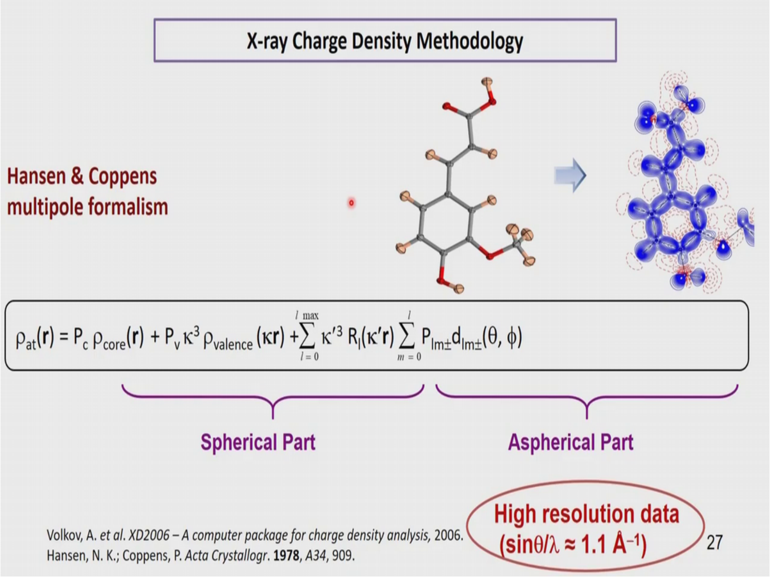

X-ray Charge Density Methodology

Hansen & Coppens multipole formalism

$$\rho_{at}(\mathbf{r}) = P_c\,\rho_{core}(\mathbf{r}) + P_v\,\kappa^3\,\rho_{valence}(\kappa\mathbf{r}) + \sum_{l=0}^{l\,max} \kappa'^3\,R_l(\kappa'\mathbf{r}) \sum_{m=0}^{l} P_{lm\pm}\,d_{lm\pm}(\theta,\phi)$$

Spherical Part

Aspherical Part

Volkov, A. *et al. XD2006 – A computer package for charge density analysis*, 2006.
Hansen, N. K.; Coppens, P. *Acta Crystallogr.* **1978**, *A34*, 909.

High resolution data
($\sin\theta/\lambda \approx 1.1$ Å^{-1})

Now; obviously, it is not true so we have to put in the information about the bonding features. How do we do it? One of the methods which is very popular which was developed by Hansen and Coppens way back in 1978 and this is in fact, the way in which most of the charge density analysis until now are being done. So, a very few which are using other methods, but this is by far the most powerful and well documented report because the charge density analysis is easily approachable by and is easily programmable by this approach.

So, here you see that the electron density at the atom now is no longer just core plus valence, the core is associated with a certain population P c that is the number of electrons with the core and P v is the number of electrons with the valence. So, we therefore, now have an expression for the electron density which has the part associated with this and then the spherical part. Now when the bonding is taking place the atom will expand and contract.

So, it will contract in the region where there is contribution coming from some other atom and it will expand when it has to push the contribution to some other atom eventually to form the molecule. And this expansion and contraction is referred to as the radial distribution or radial part and that is this part. And this part of the expression now joins the definition of the electron density and this part of the expression tells us this value of kappa tells us how the expansion and contraction is associated with this behavior.

Now, apart from that we also have the reorientation, so it is not spherical the spherical is a big approximation again, but definitely not so much of an approximation as independent atom model where we assume solid atoms atomic spheres and they are like billiard balls and you cannot bend them. In this case the expansion and contraction parameter will allow for the possibility of forming bonds.

In the early days that was what was developed again from Philip Kaufman's group and it so happened that I happened to be a part of that group at the time, so I was also involved in the development. But that was essentially the expansion and contraction of the atom it's known eventually as a radial refinement protocol. But then we also realized very quickly that there is a as spherical component. So, to build in the spherical component this additional term is added which is their spherical part.

So, effectively now the atom is described as a realistic atom, so this is now a realistic atom in a molecule. So, when the atom becomes a part of a molecule this will be the value of the electron density and not the value of electron density that we use always for determining the crystal structures. So, this is just rho core plus rho valence whereas, as you see here rho core plus rho valence plus this radial term and then this is known as the spherical harmonic term which essentially takes into account the asphericity that can be associated with the atom.

Unfortunately there is not a enough time to go to the fuller details of this except to give you the highlights of what kind of results we can get from this kind of an analysis, one of the things of course, is we get very highly accurate crystal structures. So, the atomic positions now and the atomic displacement parameters, the thermal parameters are shown in this r type diagram you see that we have a low temperature data, so the r type plots along is also showing the presence of the hydrogen atoms also shown as anisotropic.

So, this kind of a feature can come when we fit the equation of this kind which is known as a multipolar expansion components. So, we have included the multipolar components along with the polar components in some sense. So, what is happening here is that the atoms now are actually represented of the way in which they are situated in a molecule and so this now develops using the symmetry rules in this space group it puts the other atoms together. So, this is the structure of a realistic molecule, I will not give you the detail of what it is, but one once we now do this we also do what is known as a difference Fourier of this.

Now, this difference Fourier of this is slightly different they define than what we already defined. This difference Fourier is the electron density as is obtained from here minus the electron density assuming that the atoms are independent atoms. So, you have atomic positions here, so you have removed the atoms effectively and what is left out in the electron density after we allowed for their spherical refinement is plotted here this is known as the deformation density map.

So, it tells you how the atoms are deformed and how much of electron density gets shared between atoms and so on. Let us look at this part you see this is the six member ring if you look at this part you see this is an atom position here and an atom position there, you see there is electron density which develops between these two. In fact, by counting the number of contours these are measured plotted at 0.01 electrons per angstrom cube so very very small electron density, but by counting this you can also get any idea of how strong is the CC bond.

And you see that all these six bonds in this particular ring are about the same value as far as the deformation density is concerned. So, this deformation density also tells you that we are fairly accurate in our ideas about the types of atoms and the contribution of chemistry to these type of atoms. If you look at this particular atom which is the oxygen atom, this oxygen atom now appears with the two lone pairs. So, the lone pairs on the electrons can be seen here, the lone pairs on the of the on the oxygen can be seen here.

The lone pair electrons have a orientation which we believe is the direction of bonding as we know.

So, earlier days Pauling and others define these as the bonding directions, the directions where a nucleophile can approach the direction where a new electrophile can approach, all these ideas now can be visualized. See X ray diffraction is always as I kept on mentioning is for visualization; visualization and realization of the reality of what is happening to atoms. So, we are now putting our lens which we started by looking at the image of an object you remember long ago we put a convex lens and then did the focal length experiment.

Now we are actually looking at focal with a lens where we are looking at the density between the bonds. So, the density between the sorry between the atoms we can also look at the density between the bonds which are also plotted here and these red dot; dot lines show negative contours. So, essentially we have therefore and now possibility of viewing these electron densities at this level. What is required is a high resolution data as I mentioned sin theta by lambda 1 and above 1.1 angstroms in this case is a minimum requirement to do these experiments.