Symmetry and Structure in the Solid State
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Lecture – 60
Quantum Crystallography- 2

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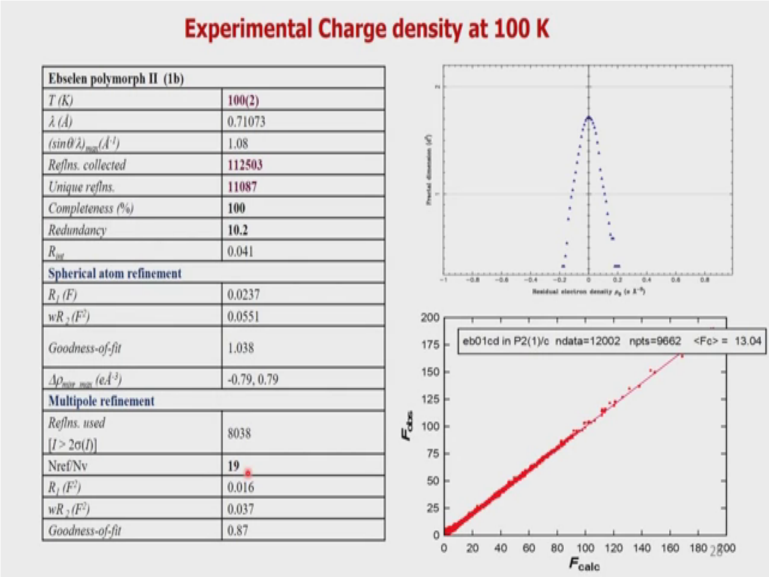

Experimental Charge density at 100 K

Ebselen polymorph II (1b)	
T (K)	100(2)
λ (Å)	0.71073
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.08
Reflns. collected	112503
Unique reflns.	11087
Completeness (%)	100
Redundancy	10.2
R_{int}	0.041
Spherical atom refinement	
R_1 (F)	0.0237
wR_2 (F^2)	0.0551
Goodness-of-fit	1.038
$\Delta\rho_{min, max}$ (eÅ^{-3})	-0.79, 0.79
Multipole refinement	
Reflns. used $[I > 2\sigma(I)]$	8038
Nref/Nv	19
R_1 (F^2)	0.016
wR_2 (F^2)	0.037
Goodness-of-fit	0.87

So, one of the good data sets is illustrated here so, when we do the data collection and collect the data over the on a crystal. It is not just a few 3 4 hours dataset. The data that is collected is now has to be complete and we have to see whether we have got the data on every reciprocal at this point which comes in the limiting sphere and in fact, beyond the limiting sphere in some sense.

We also measure all possible reflections we do not leave out the reflections now and as you see from this; this is the structure of epsilon which was done in our laboratory Ebselen polymorph II it is supposed to be a drag. And the temperature at which the data was collected is 100 this was done by my student who is now his name is Dr. Sajesh Thomas and he is now somewhere in Denmark. So, he measured the data at 100 Kelvin and the wavelength that is used is molybdenum. And as we saw from the from the table we made for resolution limits and so on lambda by 2 is the resolution to which we can go in principle right.

So, it should be half of 0.7. So, we should be able to see these bonding densities fairly clearly in this data. Sin theta by lambda he managed to go up to 1.08 and the total number of reflections collected as you see is enormously large for a very small crystal unit cell dimensions. I think the unit cell dimensions are not given here, but I remember the unit cell dimensions it is a monolithic system and it is 8 by 12 by 14, it is a very small firm.

So, you see that we have 112503 out of which of course, all the all the redundant ones are also measured; that means, we measure the Friedel equivalent also. So, the Friedel equivalents do not contribute freshly to the data, but they will allow you to average the data. So, if you now reduce this redundant data to unique reflections we have 11087 reflections. So in fact, if you look at the sphere you all sphere you will see that it is 100 percent complete data, it is all possible data points have been taken into account a very high quality data and we are measured some reflections more than 10 times. That means, you we have measured let us say in this space group we have measured 10 percent 10.2 times is the redundancy; that means, a given hkl is measured in all possible orientations 10 times so and then averaged out.

So, you are accuracy of the data measurement is extraordinarily high and that is indicated by this what is known as a fractal plot. So, I have no time to go into the detail except that this has to be symmetric with respect to the electron density the residual electron density which is shown here. So, based on this now we go to the refinement so, we now refine the unit cell in such a way that we consider this is at routine data; that means we do as spherical atom refinement.

So, when we do this spherical atom refinement we reach a R factor which is 0.02 very accurate data and rated R factor is 0.08 and the goodness of fit which should be ideally 1 it is 1.038; that means, it is an extraordinarily high quality data. And as you can see from here if you do look at the what is left after the difference Fourier map you see that an amount of electron density that is left is minus 0.79 electrons per Angstrom cube to plus 0.79 both are nearly equal; that means, it is a very flat map after you account for the entire data which the entire crystal and the atoms in the crystal. Then we go and do these multipole refinement, you see the number of reflections now used are 8038 we have made some more filtration of that.

Because we now consider reflections above the threshold of 2 sigma I sigma represents the threshold. So, the ratio see what is important in this data again is the over determination, just like any structural refinement we had over determination. Here for every variable which is now increased in number because now the variables are not just x y z we have to now refine many other parameters to define this asperity.

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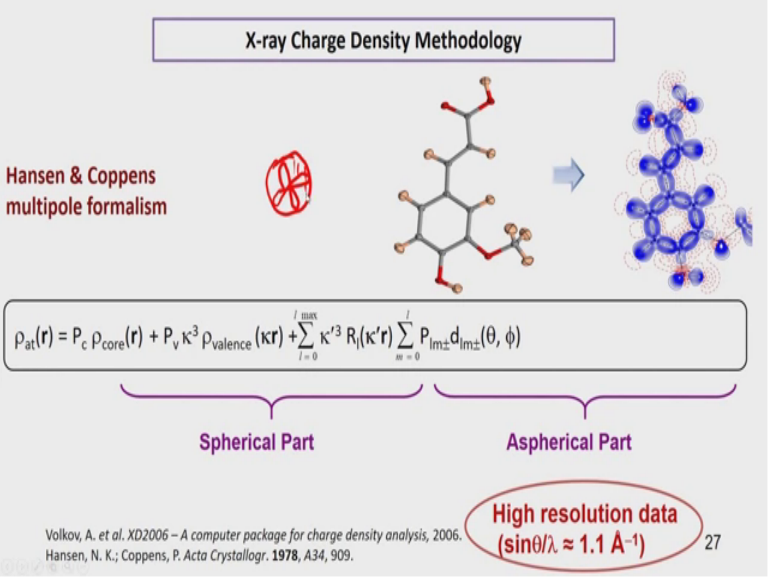

X-ray Charge Density Methodology

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})

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In fact, every atom earlier had x y z and 6 thermal parameters. So, that made it 9 parameters per atom. Now, along with this 9 parameters we now consider the atom to be a multi pole; that means, the atom is now associated with a monopole which contains the number of electrons, then it is also associated with a dipole so which we will have 3 parameters 1 parameter for the monopole, 3 parameters for the dipole and then 8 parameters for the octopole and so on. So, we will keep increasing the number as we go higher and higher to describe the atom. So, effectively what we do is the following. You just consider the atom to be made up of a monopole and this particular monopole.

Now, covers the diameter of the atom and then in that way have a dipolar contribution which will go like that with respect to the center and 3 directions, then the quadropole, the octopole and the hexa pole upon. So, effectively we fill in all the possible space here and the shape being aspherical; the space being aspherical we will have the representation of the atom in terms of multipoles that is why we call the multiple. So, there will be 26 additional, 9 plus additional parameters are accounting to total 26. So, they we therefore, define refined 26 parameters per atom.

So, considering that the number of reflections to a number of variables ratio is 19. So, it is generally recommended it should be at least 10 for a successful determination of bonding density. So, it is quite over determined in that sense. So, the R factor here you see is 0.016; that means, the error that is involved is less than 1 plus 1.6 percent, you can express the R factor as 1.6 percent; that means, the 1.6 percent is your R factor the weighted R factor is 3.7 percent goodness of it is 0.87.

In fact, if when once we compare this to F of x minus F calc you see this line where in which we have plotted every reflection that has been measured and you see if I have the beautiful straight line saying that there are not much deviations in the individual F ofs F calc measurements and calculations. So, this essentially represents a very accurate data it is P 2 1 upon c as I mentioned it is a monotonic system.

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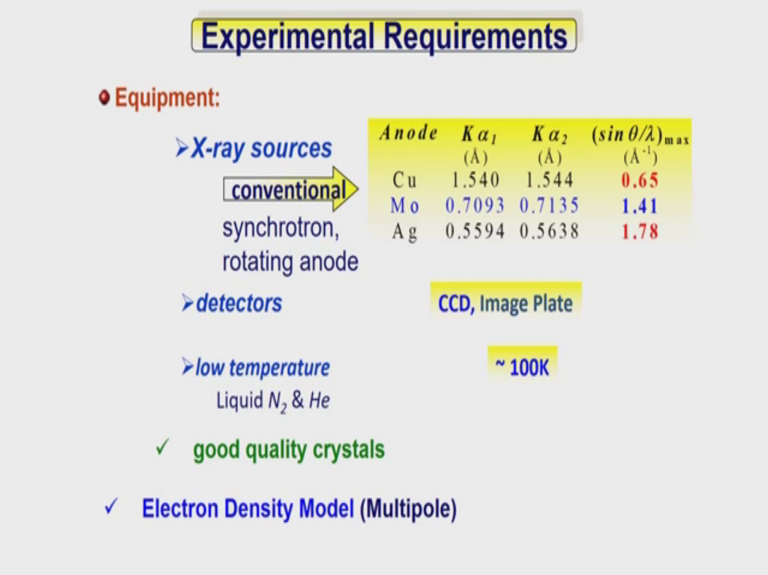

Experimental Requirements

- Equipment:
  - X-ray sources
    - conventional
    - synchrotron, rotating anode

Anode	$K\alpha_1$ (Å)	$K\alpha_2$ (Å)	$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)
Cu	1.540	1.544	0.65
Mo	0.7093	0.7135	1.41
Ag	0.5594	0.5638	1.78

  - detectors — CCD, Image Plate
  - low temperature — ~ 100K
    - Liquid N_2 & He
- ✓ good quality crystals
- ✓ Electron Density Model (Multipole)

What are the experimental requirements? How do we collect the data in such an experiment? The experimental requirements are, we can use a conventional sources good laboratory source and the preferred radiation is molybdenum. Of course, we can also use silver because the idea is to get the sin theta by lambda maximum to as high value as possible. Obviously, use of copper is disallowed because it is just up to 0.65, we need to have data beyond 1.0of sin theta by lambda and so molybdenum is the choice if you are doing charge density analysis.

We can use synchrotron radiation and tune the radiation in any range between our silver and molybdenum. So, that is also good news we can use rotating anodes as well the detectors could be CCD image plate I must be adding here CMOS detector which is nowadays the most suggested this detector on diffractometers. The low temperature data we can use either nitrogen or helium we use the nitrogen which is a about 100 K because, in all these there is 1 issue there are 2 issues in fact. The 2 issues are they were 2 which are ticked. Only when we can tick these two we can do the charge density analysis and therefore, aid in the development of the ideas of quantum crystallography.

So, we have to have good quality crystals that is the first requirement, the second requirement is that we should have a good electron density model. So, when once we have these two this is the multi pole model which we just now discussed, if we have these two properly done then we can go further.

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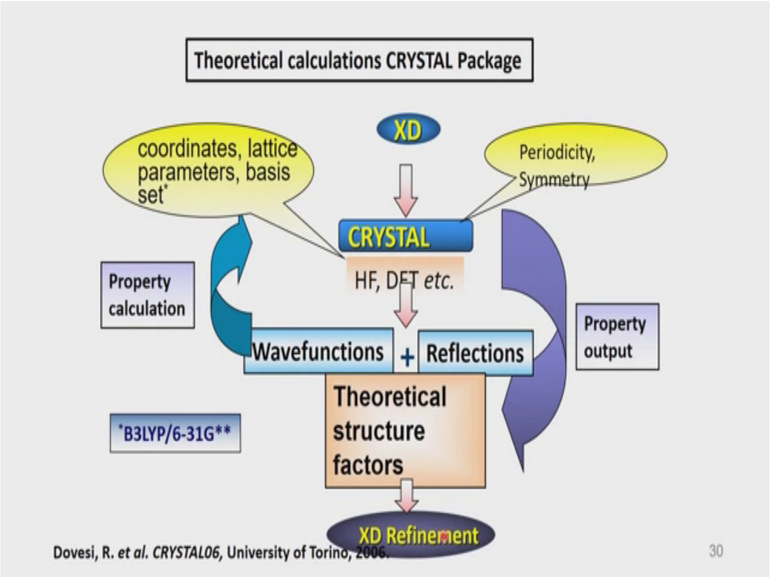

Theoretical calculations CRYSTAL Package

XD

coordinates, lattice parameters, basis set*

Periodicity, Symmetry

CRYSTAL

HF, DFT *etc.*

Property calculation

Wavefunctions + Reflections

Property output

*B3LYP/6-31G**

Theoretical structure factors

XD Refinement

Dovesi, R. *et al.* *CRYSTAL06*, University of Torino, 2006.

And now we can bring in the aspect of combining theory and experiment. One of the early ways of doing this was sorry about this overlap it is university of Torino this reference is 2006. But we have now, what is known as crystal 17, I told my students to get it, but they have not shown any further interest on that. Here we have crystals 17 and the crystals 17 is the one; which we should be having and the theoretical calculations can be performed and we can use the package XD which is the charge density package.

So, when we take the charge density package and use this program crystal from the charge density package we feed in the coordinates the lattice parameters and the basis set, then periodicity and symmetry are brought into the system, we can use Hartree Fock and DFT etcetera to calculate the way functions and reflections. So, the advantage here is we end up with theoretical structure factors.

So, if we get theoretical structure factors they are devoid of all systematic errors we do not have to worry about absorption, we do not have to worry about extinction corrections, we do not have any issues related to WLP and so on. All whatever errors we have had in the routine structure determination are avoided. So, the theoretical structure factors of the ones which we now use and of course, we use the XD protocol refinement that is the charged density refinement and process the data.

There are two ways in which we can do it one is of course, we have the wave functions this is the quantum crystallographic approach. So, we have the wave functions, we can go back here recalculate these values and then feeding to crystal and then develop the theoretical structure factors of it. So, or we if we have the reflections these theoretical structure factors are essentially the reflections. We can therefore, cycle these out such that we get finally, a high quality theoretical structural factors which can be taken to refinement. So, this is the approach which is there in crystal package.

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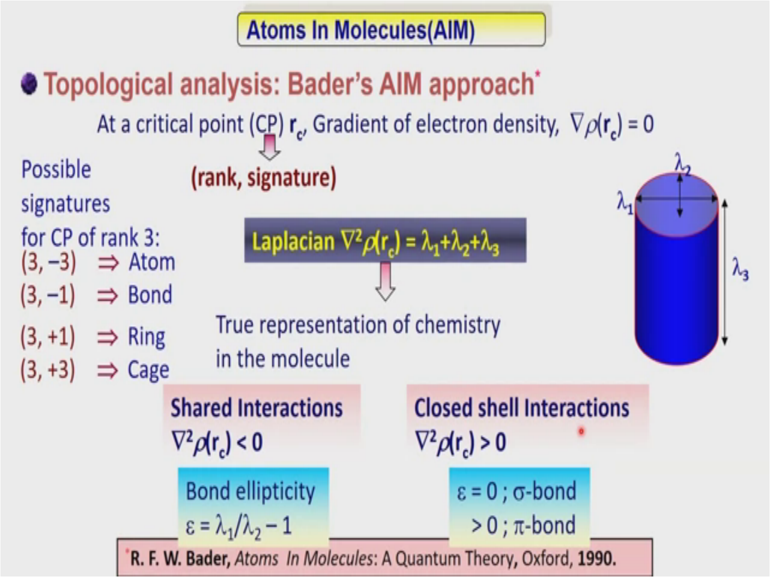

Atoms In Molecules(AIM)

- Topological analysis: Bader's AIM approach*

At a critical point (CP) r_c, Gradient of electron density, $\nabla\rho(r_c) = 0$

(rank, signature)

Possible signatures for CP of rank 3:

$(3, -3) \Rightarrow$ Atom
$(3, -1) \Rightarrow$ Bond
$(3, +1) \Rightarrow$ Ring
$(3, +3) \Rightarrow$ Cage

Laplacian $\nabla^2\rho(r_c) = \lambda_1+\lambda_2+\lambda_3$

True representation of chemistry in the molecule

Shared Interactions
$\nabla^2\rho(r_c) < 0$

Closed shell Interactions
$\nabla^2\rho(r_c) > 0$

Bond ellipticity
$\varepsilon = \lambda_1/\lambda_2 - 1$

$\varepsilon = 0$; σ-bond
> 0 ; π-bond

*R. F. W. Bader, *Atoms In Molecules*: A Quantum Theory, Oxford, 1990.

And now we have to see how to see these atoms. So, you see we have done the map the multi pole modeling, we have accounted for the overall electron density and so on. But how do we see these atoms? There is a theory due to Bader which is referred to as atoms and molecules there is a book which is atoms and molecules A Quantum Theory published by Oxford University Press in 1990, this was written by Richard Bader.

So, in this approach what we do is, we do not look at you see nobody told us that when we say a bond between an atom let us say one carbon and another carbon. Nobody told us that there should be a straight line between these two, which we call as the bond length, but there is nothing called a bond length ok. There is an electron density between the 2 atoms and it is shared and the electrons do not know that they should go in a straight line nobody told me to go in a straight line.

But we measure the straight line distance and say it is bond length and then is the same thing is true with the bond angles then we take the 2 lengths and then say this is the bond angle. What really happens is that the electron density gets distributed in this region. So, it is now a 3 dimensional issue of the electron density distribution and therefore, we call it as the topology associated with the bond.

So, effectively you see here if you take this as a carbon atom and the end other end as a carbon atom this is the CC bond, the electron density is distributed inside this cylinder. It is not necessary that it should be a straight line it can be any anywhere in this particular cylindrical entity which is characterized by three quantities lambda 1, lambda 2, lambda 3; which are essentially elements of what we call as a Hessian matrix.

Theoretically what it means is that we have the true chemistry of this bonding is represented in terms of an expression which is the second derivative of the electron density at the so called a critical point; the critical point is one in which the first derivative of the electron goes to electron goes to 0. So, between these 2 atoms the first derivative of the electron density goes to 0 at a critical point and whenever there is a critical point between 2 atoms in principle we call it a bond.

And if there is a bond that the critical point del square rho value should be lambda 1 plus lambda 2 plus lambda 3 and there are different kinds of bonding features and those are indicated here. You do not have time to explain every one of them except to tell you that these are actually tenses of rank 3. So, if it is 3 minus 3 it represents an atom position, 3 minus 1 represents a bond position and then 3 plus 1 represents a ring and 3 plus 3 represents a cage.

Effectively we are now trying to see what is the chemistry in this bonding? Rather than look at the straight line distance between atoms and so on which is important which we which is important to say find out how accurately we can determine those by a straight line distances. But what is important is now to see the electron density and the how the electron density is distributed between these two bonds.

So, whenever this value of del square rho c which is called the Laplacian is less than 0, it represents that the 2 atoms here involved are sharing the electrons, it is a covalent bond what is defined as a covenant bond by Linus Pauling is exactly the fact that the del square rho c is less than 0. If del square rho c is greater than 0 it represents closed shell interactions; that means, if you have let us say a molecule here and a molecule there and these two molecules are interacting through a hydrogen bonds or some other Van der Waal interaction.

This essentially represents the limit of the Van der Waal interaction; that means, there is no density developed at the critical point which is now del square rho c greater than 0. In both the cases there is no density of the first derivative of the electron density that goes to 0. We also now defined because we know these values lambda 1, lambda 2, lambda 3, these are the eigenvalues of the Hessian matrix as I mentioned.

These are all terms which I am using freely, these things need a full another 30 hour NPTEL course in which we can systematically go and define all these factors. But what is important from the chemistry and what is important from this particular course structure point of view, structure and symmetry in the solid state? We are now trying to see the structure in the bonding regions and the structure in the regions between molecules and see if symmetry is still there and the how the symmetry is directing the electron density distributions. So, from that point of view we are discussing this issue of quantum crystallography.

So, if we define a value epsilon which is referred to as the bond electricity, as I mentioned again that as we mentioned again and again it is not the central straight line distance between the 2 carbon atoms. So, this bond ellepticity tells us the nature of the bond. So, if the epsilon is exactly equal to 0 it represents a sigma bond, if epsilon is greater than 0 it represents the nature of a pi bond.

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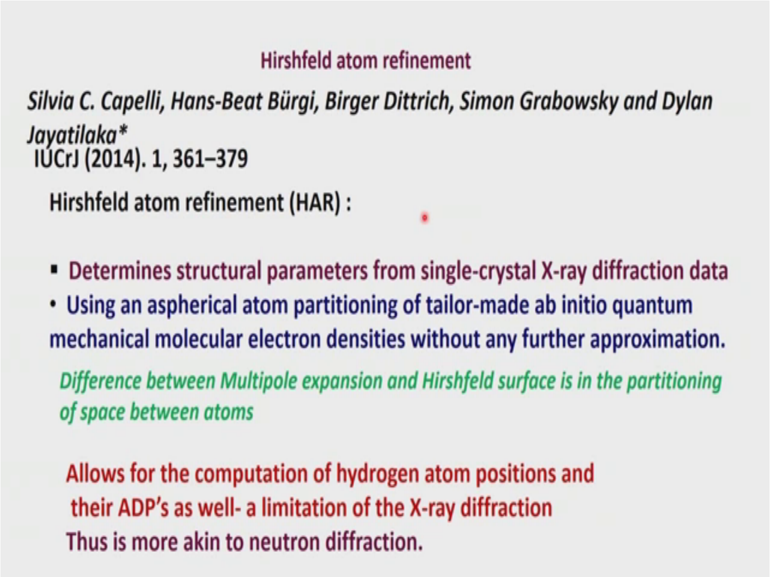

Hirshfeld atom refinement

*Silvia C. Capelli, Hans-Beat Bürgi, Birger Dittrich, Simon Grabowsky and Dylan Jayatilaka**

IUCrJ (2014). 1, 361–379

Hirshfeld atom refinement (HAR) :

- Determines structural parameters from single-crystal X-ray diffraction data
- Using an aspherical atom partitioning of tailor-made ab initio quantum mechanical molecular electron densities without any further approximation.

Difference between Multipole expansion and Hirshfeld surface is in the partitioning of space between atoms

Allows for the computation of hydrogen atom positions and their ADP's as well- a limitation of the X-ray diffraction
Thus is more akin to neutron diffraction.

The fact that we can use multiple atom modeling and use the multiple atom modeling to look into the topological distribution is a very nice idea because, we now know whether the given chemistry can be represented for a molecule and so on. We will take examples, but before we go for such examples I just wanted to introduce the other aspect which is now becoming very popular this is known as the Hirshfeld atom refinement. In this particular case what is done is to determine the structural parameters from single crystal diffraction data with very accurate possibilities of course, independent atom module.

So, the structural parameters are from the independent atom module. And then we use the aspherical atom partitioning of tailor made ab initio quantum mechanical molecular electronics densities a big word big phrase. So, let me tell you what it does. Now what it does is now that we have a molecule and let us say we are looking at inter molecular space. So, there is a molecule a and the molecule b and we want to see what is the type of interaction this molecule a can have with the molecule b.

So, there are different kinds of atoms, there are atoms which are electro negativity atoms, which are electro positive atoms which are neutral and so on in this molecule and so also in the other molecule. So, if you now consider even the case where we have only 2 atoms and for a diatomic structure let us say and this diatomic structure the interaction between 2 atoms. So, effectively you replace the molecules by single atoms. The atoms between these two the distance between these two of course, is our bond length, but the fact that there is a certain amount of overlap of the electron density from atom 1 to atom 2 and a certain amount of overlap from 2 to 1 in the topological region defined.

When we use the multi pole atom modeling the problem is that the multi pole atom modeling does not restrain the extent to which electron density can be penetrated between the 2 atoms position so; that means, there must be some position. So, the position is defined by what is known as atomic basin in which we have let us say an atom in this case we can use this diagram.

So, we can have an atom here and an atom there and del square rho the first derivative of electron density goes to 0. So, if you now plot the electron density along this particular direction the first derivative of the electron density, when it goes to 0 that represents a maxima. So, the actual amount of electron density that is at the middle of the bond is maximum and then it falls off towards the other atom it falls off towards the other atom.

On the other hand when we do the multi pole atom modeling, the multi pole atom model will have the populations of the higher terms, higher multi poles which are extended beyond this region where there is a there is an atomic basis. So, we have an atom we have an atom and between the 2 atoms. So, let me write it quickly because of lack of time. So, we have an atom here and an atom there. So, the electron density will go like that. So, this is the so called critical point.

So, the first derivative goes to 0 and this essentially means that these two atoms are held with respect to the electron density region in this topological space. So, the expressions which we have for the multi pole refinement modeling will extend beyond this particular point which is strictly not allowed because this is the place at which these two should be separated from each other. So, whatever contributions that are coming from multiple modeling has a tendency to penetrate beyond this.

And therefore, there is an error that is associated with multi pole modeling this is gets avoided when we do a different kind of modeling and that again has been developed by using mechanical molecule electron density. So, if we now consider the molecule as a whole and calculate its electron density, there is a certain form factor which can be straight away attached to the molecule as though it is a some kind of a thermal parameter. And so, we have a thermal parameter surface 1, thermal parameter surface 2 which now interact with each other.

So, the atomic based in now can be better defined. Between the 2 methodologies there is not much of a difference except that we have therefore, I have written here the difference between multiple expansion and Hirshfeld surface it is in the partitioning of space between atoms. And this in fact, allows for the competition of hydrogen atom position. So, we can actually get compute the where the hydrogen atoms are lying and also they can get their corresponding atomic displacement parameters.

So, this is a limitation in the X-ray experiment we said that we cannot determine the hydrogen positions, but we use this approach and use the either the multipole modeling or this one preferably the Hirshfeld surface modeling, then we will get the hydrogen atom positions. So, in some sense this methodology of Hirshfeld atom refinement is similar to that of neutron diffraction.

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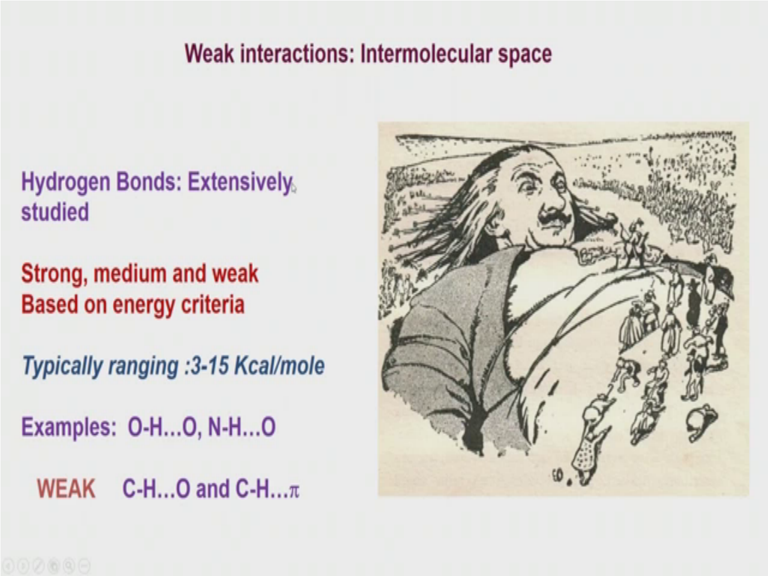

Weak interactions: Intermolecular space

Hydrogen Bonds: Extensively studied

Strong, medium and weak
Based on energy criteria

Typically ranging :3-15 Kcal/mole

Examples: O-H…O, N-H…O

WEAK C-H…O and C-H…π

I think I should not go into further detail of this or for that matter multipole model, instead what I will do is, I will start taking examples which will make your life comfortable because you will understand it better and in of course, you all know the story of Gulliver.