Chemical Crystallograhpy
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Lecture - 51
Direct Methods Part – 02

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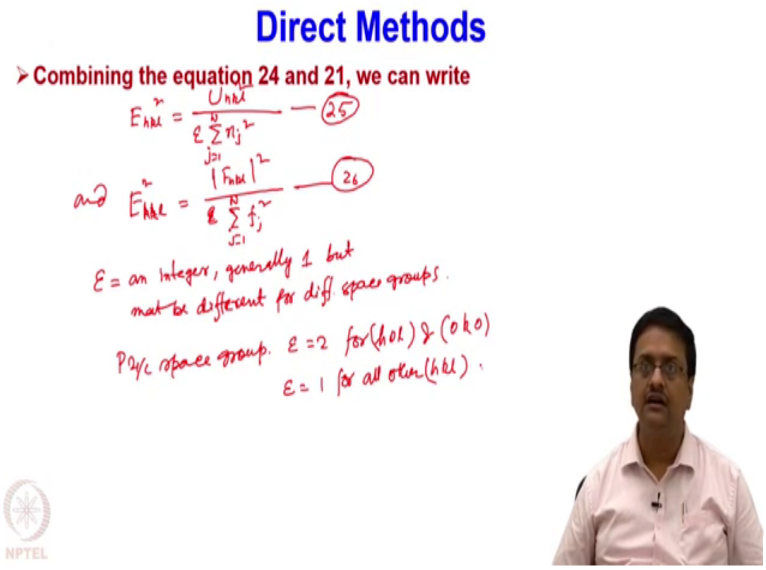

Direct Methods

- Combining the equation 24 and 21, we can write

$$E_{hkl}^2 = \frac{U_{hkl}^2}{\varepsilon \sum_{j=1}^{N} n_j^2} \quad — \text{(25)}$$

and $$E_{hkl}^2 = \frac{|F_{hkl}|^2}{\varepsilon \sum_{j=1}^{N} f_j^2} \quad — \text{(26)}$$

ε = an integer, generally 1 but may be different for diff. space groups.

$P2_1/c$ space group. $\varepsilon = 2$ for $(h0l)$ & $(0k0)$

$\varepsilon = 1$ for all other (hkl).

Welcome back to the course of Crystallography. In the previous class we were discussing about the emitter restructure factor and the E values, we will see how these E values the normalized structure factors can be utilized to determine the central electricity centrosymmetric or non-centrosymmetric behaviour of a crystal.

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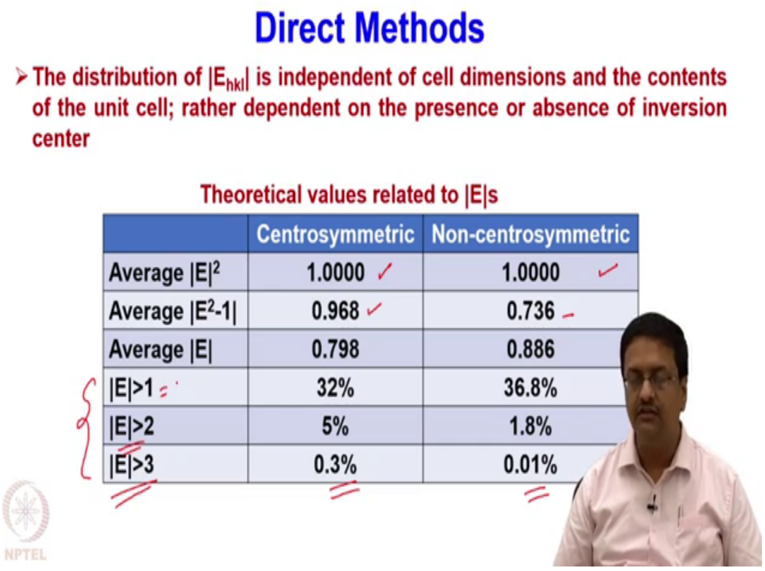

Direct Methods

- The distribution of $|E_{hkl}|$ is independent of cell dimensions and the contents of the unit cell; rather dependent on the presence or absence of inversion center

Theoretical values related to |E|s

	Centrosymmetric	Non-centrosymmetric
Average $|E|^2$	1.0000 ✓	1.0000 ✓
Average $|E^2-1|$	0.968 ✓	0.736
Average $|E|$	0.798	0.886
$|E|>1$	32%	36.8%
$|E|>2$	5%	1.8%
$|E|>3$	0.3%	0.01%

So, the distribution of E h k l is independent of cell dimensions and the contents of the unit cell rather it is dependent on the presence or absence of the inversion centre.

So, here in this table we have a set of theoretical values for the values of E and what we see here the average value of E square is same for both centrosymmetric and non-centrosymmetric structures, but when we try to calculate the E square minus 1 the mod of E square minus 1 the centrosymmetric structures would have the value very close to 1 that is 0.968. For non-centrosymmetric structures it should have value close to 0.73.

So, from a real data when these E square values are calculated and then the mod of E square minus 1 is determined, the value indicates whether it is a centrosymmetric or non-centrosymmetric structure. And then there are indications of how these E values fall rapidly in number of percentages in terms of percentages when E is mod E is greater than 1 greater than 2 greater than 3 and so on, which means the stronger values stronger reflections are less in number, where these reflections are strong reflections and these are the weak reflections.

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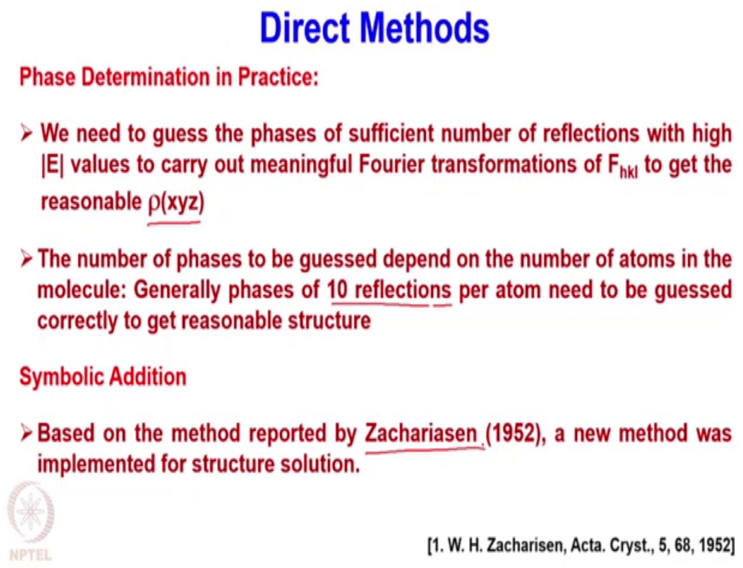

Direct Methods

Phase Determination in Practice:

- We need to guess the phases of sufficient number of reflections with high |E| values to carry out meaningful Fourier transformations of F_{hkl} to get the reasonable $\rho(xyz)$
- The number of phases to be guessed depend on the number of atoms in the molecule: Generally phases of 10 reflections per atom need to be guessed correctly to get reasonable structure

Symbolic Addition

- Based on the method reported by Zachariasen (1952), a new method was implemented for structure solution.

[1. W. H. Zacharisen, Acta. Cryst., 5, 68, 1952]

So, these are different mathematical understanding to talk about the phases, but these phases are very difficult to determine and then from there it is difficult to arrive at the atomic coordinates using the brackets and plot.

So, what we need for practice, routine practice the determine phase determination in practice that we do using computer program? We need to guess the phases of sufficient number of reflections with high E values, to carry out a meaningful Fourier transformation of h k l, F h k l to get the reasonable values for rho x y z which indicates the atom positions.

So, to do that we need the number of phases to be guessed that is depend on that depends on the number of atoms in the molecule. Generally, we need about 10 reflections the phase of 10 reflections to be guessed per atom to get a reasonable structure of a multi atomic structures. So, for this we use a method called symbolic addition. So, based on this method by Zachariasen which was introduced in 1952, a new method was implemented for structure solution.

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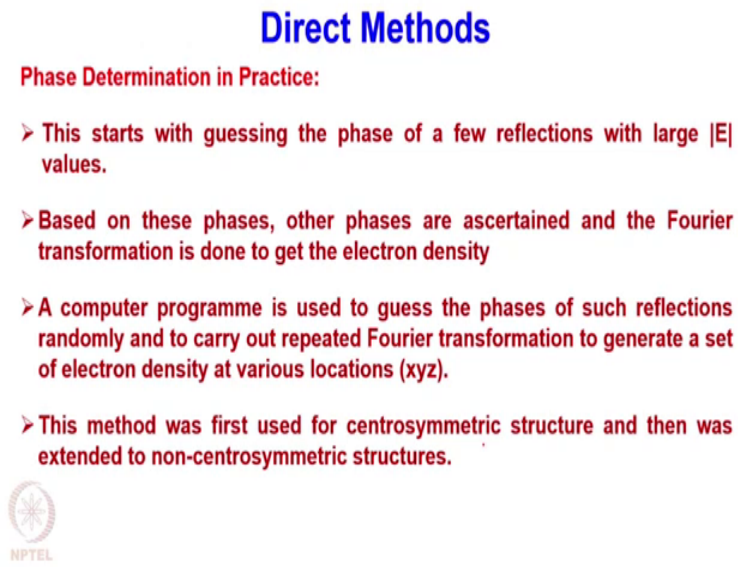

Direct Methods

Phase Determination in Practice:

- This starts with guessing the phase of a few reflections with large |E| values.
- Based on these phases, other phases are ascertained and the Fourier transformation is done to get the electron density
- A computer programme is used to guess the phases of such reflections randomly and to carry out repeated Fourier transformation to generate a set of electron density at various locations (xyz).
- This method was first used for centrosymmetric structure and then was extended to non-centrosymmetric structures.

This method starts with guessing the phases of a few reflections with very large values of E. Based on these phases other phases are ascertained and the Fourier transformation is done to get the electron density. So, this is a random process this is a guess and assumption. So, what we try to do is that, we arrange these deflections in terms of decreasing values of E. We utilize a computer program to guess the phases of such deflections randomly. And then we carry out repeated Fourier transformations and generate a set of electron density of various locations and then plot those electron densities and try to see whether those electron densities have appropriate bond connectivities or not. So, to do that initially this method was first used for centrosymmetric structures and then this was extended for non-centrosymmetric structures as well.

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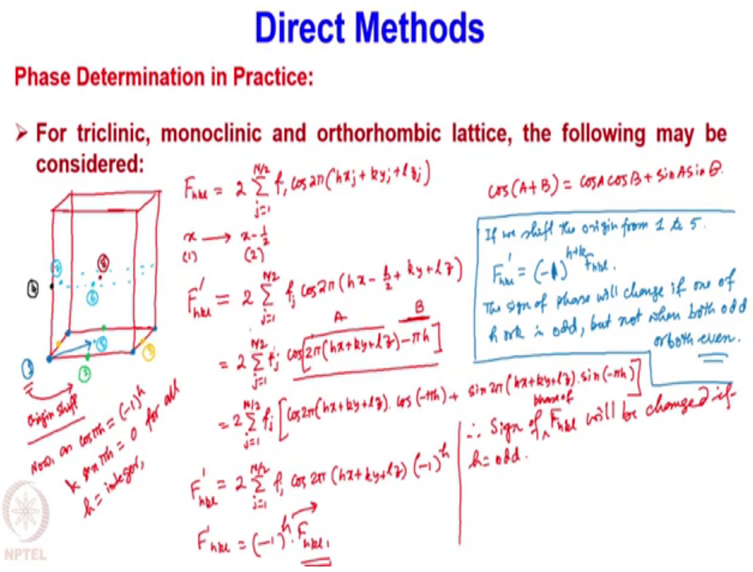

Direct Methods

Phase Determination in Practice:

- For triclinic, monoclinic and orthorhombic lattice, the following may be considered:

$$F_{hkl} = 2\sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

$$\underset{(1)}{x} \longrightarrow \underset{(2)}{x-\tfrac{1}{2}}$$

$$F'_{hkl} = 2\sum_{j=1}^{N/2} f_j \cos 2\pi\left(hx - \tfrac{h}{2} + ky + lz\right)$$

$$= 2\sum_{j=1}^{N/2} f_j \cos\left[\overset{A}{2\pi(hx+ky+lz)} - \overset{B}{\pi h}\right]$$

$$= 2\sum_{j=1}^{N/2} f_j \left[\cos 2\pi(hx+ky+lz).\cos(-\pi h) + \sin 2\pi(hx+ky+lz).\sin(-\pi h)\right]$$

$$F'_{hkl} = 2\sum_{j=1}^{N/2} f_j \cos 2\pi(hx+ky+lz)(-1)^h$$

$$F_{hkl} = (-1)^h . F_{hkl}$$

$\cos(A+B) = \cos A \cos B + \sin A \sin B$

If we shift the origin from 1 to 5.

$F'_{hkl} = (-1)^{h+k} F_{hkl}$.

The sign of phase will change if one of h or k is odd, but not when both odd or both even.

$\therefore$ Sign of phase of F_{hkl} will be changed if h = odd.

Now, as $\cos \pi h = (-1)^h$ & $\sin \pi h = 0$ for all h = integer,

So, let us concentrate on a simple system where it is either a triclinic, monoclinic or an orthorhombic lattice. So, what one can consider in these 3 different types of lattices is that if we draw an orthorhombic lattice which I am trying to draw here, we know that the inversion there are several inversion centres possible in case of a centrosymmetric orthorhombic lattice. So, we need to identify those points with a certain number.

The points which are the corner points are to be numbered as 1, the edge centres on one side these are numbered as 2, the edge centres on the third side, second sorry second side is numbered as set of 3. And the edge centre point on along z is numbered as 4. Other than these there are other symmetric equivalent positions and there are other inversion centres which is the phase centre here marked as 5, the phase centre here marked as 6, phase centre there marked as 7 and the body centre point marked here as 8.

So, there are 8 inversion centres possible in this orthorhombic unit cell. So, for this structure one can write F h k l as equal to 2 times sum over j equal to 1 to n f j cos 2 pi h x j plus k y j plus l z j. Suppose, we first considered the origin to be located at 1 and then we think we assume that we are shifting the origin to 2. So, if we do such kind of origin shift so, what should happen is the value of x which was with respect to origin 1 should become x minus half with respect to the origin 2.

So, in that case the modified F h k l, that is F h k l dash or F h k l prime should be equal to 2 times, I am sorry this should be n by 2, j equal to 1 to n by 2, f j cos 2 pi h x minus h by 2 plus k y plus l z. Or that can be written as 2 times sum over j equal to 1 to n by 2 f j cos 2 pi h x plus k y plus l z minus pi h. So, this can then be rewritten as 2 times sum over j equal to 1 to n by 2 f j cos 2 pi h x plus k y plus l z into cos minus pi h plus, sin 2 pi h x plus k y plus l z into sin minus pi h. You may be thinking how we have written that.

So, we assume this as cos A minus B. So, cos A minus B can be written as cos A cos B plus sin A sin B. So, here it is A and that is B; cos A plus B equal to cos A cos B plus sin A sine B. So now, as cos pi h is equal to minus 1 to the power h and sin pi h is equal to 0 for all h equal to integer. We can simply write F h k l prime is equal to 2 sum over j equal to 1 to n power n by 2 f j cos 2 pi h x plus k y plus l z into minus 1 to the power h or we can write F prime h k l equal to minus 1 to the power h into f h k l.

So, this particular shift of origin from 1 to 2 will change the sign of F h k l if h is odd. So, the sign of F h k l will be changed if h is odd. That is the sign of the phase of F h k l. So, similarly, if we shift the origin from 1 to 5; that means, we change it from here to there. So, what will happen is, we will arrive at an expression F h k l prime is equal to minus 1 to the power h plus k F h k l. So, in that case the sign of phase will change if one of h or k is odd, but not when both are odd or both even.

So, this signs are symbols of these phases will help us in guiding the guiding to guess the correct phases of various reflections.

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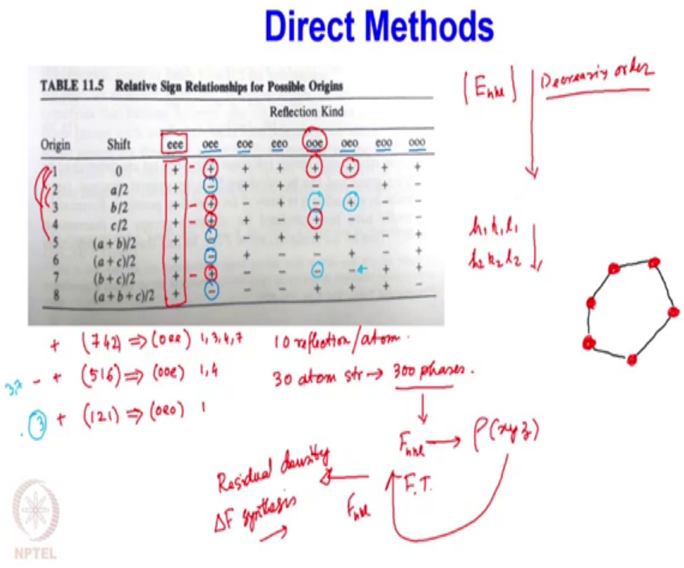

Direct Methods

TABLE 11.5 Relative Sign Relationships for Possible Origins

Origin	Shift	Reflection Kind eee	oee	eoe	eeo	ooe	oeo	eoo	ooo
1	0	+	+	+	+	+	+	+	+
2	$a/2$	+	−	+	+	−	−	+	−
3	$b/2$	+	+	−	+	−	+	−	−
4	$c/2$	+	+	+	−	+	−	−	−
5	$(a+b)/2$	+	−	−	+	+	−	−	+
6	$(a+c)/2$	+	−	+	−	−	+	−	+
7	$(b+c)/2$	+	+	−	−	−	−	+	+
8	$(a+b+c)/2$	+	−	−	−	+	+	+	−

+ (742) ⇒ (oee) 1, 3, 4, 7

3? − + (516) ⇒ (ooe) 1, 4

③ + (121) ⇒ (oeo) 1

10 reflection/atom.

30 atom str → 300 phases.

$|E_{hkl}|$ Decreasing order

$h_1 k_1 l_1$

$h_2 k_2 l_2$

$F_{hkl} \rightarrow \rho(xyz)$

F.T.

F_{hkl}

Residual density

ΔF synthesis

Here we have a particulate tabular form where we have listed, what should be the signs of phases of various sets of reflections with the values h k l even even even odd even even, like here. So, in this case there are different possibilities of the h k l deflections, having the indeed indices as all even or all odd, odd combinations of odd and even. So, this indicates that all the h k l reflections when it is all even which is the first column, they all of them have the same phase. And they do not change the phase if the origin is shifted from 1 to 2 or 1 to 3.

So, any shift of origin from 1 to 2 or 1 to 3 or 2 to 3 or 1 to 5 or whatever does not change the sign of these phases. So, it means that the reflections with all even integers, that is all even h, k and l are structure semi invariants and their phases cannot be changed in any condition.

So, what we then try to see that all other reflections have either positive. So, you have this case, where you have plus sign for 4 of them and the corresponding minus sign for 4 of them. And this is valid for all other reflections where you have 4 plus and 4 minus possibilities. So, when we have such situation, then depending on the data set what we first do is we arrange them with the E h k l, mod E h k l values in the decreasing order. And then identify some reflections h 1 k 1 l 1, h 2 k 2 l 2 from top to bottom. And then arbitrarily first assign their phases to be either positive or negative.

So, for example, suppose if we take a reflection 7 4 2 which falls in the class of odd even even. So, when we have this reflection odd even even, the 4 possibilities where the phases are plus are marked here. So, at the origin 1 3 4 and 7 they will have plus phases. So, by assuming this to be correct, which I to assign the face of some other reflection which may be falling like 5 1 6, a strong reflection and that 5 1 6 falls as odd odd even set of reflection. So, the odd odd even comes here.

So, now with plus sign of 7 4 2, the odd odd even has plus signs for 2 cases. The origin at 1 and origin at 4; that means, the choice of origin for 7 4 2 was 1, 3 4 and 7, but now for 5 1 6 reflection that choice is now reduced to 1 and 4. So now, if we then choose one reflection which is suppose like 1 to 1 which is also probably a strong reflection, which is odd even odd set of reflection. So, odd even odd should have all 3 plus the option is only 1.

So now, with this condition the phases of these reflections are all plus. You have choices of those origins. So, like that we try to assign phases of a large number of reflections. How many as we indicated 10 reflections per atom. So, if it is a 30 atom structure, then we need to guess about 300 such phases. And then after guessing those 300 phases, we use those 300 F h k l to generate the corresponding rho x y z using the Fourier Transformation method.

And then by doing a Fourier transform, we try to we what we get is some location of electron density in space. Then by applying our chemical knowledge we try to join those electron densities by bonds and try to see whether that generates something sensible. And then we take that as a starting model and continue the process of guessing phases to completely solve the structure.

So, once we have correctly guessed a molecule, part of a molecule maybe like a benzene ring or whatever, so, then these are used as known locations of the atoms. So now, the rho x y z is known. What we do is then do the inverse Fourier transformation and try to get the residual density from a delta F synthesis. And we try to complete the structure. And if this phase guessing method is wrong; that means, we start going back and forth in this method. So, if the phase of 5 1 6 had to be minus, then the choices are different.

So, if we want to have a 5 1 6 to be minus, so, with plus sign of 7 4 2 here, 5 1 6 minus is possibility here which is 3 and the possibility is 7 to that the choice of origin. So now, for 1 2 1, to have a plus sign matching with plus and minus of the first 2, so, we should have plus minus can have plus here, plus minus is having minus there.

So, the only choice is now, reduced to the origin 3. So, this method of guessing doing Fourier transformation getting the atomic coordinates trying to see whether it forms a molecule or not, going back and reassigning the phases changing the phases from plus to minus for centrosymmetric structure is done by a computer program. And nowadays, we as we have seen we have we know SHELX does this job very well. And we use SHELX, S for structure solution, which we will show in one of the lectures how SHELX does this than routine structure solution algorithm to get the correct phases. And from there it does a Fourier transformation to give you the correct positions of the atoms.

So, this method was extremely difficult until and unless the computer programs were incorporated and these phases had to be done by hand and it used to take a large amount of time to solve one structure, not too many years ago about 30 years ago, this was reasonably difficult, but after SHELX came into picture in 1970s this random phase determination and simultaneous Fourier transformation has become significantly useful for all kinds of centrosymmetric and non-centrosymmetric structures. So, with this we will conclude the part of direct methods and as I indicated there are other methods of structure determination like Patterson method. So, in the next lecture we will try to talk about this Patterson method.