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Bhanumoorthy Pullooru (✉ bhanumoorthy_p@yahoo.com)

Indian Institute of Science

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Partial Wave Direct Method Solution to Phase Problem.

P. Bhanumoorthy^{1*}

¹*Department of Physics, Indian Institute of Science, Bangalore - 560 012, India.*

Abstract.

We cast crystal diffraction as a boundary value problem with Maxwell-Schrödinger equation as the governing partial differential equation. Unitcell defined boundary conditions determine definite momentum eigen series in spherical basis to include precision angles as additional data measurable in a stationary spherical polar coordinate system with polar axis always aligned along direct beam in the experiment. Orbital structure of individual atoms is contained in angle dependence and thus in the precision angles of position and momentum vectors. Partial wave version of Parseval relation becomes probability conservation law. We show that polar angles and azimuthal angles respectively determine signs and phases of partial wave sub-amplitudes and give rise to solution to phase problem.

1 Introduction.

In conventional Cartesian Fourier transform(FT henceforth) description, we measure only intensity and its standard deviation for each diffracted Bragg beam. Apart from intensities alone, we can measure also the precision angles for vectors \mathbf{k} and \mathbf{r}_j as additional data corresponding to each diffraction intensity measurement in the experiment. Such measurement of precision angles can be accomplished in the laboratory reference frame defined stationary spherical coordinate system for

any orientation of the unit cell during data collection. The additional precision angles measured in the experiment can be incorporated in structure determination calculations for better convergence.

Sommerfeld's Cartesian FT relations have no provision for precision angles of \mathbf{k} and \mathbf{r}_j measured in the experiment. Therefore a mathematical description that permits to incorporate precision angles is necessary to exhaustively use the entire measurable data in the experiment. We now formulate such a mathematical description from quantum theory of scattering derived partial wave analysis. From Rayleigh expansion and Sommerfeld's Cartesian FT relations, we derive forward and inverse eigen series expansions that naturally give rise to the direct method solution to phase problem from experimental precision angles for macromolecular crystallography. The description is equivalent to generalizing the partial wave analysis of quantum theory of scattering to the periodic scattering potential of unitcell periodicity in the crystal.

The probability theory derived triple phase tangent formula¹ based direct methods is in Cartesian description with no provision to use the precision angles from the experiment and hence fails as solution to phase problem for macromolecular crystallography. We note that partial wave analysis in spherical coordinates^{2,3} overcomes several limitations of Cartesian crystallography.

2 Both FT domains as complex-valued.

Wennerström already described FT relations between position and momentum state functions for scattering and diffraction⁴. In the description of a quantum system, state function is synonymous to wave function. According to Max Born's probability interpretation⁵, modulus square of a wave

function gives probability density. In terms of position wave function $\psi(\mathbf{r})$ and momentum wave function $\phi(\mathbf{k})$, the probability densities in position space and in momentum space are given by $|\psi(\mathbf{r})|^2$ and $|\phi(\mathbf{k})|^2$ respectively. Following FT relation between position and momentum wave functions, we also likewise prescribe the FT relation $u(\mathbf{r}) \rightleftharpoons F(\mathbf{k})$ with electron density given by $\rho(\mathbf{r}) = |u(\mathbf{r})|^2$ for crystal diffraction, where $u(\mathbf{r})$ is solution to a governing Sturm-Liouville(self-adjoint) partial differential equation as in quantum mechanics. We term $u(\mathbf{r})$ as the unitcell function as equivalent to position wave function such that $|u(\mathbf{r}_j)| = f(\mathbf{r}_j)$ where $f(\mathbf{r}_j)$ is the atomic form factor.

The conflict and its resolution. A complex-valued unitcell function in place of an atomic scattering factor conflicts with purely real-valued $f(\mathbf{r}_j)$ in the absence of absorption. We note that such a constraint is limited only to Cartesian description. Partial wave description does not require such a constraint and overcomes positivity constraint on position domain. With complex-valued unitcell function, auto-correlation of structure factors assumes the form of Sayre's equation⁶.

FT relations with complex-valued $u(\mathbf{r}_j)$. It can be shown that an infinite number of Friedel phase relations can effect Friedel's law in the description with a complex-valued unitcell function.

Following unitarity property of FT , we introduce a symmetric constant in the transform relations.

Then Cartesian FT relations for the unitcell function $u(\mathbf{r}_j)$ become,

$$u(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} |F(\mathbf{k})| e^{-2\pi i \mathbf{k} \cdot \mathbf{r}_j + i\alpha[F(\mathbf{k})]} \quad (1)$$

$$F(\mathbf{k}) = \frac{1}{\sqrt{V}} \sum_j |u(\mathbf{r}_j)| e^{+2\pi i \mathbf{k} \cdot \mathbf{r}_j + i\alpha[u(\mathbf{r}_j)]} \quad (2)$$

where V is the volume of unitcell and both non-zero phases $\alpha[F(\mathbf{k})]$ and $\alpha[u(\mathbf{r}_j)]$ are given by,

$$\tan \alpha[F(\mathbf{k})] = \frac{\sum_j |u(\mathbf{r}_j)| \sin(2\pi\mathbf{k} \cdot \mathbf{r}_j + \alpha[u(\mathbf{r}_j)])}{\sum_j |u(\mathbf{r}_j)| \cos(2\pi\mathbf{k} \cdot \mathbf{r}_j + \alpha[u(\mathbf{r}_j)])} \quad (3)$$

$$\tan \alpha[u(\mathbf{r}_j)] = \frac{-\left(\sum_{\mathbf{k}} |F(\mathbf{k})| \sin(2\pi\mathbf{k} \cdot \mathbf{r}_j + \alpha[F(\mathbf{k})])\right)}{\sum_{\mathbf{k}} |F(\mathbf{k})| \cos(2\pi\mathbf{k} \cdot \mathbf{r}_j + \alpha[F(\mathbf{k})])} \quad (4)$$

as both FT domains have by now become complex-valued in crystal diffraction similar to both FT domains in quantum mechanics. But Cartesian description cannot accept such a prescription because we cannot define phase problem when both FT domains are complex-valued in which case, unknown phases exist in both FT domains. Then phases in which domain do we solve for, to solve phase problem. Hence, Cartesian description demands unknown phases exist only on momentum domain, i.e., only on structure factors. Such a constraint is the limitation of Cartesian description. Partial wave analysis overcomes such a limitation of Cartesian description with complex-valued $u(\mathbf{r}_j)$ as solution to a governing partial wave differential equation for crystal diffraction.

3 The governing partial differential equation.

Fourier discovered Fourier series while solving heat equation in the context of heat reservoir problem. Hence in crystal diffraction too, we expect to start our analysis from an eigen series expansion, which is derived from a governing partial differential equation. In crystal diffraction, Schrödinger equation describes fermion modes within unitcell and reduced classical wave equation describes boson modes in momentum lattice space. Both equations become Helmholtz equation, which whence becomes Maxwell-Schrödinger equation as the governing partial differential equation⁷ for both Schrödinger field and Maxwell radiation field within unitcell in crystal diffraction.

Fourier basis functions are eigen solutions to position and momentum operators as well as Helmholtz equation. Linear momentum and energy operator commute. Two commuting operators admit of simultaneous eigen functions and Fourier series therefore can be viewed as eigen series in crystal diffraction. Being a stationary state quantum system with no time variable in the description, crystal diffraction can be viewed as a Sturm-Liouville boundary value problem with Dirichlet vanishing boundary conditions applied to eigen solution at unitcell boundaries. In such a description, unitcell becomes a bound state quantum system and bound state eigen solutions and wave functions are known to exclusively describe standing waves. Thus the atomic orbitals and the intensity pattern, respectively as fermion modes in the position space unitcell and as boson modes in the momentum space, become standing wave bound state position and momentum wave functions as solutions to Helmholtz equation.

We now derive partial wave eigen series for crystal diffraction with definite momentum eigen solutions to Helmholtz equation to incorporate experimental precision angles in structure determination calculations to overcome the phase problem in macromolecular crystallography.

4 The partial wave eigen series description.

Angular momentum operator is given by $L = -i\hbar(\mathbf{r} \times \nabla_{\mathbf{r}})$ and $L = +i\hbar(\nabla_{\mathbf{k}} \times \mathbf{k})$ respectively in position space and in momentum space and corresponds to eigen value equations,

$$L^2 Y_l^m(\hat{\mathbf{r}}) = l(l+1)\hbar^2 Y_l^m(\hat{\mathbf{r}}) \quad (5)$$

$$L^2 Y_l^m(\hat{\mathbf{k}}) = l(l+1)\hbar^2 Y_l^m(\hat{\mathbf{k}}) \quad (6)$$

Momentum Schrödinger equation, as FT of position Schrödinger equation, is generally believed to be an algebraic equation or at the most a mixed integral-differential equation⁸. But we identify the normalized spherical harmonics in eq. (5) and in eq. (6) respectively as angular part of eigen solutions to partial differential equations given by,

$$(\nabla_{\mathbf{r}}^2 + k^2)j_l(kr)P_l^m(\cos \theta_{\mathbf{r}})e^{im\phi_{\mathbf{r}}} = 0 \quad (7)$$

$$(\nabla_{\mathbf{k}}^2 + r^2)j_l(kr)P_l^m(\cos \theta_{\mathbf{k}})e^{im\phi_{\mathbf{k}}} = 0 \quad (8)$$

Due to the absence of spherical symmetry in crystal diffraction, angular momentum is only quantized, but not conserved. In which case, angular momentum does not commute with energy operator and hence spherical harmonics alone cannot become energy eigen functions. The definite momentum eigen solutions to eq. (7) and eq. (8) become the energy eigen functions as basis functions in the eigen series expansion. The basis functions are without normalization constants as the Sturm-Liouville eigen series basis functions are only orthogonal, not orthonormal.

We have no objection to identify eq. (8) as Helmholtz equation in momentum space. Thus, the description of crystal diffraction experiment necessitates the momentum wave equation too to necessarily become a partial differential equation.

Rayleigh expansion^{9,10,11,12} is given by,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(kr) Y_l^{m*}(\hat{\mathbf{k}}) Y_l^m(\hat{\mathbf{r}}) \quad (9)$$

The Dirichlet vanishing boundary conditions on spherical Bessel function $j_l(kr) = 0$ at $r = a$ for $l = 0$ in the absence of angular dependence¹³ give rise to $k = n\pi/a$. For one spherical Bessel

function along each axial dimension gives, $k_x = h\pi/a$, $k_y = k\pi/b$, $k_z = l\pi/c$. We note that Cartesian FT dictates that $k_x = 2h\pi/a$, $k_y = 2k\pi/b$, $k_z = 2l\pi/l$ with 2π as the multiplicative factor. Hence, the application of unitcell boundaries defined vanishing boundary conditions on radial solution, one along each axial dimension, derives definite momentum values with factor π and hence define the radial solution as $j_l(\pi kr)$. From Cartesian FT relations eq. (1), eq. (2) and Rayleigh expansion, we identify the basis functions in eq. (7), eq. (8) and write,

$$u(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}, lm} A_{\mathbf{r}_j}^{lm}(\mathbf{k}) j_l(\pi kr_j) P_l^m(\cos \theta_{\mathbf{k}}) e^{im\phi_{\mathbf{k}}} \quad (10)$$

$$F(\mathbf{k}) = \frac{1}{\sqrt{V}} \sum_{j, lm} a_{\mathbf{k}}^{lm}(\mathbf{r}_j) j_l(\pi kr_j) P_l^m(\cos \theta_{\mathbf{r}_j}) e^{im\phi_{\mathbf{r}_j}} \quad (11)$$

Transforming and transformed amplitudes are viewed as vectors in the vector space description of crystal diffraction¹⁴. In any Sturm-Liouville theory derived eigen series or integral transform, summation or integration can only be on the variable of the transforming domain. Hence, we introduce orthonormal Hilbert sub-spaces with metric space modulus square relations,

$$u(\mathbf{r}_j) = \sum_{lm} |u^{lm}(\mathbf{r}_j)|^2 \quad ; \quad F(\mathbf{k}) = \sum_{lm} |F^{lm}(\mathbf{k})|^2 \quad (12)$$

and derive lm eigen series relations from eq. (10), eq. (11) without summation over lm as,

$$u^{lm}(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} A_{\mathbf{r}_j}^{lm}(\mathbf{k}) j_l(\pi kr_j) P_l^m(\cos \theta_{\mathbf{k}}) e^{im\phi_{\mathbf{k}}} \quad (13)$$

$$F^{lm}(\mathbf{k}) = \frac{1}{\sqrt{V}} \sum_j a_{\mathbf{k}}^{lm}(\mathbf{r}_j) j_l(\pi kr_j) P_l^m(\cos \theta_{\mathbf{r}_j}) e^{im\phi_{\mathbf{r}_j}} \quad (14)$$

where $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ is the transforming sub-amplitude in the position space derived from atomic scattering factor and $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ is the transforming sub-amplitude in the momentum space derived from the structure factor. We may call the eigen series eq. (13) and eq. (14) as discrete Sturm-Liouville

integral transform relations for crystal diffraction. From Rayleigh expansion, the complex-valued transforming sub-amplitudes together with phases become,

$$A_{\mathbf{r}_j}^{lm}(\mathbf{k}) = |F(\mathbf{k})|(2l+1)\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta_{\mathbf{r}_j})e^{i\alpha[F(\mathbf{k})]-im\phi_{\mathbf{r}_j}-il\pi/2} \quad (15)$$

$$a_{\mathbf{k}}^{lm}(\mathbf{r}_j) = |u(\mathbf{r}_j)|(2l+1)\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta_{\mathbf{k}})e^{i\alpha[u(\mathbf{r}_j)-im\phi_{\mathbf{k}}+il\pi/2]} \quad (16)$$

with no normalization constants as the eigen basis set is only orthogonal, not orthonormal. Hence, the normalization constant for spherical Bessel function is not needed. The normalization constants for spherical harmonics that appear in the expressions come from Rayleigh expansion.

We note that the angle dependence in eq. (15) is on \mathbf{r}_j and in eq. (16) is on \mathbf{k} . We now define the partial wave sub-amplitudes that contain angle dependence on both vectors as,

$$F_{\mathbf{r}_j}^{lm}(\mathbf{k}) = A_{\mathbf{r}_j}^{lm}(\mathbf{k})j_l(\pi kr_j)P_l^m(\cos\theta_{\mathbf{k}})e^{im\phi_{\mathbf{k}}} \quad (17)$$

$$u_{\mathbf{k}}^{lm}(\mathbf{r}_j) = a_{\mathbf{k}}^{lm}(\mathbf{r}_j)j_l(\pi kr_j)P_l^m(\cos\theta_{\mathbf{r}_j})e^{im\phi_{\mathbf{r}_j}} \quad (18)$$

and Parseval relation in terms of partial wave sub-amplitudes defines the orthonormal Hilbert sub-space metric relations,

$$|F(\mathbf{k})|^2 = \sum_{lm,j} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 \quad (19)$$

$$|u(\mathbf{r}_j)|^2 = \sum_{lm,\mathbf{k}} |u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 = |f(\mathbf{r}_j)|^2 \quad (20)$$

In eq. (17) and eq. (18), we define $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ as transforming sub-amplitudes and $F_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $u_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ as partial wave sub-amplitudes so as not to violate partial wave Parseval relation as the probability conservation law.

5 The partial wave Parseval relation.

Full-wave Parseval relation as the statement of unitarity property of FT and as conservation of energy in Fraunhofer diffraction¹³ becomes probability conservation law in crystal diffraction. Hence from eq. (19) and eq. (20), the partial wave Parseval relation becomes,

$$\sum_{j, \mathbf{k}', lm} |u_{\mathbf{k}'}^{lm}(\mathbf{r}_j)|^2 = \sum_{\mathbf{k}, j' l' m'} |F_{\mathbf{r}_{j'}}^{l' m'}(\mathbf{k})|^2 \quad (21)$$

as probability conservation law in partial wave description of crystal diffraction. From eq. (10) and eq. (11) and from eq. (17) and eq. (18), we observe that the probability conservation law can exist only in terms of $F_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $u_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ and no conservation law is possible in terms of transforming sub-amplitudes $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ in the eigen series relations for the following reasons.

Due to the diffraction geometry, measurement of a particular $\mathbf{k} = \mathbf{k}(hkl)$ diffraction intensity occurs exclusively at a unique orientation of the unitcell in the experiment, i.e., each diffraction intensity exclusively corresponds to a unique orientation of the position vectors $\mathbf{r}_j = \mathbf{r}_j(r_j, \theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j})$. And the unitcell coordinate system is moving from one diffraction intensity measurement to another. As crystal is moving, experimental precision angles and thus laboratory coordinate system dependence contained in the sub-amplitudes with subscripts prevents formal analytical derivation of the partial wave Parseval relation. But that does not mean crystal diffraction does not obey Parseval relation as the probability conservation law.

We note that the sub-amplitudes with subscripts can be defined only in the laboratory spherical polar coordinate system. All the rest full-amplitudes and sub-amplitudes without subscripts in

them are defined in the respective unitcell and momentum lattice Cartesian coordinate systems.

The angle dependence in sub-amplitudes disappears in the presence of spherical symmetry rendering experimental precision angles useless, hence the presence of spherical symmetry in analytically deriving the relation eq. (21) has no significance at all. With no analytical derivation for eq. (21), we numerically integrate angle dependence into the Sturm-Liouville eigen series with the precision angles from the experiment to extract $|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|$ for structure determination using eq. (10).

6 The amplitudes and phases of $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$.

From eq. (15) and eq. (16),

$$|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 = |F(\mathbf{k})|^2 \left| (2l+1) \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_{\mathbf{r}_j}) \right|^2 \quad (22)$$

$$|a_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 = |u(\mathbf{r}_j)|^2 \left| (2l+1) \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_{\mathbf{k}}) \right|^2 \quad (23)$$

eq. (10) and eq. (11) together with eq. (17) and eq. (18) and partial wave Parseval relation define the relations,

$$|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 = |A_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 |j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{k}})|^2 \quad (24)$$

$$|u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 = |a_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 |j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{r}_j})|^2 \quad (25)$$

Partial wave Parseval relation dictates scaling of the partial wave sub-amplitudes using the relations eq. (19) and eq. (20).

In an eigen series expansion, the radial solution and the polar and azimuthal solutions with angle dependence cannot simultaneously belong in both transforming sub-amplitudes and basis

functions. Hence, the sub-amplitudes extracted from the Partial wave Parseval relation as the probability conservation law as such cannot become the transforming sub-amplitudes in the eigen series. We must exclude the basis function dependence from partial wave sub-amplitudes $F_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $u_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ to obtain the transforming sub-amplitudes $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ for the eigen series to be valid. Which means, we extract the transforming sub-amplitudes $|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|$ and $|a_{\mathbf{k}}^{lm}(\mathbf{r}_j)|$ that go into the eigen series using the relations eq. (24) and eq. (25) so as not to violate partial wave Parseval relation as the probability conservation law.

From eq. (15) and eq. (16), the phases of the transforming sub-amplitudes are given by,

$$\alpha[A_{\mathbf{r}_j}^{lm}(\mathbf{k})] = \alpha[P_l^m(\cos \theta_{\mathbf{r}_j})] + \alpha[F(\mathbf{k})] - m\phi_{\mathbf{r}_j} - l\pi/2 \quad (26)$$

$$\alpha[a_{\mathbf{k}}^{lm}(\mathbf{r}_j)] = \alpha[P_l^m(\cos \theta_{\mathbf{k}})] + \alpha[u(\mathbf{r}_j) - m\phi_{\mathbf{k}} + l\pi/2] \quad (27)$$

we note that $P_l^m(\cos \theta_{\mathbf{k}})$ and $P_l^m(\cos \theta_{\mathbf{r}_j})$ are purely real-valued functions hence phases can only be either zero or π depending on whether positive or negative. It now becomes evident from eq. (26) and eq. (27) that the subscripts in the transforming sub-amplitudes in the integral transform relations eq. (10) and eq. (11) describe the angle dependence of the transforming sub-amplitudes.

Cartesian description can define the phase only on full-amplitude of Cartesian structure factor. Hence, we call the unknown Cartesian phase $\alpha[F(\mathbf{k})]$ on a structure factor that gives rise to phase problem as "the phase problem phase". We now prove that Cartesian full wave phase problem phase has no role in the phase of a partial wave sub-amplitude in partial wave analysis. Which means we now prove that the partial wave analysis description overcomes the phase problem.

7 Theoretical and hypothetical crystals corresponding to partial waves.

Both transforming and transformed sub-amplitudes in both the forward and inverse partial wave Sturm-Liouville integral transform relations are complex-valued sub-amplitudes. Hence, the partial wave analysis divides a crystal into mathematically visible, hypothetical and theoretical partial wave crystals, each designated by a unique pair of l and m values. A unitcell in such a partial wave crystal is made up of only the l and m designated orbital of each atom and nothing else. The partial wave sub-intensities, not sub-amplitudes, from each such partial wave crystal add up into each full-wave intensity and constitute the diffraction intensity pattern in the experiment.

8 The direct method solution to the phase problem.

From Cartesian FT relations with both FT domains as complex-valued and Rayleigh expansion we derive relations eq. (15) and eq. (16) for the transforming sub-amplitudes. Quantum numbers l and m represent orbital structures of individual atoms in position domain and three dimensional electromagnetic modes of individual diffraction intensities similar to longitudinal and transverse modes of an electromagnetic wave guide.

For $l = 0$, angle dependence and thus the subscripts in $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ vanish. We have $P_0^0(\cos \theta_{\mathbf{r}_j}) = 1$ and hence eq. (15) and eq. (16) become,

$$A^{00}(\mathbf{k}) = |F(\mathbf{k})|e^{i\alpha[F(\mathbf{k})]} \quad (28)$$

$$a^{00}(\mathbf{r}_j) = |u(\mathbf{r}_j)|e^{i\alpha[u(\mathbf{r}_j)]} \quad (29)$$

In extracting the amplitudes $|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|$, $|a_{\mathbf{k}}^{lm}(\mathbf{r}_j)|$ respectively from $|F(\mathbf{k})|$, $|u(\mathbf{r}_j)|$ using eq. (15) and eq. (16), we use the scaling relations,

$$c \sum_{j,lm} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{unscaled}}^2 = |F(\mathbf{k})|^2 \quad ; \quad |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}} = \sqrt{c} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{unscaled}} \quad (30)$$

$$c \sum_{\mathbf{k},lm} |u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|_{\text{unscaled}}^2 = |u(\mathbf{r}_j)|^2 \quad ; \quad |u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|_{\text{scaled}} = \sqrt{c} |u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|_{\text{unscaled}} \quad (31)$$

The amplitudes $A^{00}(\mathbf{k})$ and $a^{00}(\mathbf{r}_j)$ are unscaled in eq. (28) and eq. (29). With scaled amplitudes in eq. (22) and eq. (23), we have,

$$|A^{00}(\mathbf{k})|_{\text{scaled}} \neq |F(\mathbf{k})| \quad (32)$$

$$|a^{00}(\mathbf{r}_j)|_{\text{scaled}} \neq |u(\mathbf{r}_j)| \quad (33)$$

In Cartesian description, purely real-valued X-ray atomic form factor with positivity constraint on the position domain, i.e., $\alpha[f(\mathbf{r}_j)] = 0$ corresponds to spherical atoms. And $l = 0$ corresponds to spherical symmetry with no angle dependence and hence both $A^{00}(\mathbf{k})$ and $a^{00}(\mathbf{r}_j)$ can be taken as purely real-valued with positivity constraint. Thus $l = 0$ corresponds to s -wave scattering in both forward and inverse eigen series relations. Purely positive real-valued $A^{00}(\mathbf{k})$ and $a^{00}(\mathbf{r}_j)$ provide proof for the relations,

$$\alpha[F(\mathbf{k})] = 0 \quad (34)$$

$$\alpha[u(\mathbf{r}_j)] = 0 \quad (35)$$

as applied in eq. (28) and eq. (29). This is where the partial wave analysis overcomes the unknown Cartesian full-wave phases and naturally solves the phase problem. Though independent of angles, both the $l = 0$ and $m = 0$ transforming sub-amplitudes $A^{00}(\mathbf{k})$, $a^{00}(\mathbf{r}_j)$ retain a specific direction

in the experiment as both are respectively extracted from $F(\mathbf{k})$ and $u(\mathbf{r}_j)$ with unique directions in the measurement. The specific directions define $A^{00}(\mathbf{k})$, $a^{00}(\mathbf{r}_j)$ in the unitcell coordinate system by coordinate transformation from the laboratory spherical polar coordinate system to unitcell coordinate system.

Cartesian description is in terms of the amplitudes and phases of full-wave structure factors and involves two Cartesian coordinate systems defined by the unitcell and the momentum lattice. The "Cartesian phase problem phase" defined by eq. (3) with positivity constraint $\alpha[u(\mathbf{r}_j)]$ in position space that gives rise to phase problem in Cartesian description is defined in Cartesian coordinate system in position space. The definite momentum eigen series given in eq. (11) and eq. (10) are defined in the stationary spherical polar coordinate system and hence a term in the series has no reference to the Cartesian coordinate systems. Which means, each term in the series is defined in the stationary spherical polar coordinate system in the laboratory reference frame. Thus the Sturm-Liouville partial wave discrete integral transform relations eq. (10) and eq. (11) cannot define the phase for a Cartesian full-wave full-amplitude and hence the "Cartesian phase problem phases full-wave structure factors have no role in the partial wave integral transform or definite momentum eigen series relations". Furthermore, crystal is moving from measurement of one diffraction intensity to another. Hence, we need to coordinate transform the unitcell coordinate system defined position vector into laboratory stationary Cartesian coordinate system and then calculate the required precision angles for \mathbf{r}_j . We scale the partial wave sub-amplitudes using the relations eq. (19) and eq. (20) and we scale the transforming sub-amplitudes using the relations eq. (24) and eq. (25).

We have $j_0(kr_j) = \sin(kr_j)/(kr_j)$ and $P_0^0(\cos \theta_{\mathbf{r}_j}) = 1$ and $P_0^0(\cos \theta_{\mathbf{k}}) = 0$. Hence from eq. (17) and eq. (18), the $l = 0$ transforming sub-amplitudes and the partial wave sub-amplitudes are related as,

$$F^{00}(\mathbf{k}) = |A^{00}(\mathbf{k})| \frac{\sin(\pi kr_j)}{\pi kr_j} \quad (36)$$

$$u^{00}(\mathbf{r}_j) = |a^{00}(\mathbf{k})| \frac{\sin(\pi kr_j)}{\pi kr_j} \quad (37)$$

The factor $e^{-il\pi/2}$ does not involve any experimental parameter and we identify each partial wave definite momentum eigen series relation with unique l and m values. Hence in eq. (26) and eq. (27), the factor $e^{-il\pi/2}$ becomes a constant multiplicative unitary phase factor which can be excluded without loss of generality of integral transform relations for crystal diffraction.

The amplitude $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ contains $P_l^m(\cos \theta_{\mathbf{r}_j})$ in it and the amplitude $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ contains $P_l^m(\cos \theta_{\mathbf{k}})$ in it. The functions $P_l^m(\cos \theta_{\mathbf{r}_j})$ and $P_l^m(\cos \theta_{\mathbf{k}})$ oscillate between positive and negative depending on l, m and the polar angle in the argument. Hence, we cannot exclude the signs of $P_l^m(\cos \theta_{\mathbf{r}_j})$ and $P_l^m(\cos \theta_{\mathbf{k}})$ and write the phases of transforming sub-amplitudes as,

$$A_{\mathbf{r}_j}^{lm}(\mathbf{k}) = |A_{\mathbf{r}_j}^{lm}(\mathbf{k})| e^{-im\phi_{\mathbf{r}_j}} \quad (38)$$

$$a_{\mathbf{k}}^{lm}(\mathbf{r}_j) = |a_{\mathbf{k}}^{lm}(\mathbf{r}_j)| e^{-im\phi_{\mathbf{k}}} \quad (39)$$

We can only write the phases of transforming sub-amplitude only as,

$$A_{\mathbf{r}_j}^{lm}(\mathbf{k}) = |A_{\mathbf{r}_j}^{lm}(\mathbf{k})| e^{i\alpha[P_l^m(\cos \theta_{\mathbf{r}_j})] - im\phi_{\mathbf{r}_j}} \quad (40)$$

$$a_{\mathbf{k}}^{lm}(\mathbf{r}_j) = |a_{\mathbf{k}}^{lm}(\mathbf{r}_j)| e^{i\alpha[P_l^m(\cos \theta_{\mathbf{k}})] - im\phi_{\mathbf{k}}} \quad (41)$$

where $e^{i\alpha[P_l^m(\cos\theta_{\mathbf{r}_j})]} = e^{i0}$ if positive, $e^{i\alpha[P_l^m(\cos\theta_{\mathbf{r}_j})]} = e^{i\pi}$ if negative and $e^{i\alpha[P_l^m(\cos\theta_{\mathbf{k}})]} = e^{i0}$ if positive, $e^{i\alpha[P_l^m(\cos\theta_{\mathbf{k}})]} = e^{i\pi}$ if negative with the azimuthal angles measured as precision angles in the experiment.

We observe that only the transforming sub-amplitudes $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ derived from the atomic scattering factor become complex-valued, the full wave atomic scattering factor $f(\mathbf{r})$ as defined in eq. (20) remains purely real-valued in the absence of absorption and thus does not conflict with Cartesian crystallography.

Hence, the relations eq. (40) and eq. (41) are the solution to phase problem in crystal diffraction. With phases of transforming sub-amplitudes from eq. (40), the inverse eigen series in terms of transforming sub-amplitudes $|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}}$ becomes,

$$u^{lm}(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \left[|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}} e^{i\alpha[P_l^m(\cos\theta_{\mathbf{r}_j})] - im\phi_{\mathbf{r}_j}} \right] \left[j_l(\pi k r_j) P_l^m(\cos\theta_{\mathbf{k}}) e^{im\phi_{\mathbf{k}}} \right] \quad (42)$$

where the factor within first square brackets is the sub-amplitude and the factor in the second square brackets is the basis function. Eq. (42) can also be written in terms of partial wave sub-amplitudes $|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}}$ as,

$$u^{lm}(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}} \left(e^{i\alpha[P_l^m(\cos\theta_{\mathbf{r}_j})] + i\alpha[j_l(\pi k r_j)] + i\alpha[P_l^m(\cos\theta_{\mathbf{r}_j})]} \right) \left(e^{-im(\phi_{\mathbf{r}_j} - \phi_{\mathbf{k}})} \right) \quad (43)$$

In each term, first parenthesis contains only purely real-valued functions in the exponential and hence can only be equal to either e^{i0} or $e^{i\pi}$ whereas exponential in second parenthesis contains the difference of azimuthal angles from the experiment. Hence, we may call the first parenthesis as

sign factor and the second parenthesis as phase factor. The structure $\rho(\mathbf{r}_j)$ is given by,

$$\rho(\mathbf{r}_j) = |u(\mathbf{r}_j)|^2 = \sum_{lm} |u^{lm}(\mathbf{r}_j)|^2 \quad (44)$$

In each term, the sign is determined by the modulus values of vectors \mathbf{k} and \mathbf{r}_j and polar angles and the phase factor is determined by the azimuthal angles. Thus in the partial wave direct method, the precision angles from the experiment solve the phase problem.

We process the diffraction intensity data in the format,

$h, k, l,$	$F(hkl), \sigma(hkl),$	$(\theta_{\mathbf{a}}\phi_{\mathbf{a}}, \theta_{\mathbf{b}}\phi_{\mathbf{b}}, \theta_{\mathbf{c}}\phi_{\mathbf{c}}),$	$(\mathbf{a} , \mathbf{b} , \mathbf{c}),$	$(\theta_{hkl}, \phi_{hkl})$
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The orientation of the unitcell is necessary for every hkl intensity to calculate the angles $(\theta_{\mathbf{r}}, \phi_{\mathbf{r}})$ for a grid point position vector. Hence the partial wave direct method shows that the most efficient way to acquisition the diffraction data is to process the intensity data in $P1$ space group together with the required angle parameters corresponding to each intensity irrespective of the space group symmetry present in the unitcell. Such data acquisition process is justified by the statement in Fourier theory that Fourier series coefficients of a periodic function are the sampled values of FT of only one period of the function.

9 Practical steps in computer program development.

We have four steps in developing the computer program for partial wave direct method.

i. We calculate $\theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j}$ from the experimental precision angles. Then from eq. (22) and eq. (24) and precision angles from the experiment, we calculate the unscaled partial wave sub-amplitudes $|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{unscaled}}$. We note that the azimuthal angles disappear due to squaring and the partial wave sub-amplitude calculation uses only polar angles of \mathbf{k} and \mathbf{r}_j .

ii. We now do local scaling, i.e., at the level of individual diffraction intensity using the relations,

$$|F(\mathbf{k})|^2 = c \sum_{j,lm} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{unscaled}}^2 \quad ; \quad |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}} = \sqrt{c} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{unscaled}} \quad (45)$$

to determine the local scale factor \sqrt{c} corresponding to a given $|F(\mathbf{k})|^2$. Local scale factor because it is one single scale factor for all partial wave sub-amplitudes $|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}}$ extracted from each diffraction intensity $|F(\mathbf{k})|^2$.

iii. Each term in the eigen series is defined in the stationary spherical polar coordinate system in the laboratory reference frame. Hence, we calculate $\mathbf{r}_j = \mathbf{r}_j(r, \theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j})$ in each term separately from the precision angle data corresponding to each term in the eigen series.

iv. Then we calculate $u^{lm}(\mathbf{r}_j)$ using eq. (43) and determine the electron density and the structure using the relation,

$$\rho(\mathbf{r}_j) = \sum_{lm} |u^{lm}(\mathbf{r}_j)|^2 \quad (46)$$

in the unitcell coordinate system.

10 As another historic success of quantum physics.

Historically, classical physics could not explain phenomenon observed in certain experiments viz., Stern-Gerlach, Davisson-Germer, Frank-Hertz experiments, Compton effect, photo-electric effect and Blackbody radiation, quantum physics alone could explain through quantization as a natural phenomenon in physical systems. In blackbody radiation, the Stefan-Boltzmann law, the Wein's distribution law and the Rayleigh-Jean's law testify to the limitations of classical physics. The quantization of radiation by Planck unequivocally led to Planck's radiation law that successfully explained the spectral emissivity in blackbody radiation problem, which hence is generally believed to be the birth place of quantum mechanics.

Blackbody radiation resonant cavity with no directionality in emission is viewed as a diffuse radiator, whereas crystal unitcell too can be physically viewed as a resonant cavity that too is radiating, but the distinction lies in that crystal unitcell is a directional radiator. Though Fourier series basis functions $e^{\pm i\mathbf{k}\cdot\mathbf{r}}$ are from the eigen solution to Helmholtz equation, application of Dirichlet vanishing boundary conditions on the eigen solution does not lead to definite momentum values $2\pi h$, $2\pi k$, $2\pi l$ in the Fourier series basis functions. Because the vanishing boundary conditions $\sin kx = 0$ gives $k = n\pi$ and $\cos kx = 0$ gives $(2n + 1)\pi/2$, each gives a different definite momentum value, also neither gives 2π as the multiplicative factor. Hence in crystal diffraction, Sommerfeld's FT relations cannot be viewed as Sturm-Liouville eigen series derived integral transform relations. Which means that Sommerfeld's Cartesian FT relations are only classical, not quantum mechanical. Also in retrospect, Arnold Sommerfeld enunciated his Cartesian FT relations for

crystal diffraction almost a decade prior to the advent of Schrödinger equation.

The application of Dirichlet vanishing boundary condition on the radial solution, one along each dimension of the unitcell, gives unique solutions that involve no ambiguity in deriving the definite momentum values. Hence, the partial wave integral transform relations alone derive from the Sturm-Liouville theory based quantum theory of scattering. Thus the partial wave analysis solution to phase problem in crystal diffraction can be viewed as one of the historical successes of quantum physics over the limitations of the classical physics.

11 Conclusions.

Crystal diffraction obviously and conspicuously permits measurement of precision angles too as part of diffraction data in addition to diffraction intensities alone. To incorporate experimental precision angles too in structure determination calculations, we formulate the quantum mechanics derived partial wave eigen series. Such a formalism alone can exclusively become the only acceptable and permissible mathematical description to exhaustively use the entire data without leaving out any part of measurable data in the experiment.

In Cartesian description, diffraction angle is twice Bragg angle and is used in conjunction with temperature factor to address the intensity fall off at higher angles. In addition to diffraction angle, the obviously measurable azimuthal angles of position vector and momentum vector are never used in Cartesian description. In partial wave eigen series description, the azimuthal angles of position vector and momentum vector respectively become the phases of the transforming sub-

amplitudes in the forward and inverse definite momentum eigen series giving rise to the solution to phase problem.

In Cartesian Fourier transform, an angle is not a generic variable. Orbital structure of individual atoms is contained in directional dependence in the experiment, i.e., in precision angles as measured in the stationary spherical polar coordinate system defined in laboratory reference. Hence, the definite momentum eigen series that can incorporate precision angles from the experiment alone can give orbital structure and thus the coordination numbers and bonding schemes of individual atoms as opposed to Sommerfeld's Cartesian description which can give only the spherical atom structure.

With Parseval relation as the probability conservation law, crystal diffraction necessitates a unitcell function as inverse FT of the structure factor. The partial wave Parseval relation as the probability conservation law alone can subdivide the experimental full wave full-amplitudes into partial wave sub-amplitudes as required in partial wave analysis to overcome the phase problem. Then electron density becomes proportional to modulus square of unitcell function. And from Fourier theory, electron density becomes inverse FT of the auto-correlation of structure factors and diffraction intensities become forward FT of the auto-correlation of unitcell function. Auto-correlation of the structure factors assumes the form of Sayre's equation.

Rayleigh expansion and partial wave Parseval relation derived eigen series defines atom-wise or position space grid-point wise phase of partial wave sub-amplitudes with angle dependence in both position and momentum spaces. Azimuthal angle dependence defines the phase of transform-

ing sub-amplitude, which therefore can be measured in the experiment.

Transforming sub-amplitudes in both forward and inverse eigen series derived transform relations become complex-valued in parallel with both the complex-valued position and momentum wave functions in FT relation in quantum mechanics. We note that such symmetry does not exist in Sommerfeld's Cartesian FT relations with always real-valued atomic scattering factor in the absence of absorption. Partial wave eigen series description conforms to the angular momentum quantization condition as the quantum diffraction law and defines highest possible resolution that corresponds to orbital structure of atoms. Hence, partial wave direct method may as well be called the crystal diffraction imaging of molecular structure in the unitcell using precision angle data from the experiment.

Phase problem arises only in Sommerfeld's Cartesian FT relations based description and thus can be viewed as a limitations of classical physics. Transition to quantum physics based partial wave analysis naturally overcomes the phase problem for macromolecular crystallography.

Cartesian full-wave phases as defined by Sommerfeld's Cartesian FT relation are not measurable in the experiment. Whereas partial wave description defined transforming sub-amplitude phases are measurable as azimuthal angles in the laboratory spherical polar coordinate system.

Partial wave description derived direct method solution to phase problem unites both small molecule crystallography and macromolecule crystallography into one. Quantum theory of scattering derived partial wave analysis description alone can exclusively qualify the term quantum

crystallography.

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***Correspondence email :** bhanumoorthy_p@yahoo.com.

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