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Research Article

Keywords: quantum theory, Maxwell-Schrödinger equation, azimuthal angles

Posted Date: June 24th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-645037/v1>

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Partial Wave Direct Method Solution to Phase Problem.

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Abstract.

We present the quantum theory derived partial wave direct method solution to phase problem. We cast crystal diffraction as a boundary value problem with Maxwell-Schrödinger equation as the governing partial differential equation. We show that phases of transforming sub-amplitudes in definite momentum eigen series become physically measurable as experimental azimuthal angles in the stationary spherical coordinate system with polar axis aligned along primary beam.

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 additional data, viz., the precision angles for vectors $\mathbf{k}$ and $\mathbf{r}_j$ corresponding to each diffraction intensity measurement. Such measurement of precision angles can be accomplished in the laboratory reference frame defined stationary spherical coordinate system for any given orientation of the unit cell during data collection. The additional precision angle data from the experiment can be incorporated in structure determination calculations for better convergence.

Sommerfeld's Cartesian FT relations have no provision to incorporate the precision angles of $\mathbf{k}$ and $\mathbf{r}$ from the experiment. Therefore a mathematical description that permits to incorporate the experimentally measured precision angles is necessary to exhaustively use the entire measurable data. 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.

We note that partial wave analysis in spherical coordinates^{8,9} 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 diffraction¹. In the description of a quantum system, state function is synonymous to wave function. Following FT relation in quantum mechanics, 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.

Born interpretation of probability. According to Max Born's interpretation of wave function², 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 mo-

momentum space are given by $|\psi(\mathbf{r})|^2$ and $|\phi(\mathbf{k})|^2$ respectively. Accordingly in parallel with $\psi(\mathbf{r})$, $u(\mathbf{r})$ becomes the solution to governing partial differential equation in crystal diffraction. We term $u(\mathbf{r})$ as the unitcell function in parallel with position wave function and $u(\mathbf{r}_j) = f(\mathbf{r}_j)$ 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 analysis description does not require such a constraint and overcomes purely real-valued position domain constraint.

FT relations with $u(\mathbf{r}_j)$. It can be shown that an infinite number of 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 the Cartesian FT relation for the unitcell function $u(\mathbf{r}_j)$ becomes,

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

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

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

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

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

as both FT domains have by now become complex-valued in crystal diffraction similarly as in the FT domains in quantum mechanics. But Cartesian description cannot accept such a prescription

because we cannot define phase problem when both the FT domains are complex-valued. Partial wave analysis overcomes such a limitation of Cartesian description.

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 equation for both Schrödinger field and Maxwell radiation field 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 and thus admit of simultaneous eigen functions and Fourier series therefore can also be viewed as eigen series in crystal diffraction. Crystal diffraction, being a stationary state quantum system with no time variable in the description, can be viewed as a Sturm-Liouville boundary value problem with Dirichlet vanishing boundary conditions applied to eigen solution at unitcell boundaries. In such description, unitcell becomes a bound state quantum system and the 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 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 equation³. 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, the 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^{4, 11, 5} given by,

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

Application of unitcell boundaries defined vanishing boundary conditions on radial solution, one alone each axial dimension, derive definite momentum values with factor π and hence define the radial solution as $j_l(\pi kr)$. From the 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 diffraction⁶. 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) as,

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

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

where $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ is the amplitude in the position space derived from atomic scattering factor and $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ is the amplitude in the momentum space derived from the structure factor. 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 constant for spherical harmonics that appears in the expressions comes from Rayleigh expansion.

The transforming sub-amplitudes in eq. (10) and eq. (11) contain the angle dependence of only one vector which is contained in the subscript such that we write,

$$a_{\mathbf{k}}^{lm}(\mathbf{r}_j) = a_{\theta_{\mathbf{k}}, \phi_{\mathbf{k}}}^{lm}(x_j, y_j, z_j) \quad (17)$$

$$A_{\mathbf{r}_j}^{lm}(\mathbf{k}) = A_{\theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j}}^{lm}(k_x, k_y, k_z) \quad (18)$$

We now define the partial wave sub-amplitudes that contain angle dependence on both vectors as,

$$F_{\mathbf{r}_j}^{lm}(\mathbf{k}) = \frac{1}{\sqrt{V}} A_{\mathbf{r}_j}^{lm}(\mathbf{k}) j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{k}}) e^{im\phi_{\mathbf{k}}} \quad (19)$$

$$u_{\mathbf{k}}^{lm}(\mathbf{r}_j) = \frac{1}{\sqrt{V}} a_{\mathbf{k}}^{lm}(\mathbf{r}_j) j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{r}_j}) e^{im\phi_{\mathbf{r}_j}} \quad (20)$$

where,

$$u_{\mathbf{k}}^{lm}(\mathbf{r}_j) = u_{\theta_{\mathbf{k}}, \phi_{\mathbf{k}}}^{lm}(r_j, \theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j}) \quad (21)$$

$$F_{\mathbf{r}_j}^{lm}(\mathbf{k}) = F_{\theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j}}^{lm}(k, \theta_{\mathbf{k}}, \phi_{\mathbf{k}}) \quad (22)$$

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

$$|F(\mathbf{k})|^2 = \sum_{lm,j} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 \quad (23)$$

$$|u(\mathbf{r}_j)|^2 = \sum_{lm,\mathbf{k}} |u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 = |f(\mathbf{r}_j)|^2 \quad (24)$$

We define $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ in eq. (19) as transforming sub-amplitudes and eq. (20) and $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ 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.

The full-wave Parseval relation as the statement of the unitarity property of FT and as the statement of conservation of energy in Fraunhofer diffraction⁷(Arfken, 1985) becomes the probability conservation law in crystal diffraction. Hence from eq. (23) and eq. (24), the partial wave Parseval

relation becomes,

$$\sum_{j, \mathbf{k}', lm} |u_{\mathbf{k}'}^{lm}(\mathbf{r}_j)|^2 = \sum_{\mathbf{k}, j'l'm'} |F_{\mathbf{r}_{j'}}^{l'm'}(\mathbf{k})|^2 \quad (25)$$

as the probability conservation law in the partial wave description of crystal diffraction. From eq. (10) and eq. (11) and from eq. (19) and eq. (20), 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.

The experimental precision angle dependence and thus the laboratory coordinate system dependence contained in the sub-amplitudes with subscripts prevents the formal analytical derivation of the partial wave Parseval relation. But that does not mean that crystal diffraction does not obey Parseval relation as the probability conservation law.

Due to the diffraction geometry, the 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 $\mathbf{r}_j = \mathbf{r}_j(r_j, \theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j})$.

We note that the angle dependence in sub-amplitudes disappears in the presence of spherical symmetry rendering the experimental precision angles useless, hence the presence of spherical symmetry in analytically deriving the relation eq. (25) has no significance at all. With no analytical derivation for eq. (25), 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).

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 with no subscripts are defined in the respective unitcell and momentum lattice Cartesian coordinate systems.

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),

$$|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 = |F(\mathbf{k})|^2 \left| (2l+1) \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_{\mathbf{r}_j}) \right|^2 \quad (26)$$

$$|a_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 = |u(\mathbf{r}_j)|^2 \left| (2l+1) \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_{\mathbf{k}}) \right|^2 \quad (27)$$

eq. (10) and eq. (11) together with eq. (19) and eq. (20) and partial wave Parseval relation define the relations,

$$|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 = |A_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 |j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{k}})|^2 \quad (28)$$

$$|u_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 = |a_{\mathbf{k}}^{lm}(\mathbf{r}_j)|^2 |j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{r}_j})|^2 \quad (29)$$

Partial wave Parseval relation dictates scaling of the partial wave sub-amplitudes using the relations eq. (23) and eq. (24).

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 $F_{\mathbf{r}_j}^{lm}(\mathbf{k})$ and $u_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ to obtain $A_{\mathbf{r}_j}^{lm}(\mathbf{k})$ 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. (28) and eq. (29) 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,

$$\alpha[A_{\mathbf{r}_j}^{lm}(\mathbf{k})] = \alpha[F(\mathbf{k})] - m\phi_{\mathbf{r}_j} - l\pi/2 \quad (30)$$

$$\alpha[a_{\mathbf{k}}^{lm}(\mathbf{r}_j)] = \alpha[u(\mathbf{r}_j)] - m\phi_{\mathbf{k}} + l\pi/2 \quad (31)$$

It now becomes evident from eq. (30) and eq. (31) 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.

We now prove that the 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 partial wave crystals.

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 par-

tial 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 the 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 structure of individual atoms in position domain and three dimensional electromagnetic modes of 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,

$$A^{00}(\mathbf{k}) = |F(\mathbf{k})|e^{i\alpha[F(\mathbf{k})]} \quad (32)$$

$$a^{00}(\mathbf{r}_j) = |u(\mathbf{r}_j)|e^{i\alpha[u(\mathbf{r}_j)]} \quad (33)$$

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 $a^{00}(\mathbf{r}_j)$ prove that both,

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

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

in eq. (32) and eq. (33). This is where the partial wave analysis overcomes the unknown Cartesian full-wave phases and naturally solves the phase problem. This fact is corroborated by the observation that the Sturm-Liouville partial wave integral transform relations eq. (10) and eq. (11) cannot define the phases for a Cartesian full-wave full-amplitudes and hence the "Cartesian phase problem phases have no role in the partial wave integral transform or definite momentum eigen series relations".

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. (19) and eq. (20), the $l = 0$ transforming sub-amplitudes and the partial wave sub-amplitudes are related as,

$$F^{00}(\mathbf{k}) = \frac{1}{\sqrt{V}} |A^{00}(\mathbf{k})| \frac{\sin(\pi kr_j)}{\pi kr_j} \quad (36)$$

$$u^{00}(\mathbf{r}_j) = \frac{1}{\sqrt{V}} |a^{00}(\mathbf{k})| \frac{\sin(\pi kr_j)}{\pi kr_j} \quad (37)$$

As each partial wave integral transform relation is identified with unique l and m values, the factor $e^{-il\pi/2}$ becomes a constant unitary phase factor which can be excluded without loss of generality of integral transform relations for crystal diffraction. Thus, the phases of transforming sub-amplitudes

become,

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

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

which can be measured in the experiment. We observe that the transforming sub-amplitude $a_{\mathbf{k}}^{lm}(\mathbf{r}_j)$ derived from the atomic scattering factor only becomes complex-valued, the full wave atomic scattering factor $f(\mathbf{r})$ as defined in eq. (24) remains purely real-valued in the absence of absorption and thus does not conflict with Cartesian crystallography.

Hence, the relations eq. (38) and eq. (39) are the solution to phase problem in crystal diffraction. The structure is given by eq. (10) with the phases from eq. (38) as,

$$\rho(\mathbf{r}_j) = \sum_{lm} |u^{lm}(\mathbf{r}_j)|^2 \quad (40)$$

Hence, the Rayleigh expansion derived partial wave analysis physically shows that the phase on a partial wave sub-amplitude comes about as its azimuthal angle as measured in the laboratory spherical coordinate system in the experiment.

We can experimentally measure the phase of each partial wave sub-amplitude as an azimuthal angle in the experiment. We process the diffraction intensity data in the format,

$$h, k, l, \quad F(hkl), \sigma(hkl), \quad (\theta_{\mathbf{a}}\phi_{\mathbf{a}}, \theta_{\mathbf{b}}\phi_{\mathbf{b}}, \theta_{\mathbf{c}}\phi_{\mathbf{c}}), \quad (\mathbf{a}, \mathbf{b}, \mathbf{c}), \quad (\theta_{hkl}, \phi_{hkl})$$

.....

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 analysis 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 Flow chart for computer program development.

We have six steps in developing the computer program.

i. From each $|F(\mathbf{k})|$ and precision angles $(\theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j})$ from the experiment, we calculate,

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

the relation simply follows by substituting Rayleigh expansion in the corresponding Cartesian FT relation and rearranging factors after separating the eigen basis functions.

The actual solution to phase problem is coming from the transition,

$$|A_{\mathbf{r}_j}^{lm}(\mathbf{k})| e^{i\alpha[A_{\mathbf{r}_j}^{lm}(\mathbf{k})]} = |A_{\mathbf{r}_j}^{lm}(\mathbf{k})| e^{i\alpha[F(\mathbf{k})] - il\pi/2 - im\phi_{\mathbf{r}_j}} \quad (41)$$

$$\longrightarrow |A_{\mathbf{r}_j}^{lm}(\mathbf{k})| e^{-im\phi_{\mathbf{r}_j}} \quad (42)$$

in the above relation, which transition is perfectly allowed.

ii. From these values and using precision angles $(\theta_{\mathbf{k}}, \phi_{\mathbf{k}})$ from the experiment, we then calculate the partial wave sub-amplitudes,

$$F_{\mathbf{r}_j}^{lm}(\mathbf{k}) = \frac{1}{\sqrt{V}} A_{\mathbf{r}_j}^{lm}(\mathbf{k}) j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{k}}) e^{im\phi_{\mathbf{k}}} \quad (43)$$

iii. But these are unscaled. We scale them using Parseval relation, which process we call as local scaling,

$$|F(\mathbf{k})|^2 = c \sum_{j,lm} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|^2 \quad (44)$$

$$|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}} = \sqrt{c} |F_{\mathbf{r}_j}^{lm}(\mathbf{k})| \quad (45)$$

where c is the scale factor for individual diffraction intensity.

iv. Using these scaled $|F_{\mathbf{r}_j}^{lm}(\mathbf{k})|$, we determine the scaled $|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|$ from the relation,

$$|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}}^2 = \frac{V |F_{\mathbf{r}_j}^{lm}(\mathbf{k})|_{\text{scaled}}^2}{|j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{k}})|^2} \quad (46)$$

and we note that none of the above relations involve summation, hence the above relations are for local scaling of partial wave sub-amplitudes using Parseval relation.

v. We have the phase for $|A_{\mathbf{r}_j}^{lm}(\mathbf{k})|$ from the experimental azimuthal angle $\phi_{\mathbf{r}_j}$. Hence, we calculate individual term in the inverse definite momentum eigen series summation,

$$u^{lm}(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} |A_{\mathbf{r}_j}^{lm}(\mathbf{k})| e^{-im\phi_{\mathbf{r}_j}} j_l(\pi k r_j) P_l^m(\cos \theta_{\mathbf{k}}) e^{im\phi_{\mathbf{k}}} \quad (47)$$

using the scaled transforming sub-amplitudes and using the four precision angles $(\theta_{\mathbf{k}}, \phi_{\mathbf{k}}, \theta_{\mathbf{r}_j}, \phi_{\mathbf{r}_j})$ from the experiment and transform each term into unitcell coordinate system prior to series summation and determine $u^{lm}(\mathbf{r}_j)$.

vi. We then determine the electron density and the structure using the relation,

$$\rho(\mathbf{r}_j) = \sum_{lm} |u^{lm}(\mathbf{r}_j)|^2 \quad (48)$$

in the unitcell coordinate system.

10 As another historic success of quantum physics.

Historically, classical physics could not explain Stern-Gerlach, Davisson-Germer, Frank-Hertz experiments, Compton effect, photo-electric effect and Blackbody radiation, quantum mechanics alone could explain these phenomena. 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 momen-

tum 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 the 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 the 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.

Orbital structure of individual atoms is contained in directional dependence in the experi-

ment, i.e., in precision angles as measured in the stationary spherical polar coordinate system defined in laboratory reference frame in the experiment. 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.

With such unitcell function, electron density becomes the modulus square of unitcell function. Then from Fourier theory, electron density becomes the inverse FT of the auto-correlation of structure factors and the diffraction intensities become the forward FT of the auto-correlation of the unitcell function. The auto-correlation of the structure factors assumes the form of the Sayre's equation.

The Rayleigh expansion and partial wave Parseval relation derived eigen series defines the atom-wise phase of partial wave sub-amplitudes with angle dependence in both position and momentum spaces. The azimuthal angle dependence defines the phase of the transforming sub-amplitude, which therefore can be measured in the experiment.

The 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. The eigen series description conforms to the angular momentum quantization condition as the quantum diffraction law and defines the highest possible resolution that corresponds to the orbital structure of atoms. Hence, the method may as well be called the crystal diffraction imaging of the molecular structure in the unitcell using precision angle data from the experiment.

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

The Cartesian full-wave phases as defined by Sommerfeld's Cartesian FT relation is not visible in the experiment. Whereas the partial wave description defined transforming sub-amplitude phases are visible in the experiment as azimuthal angles in the laboratory spherical polar coordinate system, which can be measured in the experiment.

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

Acknowledgements : Author acknowledges Professors David E. Timm, Thomas D. Hurley, Jean A. Hamilton for postdoctoral opportunity and conveys special gratitudes to Professor Cynthia V. Stauffacher for Research Associate support during which time author published preliminary abstract on spherical basis description. Acknowledgments are due to Professors Jeffrey T. Bolin and Janet L. Smith for encouragement. Author is grateful to Dr. Frank Schlutzenzen and Dr. William S. Bennett Jr for very subtle and distinctive discussions in initial stages. Author acknowledges Professors Dilano K. Saldin and Paul F. Lyman for Research Associate support in diffraction physics that enabled the author to continue studies and Professors Micheal T. Weinert and Abbas Ourmazd for discussions. Author records earnest gratitudes to Professor Jorge Navaza for a very insightful advice on spherical basis expansion and for time to time encouragement over years since 2002 when author published preliminary abstract.

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Author contributions : P. Bhanumoorthy conceptualized the work, wrote and reviewed the manuscript.

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Competing interests : The author declares no competing financial interests.