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The Partial Wave Sub-Amplitude Fourier Transform with Born Probability Interpretation in Crystallography

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Abstract.
We identify Maxwell-Schrödinger equation as the governing partial differential equation. We name the solution as unitcell function such that Born probability rule interprets electron density as modulus square of the unitcell function. The existing traditional full-amplitude Fourier transform relation with electron density as directly the inverse Fourier transform of structure factors therefore violates Born probability rule. We derive the partial wave Parseval relation as the probability conservation law using Rayleigh expansion. We subdivide the experimental full-amplitudes into partial wave sub-amplitudes, which become amplitudes of spherical waves. The subscript on a sub-amplitude represents localization within the unitcell and therefore spherical waves become localized wave packets. As a probability measure, the amplitude of a localized wave packet is exact and merits over the amplitude of a non-localized plane wave. We measure angle dependence as the precision angles data. We derive the partial wave sub-amplitude Fourier transform relation to determine orbital structures of individual atoms using the precision angles data. The partial wave sub-amplitude Fourier transform relation alone obeys Born probability rule and hence becomes the only acceptable Fourier transform relation in quantum crystallography.
1 Introduction.

**Fourier transform between wave functions.** In quantum physics, Fourier transform (FT henceforth) relates position and momentum wave functions as solutions to Schrödinger equation respectively in position and momentum representations\(^1\). Max Born probability interpretation\(^2\), or simply Born probability rule, states that probability in position space is the modulus square of position wave function and probability in momentum space is the modulus square of momentum wave function. Probability density is probability per unit volume and hence electron density becomes proportional to probability density. More specifically, the charge density is given by

\[ \rho(r_j) = e|\psi(r_j)|^2 \]

where \(e\) is charge on electron and \(\psi(r_j)\) is the solution to position space Schrödinger equation. Wennerström already described FT relations between position and momentum state functions for scattering and diffraction\(^3\). A state function is synonymous to a wave function.

2 Born probability rule in crystallography.

Currently we use the traditional full-amplitude FT relation \(\rho(r_j) \xrightarrow{FT} F(k)\) given by,

\[ \rho(r_j) = \frac{1}{V} \sum_k |F(k)| e^{i\alpha[F(k)]} e^{-i2\pi k \cdot r_j} \]  

(1)

to calculate the electron density map as \(\text{Re}(\rho(r_j))\) using only the real-part. Such practice of using only real-part of \(\rho(r_j)\) derives from the Friedel phase relation \(\alpha[F(-k)] = -\alpha[F(k)]\) which relation is intrinsic in Fourier expansion coefficients of a purely real-valued and positive function.

We note that the Friedel phase relation \(\alpha[F(-k)] = -\alpha[F(k)]\) makes \(\rho(r_j)\) purely real-
valued only when all the amplitudes in the series summation have Friedel mates. If all the amplitudes do not have Friedel mates, \( \rho(r_j) \) becomes complex-valued. Then, the modulus value of \( \rho(r_j) \) varies depending on the number of Friedel mates included in the series summation. Such variation in the map is unacceptable. Hence, the only way to calculate a map that is independent of the number of Friedel mates is to calculate the map only from the real-part of \( \rho(r_j) \). Hence is the traditional practice of taking only the real-part of \( \rho(r_j) \) in calculating the electron density map.

**Born probability rule on the solution to Maxwell-Schrödinger equation.** Within the unitcell, electrons constitute Schrödinger field and the momentum lattice points as Fourier modes constitute the Maxwell radiation field. Accordingly, we identify Maxwell-Schrödinger equation as the governing Sturm-Liouville partial differential equation for crystal diffraction. We call the solution as the unitcell function \( u(r_j) \). In the viewpoint of \( FT \) between wave functions, the unitcell function becomes the parallel to position wave function and structure factor becomes the parallel to momentum wave function. Following Born probability interpretation, intensity \( I(k) = |F(k)|^2 \) becomes the probability in momentum space and the electron density is given by \( \rho(r_j) = |u(r_j)|^2 \) in position space. We may calculate the modulus square Born map using only the real-part as \( \rho(r_j) = |\text{Re}(u(r_j))|^2 \) for the same reason of using only real-part in calculating the traditional map.

**Violation of Born probability rule in calculating the electron density map.** Born probability rule dictates that probability density is equal to the modulus square of a wave function. A density such as electron density is directly proportional to the probability density which is \( |u(r_j)|^2 \) where \( u(r_j) \) is the solution to the governing partial differential equation. Current practice of electron
density map calculation is in violation of Born probability rule in two ways. First is ignoring unitcell function in the $FT$ relation and taking electron density directly as inverse $FT$ of the structure factors. The second is calculating the electron density map from only the real-part of the inverse $FT$ of structure factors. But taking only the real-part in calculating the map is acceptable when we do not have Friedel mates for all the diffraction intensities in the series summation.

The unitcell function as solution to the Maxwell-Schrödinger equation is equivalent to position wave function and hence replaces $\rho(\mathbf{r}_j)$ in eq. (1). Then the $FT$ relation $u(\mathbf{r}_j) \rightleftharpoons F(\mathbf{k})$,

$$u(\mathbf{r}_j) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} |F(\mathbf{k})| e^{i\alpha |F(\mathbf{k})|} e^{-i2\pi \mathbf{k} \cdot \mathbf{r}_j}$$

(2)

with unitcell function within it becomes the $FT$ relation for crystal diffraction. The unitarity of $FT$ requires the symmetric constant $1/\sqrt{V}$ in both forward and inverse $FT$ relations. Then, Born probability rule with modulus squaring dictates that only the map calculated using the relation $\rho(\mathbf{r}_j) = |u(\mathbf{r}_j)|^2$ or with only real-part $\rho(\mathbf{r}_j) = |\text{Re}(u(\mathbf{r}_j))|^2$ must give the acceptable structure.

The $FT$ relation must obey Born probability interpretation to be acceptable in quantum crystallography. Which means the Born map with modulus squaring of the unitcell function must give the correct structure. But we note that the modulus squaring in the $\rho(\mathbf{r}_j) = |\text{Re}(u(\mathbf{r}_j))|^2$ using the relation $u(\mathbf{r}_j) \rightleftharpoons F(\mathbf{k})$ makes the low density too low and high density too high and the Born map becomes Sayre’s squared crystal structure$^6$ which is uninterpretable. Hence, we cannot simply replace $\rho(\mathbf{r}_j)$ by $u(\mathbf{r}_j)$ and calculate Born map. We note that both the $FT$ relations $\rho(\mathbf{r}_j) \rightleftharpoons F(\mathbf{k})$ and $u(\mathbf{r}_j) \rightleftharpoons F(\mathbf{k})$ are the full-amplitude $FT$ relations.
To follow Born probability rule and obtain an interpretable Born map, we necessarily modify the currently existing full-amplitude $FT$ relation into the partial wave sub-amplitude $FT$ relation in which the transforming and the transformed amplitudes are partial wave sub-amplitudes. In the partial wave analysis, the spherical waves become wave packets and derive the partial wave sub-amplitude $FT$ relation in terms of localized sub-amplitudes of wave packets. The partial wave sub-amplitude $FT$ relation alone obeys Born probability rule and gives the structure from Born map. Hence, the partial wave sub-amplitude $FT$ relation alone becomes the valid $FT$ relation acceptable in quantum crystallography.

The autocorrelation theorem on the $FT$ relation $u(r_j)^{FT} \rightleftharpoons F(k)$ with unitcell function states that the forward $FT$ of autocorrelation of unitcell function becomes the diffraction intensities and inverse $FT$ of the autocorrelation of structure factors becomes the electron density which is the modulus square of the unitcell function. Hence, Sayre’s equation$^5$ and Sayre’s squared crystal$^6$ are in conflict with Born’s probability interpretation of the unitcell function. The Born map $\rho(r_j) = |\text{Re}(u(r_j))|^2$ from $u(r_j)^{FT} \rightleftharpoons F(k)$ does not give interpretable map and hence the full-amplitudes may not obey the autocorrelation theorem. The partial wave sub-amplitude $FT$ relation alone gives the interpretable Born map and hence can readily obey the autocorrelation theorem.

3 The precision angles data as the angle dependence in crystal diffraction.

Besides diffraction intensity data alone, we can measure precision angles data for $k$ and $r_j$ vectors in a stationary spherical polar coordinate system defined in the laboratory reference frame$^{11}$. Each
intensity measurement corresponds to a unique orientation of the unitcell. Hence, the precision angles data constitutes a huge part of experimental data. Despite being huge part of data, the precision angles data is being grossly ignored because the full-amplitude $FT$ relation currently in practice does not have provision to accommodate the precision angles data. For a method to be effective, we must exhaustively use all the data measurable in the experiment. The partial wave sub-amplitude $FT$ relation with sub-amplitudes in place of full-amplitudes alone can accommodate the precision angles data from the experiment.

The precision angles data carry orientations of $k$ and $r_j$ vectors in the experiment. The only angle in the full-amplitude $FT$ relation is the inter-vector angle present in the kernel which means the full-amplitude $FT$ relation does not carry angle dependence measured in the laboratory coordinate system. In consequence, the full-amplitude $FT$ relation can only represent spherical atoms and spherical diffraction amplitudes. The only way to incorporate the precision angles data and thus the dependence in calculations is to use the $FT$ between partial wave sub-amplitudes that carry precision angles data.

We note that we can formulate a diffraction law from the standing wave description\(^8\) of crystal diffraction. Such a diffraction law becomes the diffraction condition in terms diffraction angle, which is the polar angle $\theta_k$ of the $k$th diffracted beam\(^8,9,10\).

To measure the precision angles data, we process the experimental diffraction data in the format \(^{11}\) given by,
Each $|F(hkl)|$ measurement corresponds to a unique orientation of the unitcell. Hence we necessarily record precision angles for the axial vectors of the unitcell in the unique orientation corresponding to each $|F(hkl)|$. Only then we can calculate the angles $(\theta_{r_j}, \phi_{r_j})$ for each grid point position vector in that unique orientation.

To calculate the precision angles $(\theta_{r_j}, \phi_{r_j})$, we transform $r_j = r_j(x_j, y_j, z_j)$ in the unitcell coordinate system to $r_j' = r_j'(x_j', y_j', z_j')$ in the laboratory Cartesian coordinate system. The transformation matrix is given by,

$$
\begin{pmatrix}
    x_j' \\
    y_j' \\
    z_j'
\end{pmatrix} =
\begin{pmatrix}
    \sin \theta_a \cos \phi_a & \sin \theta_a \sin \phi_a & \cos \theta_a \\
    \sin \theta_b \cos \phi_b & \sin \theta_b \sin \phi_b & \cos \theta_b \\
    \sin \theta_c \cos \phi_c & \sin \theta_c \sin \phi_c & \cos \theta_c
\end{pmatrix}
\begin{pmatrix}
    x_j \\
    y_j \\
    z_j
\end{pmatrix}
$$

Then the spherical polar coordinates become,

$$
r_j = \sqrt{x_j^2 + y_j^2 + z_j^2} = \sqrt{x_j'^2 + y_j'^2 + z_j'^2} ; \quad \theta_{r_j} = \cos^{-1} \left( \frac{z_j'}{r_j} \right) ; \quad \phi_{r_j} = \tan^{-1} \left( \frac{y_j'}{x_j'} \right)$$

We subdivide the experimental full-amplitudes into partial wave sub-amplitudes using the partial wave Parseval relation as the probability conservation law and the precision angles data from the experiment. To use the precision angles data derived sub-amplitudes thus obtained, we define the new partial wave sub-amplitude $FT$ relation for crystallography.
4 The partial wave sub-amplitudes.

Partial wave Parseval relation as the probability conservation law. Parseval relation is energy conservation law\textsuperscript{12} in Fraunhofer diffraction and hence becomes probability conservation law in crystal diffraction. For a unitcell, we may replace integration with summation over discrete locations of atoms and equivalently write as,

\[
\int_V |u(r)|^2 dr = \sum_j |u(r_j)|^2 \quad (5)
\]

when \( j \) ranges over positions of all atoms within the unitcell. But we do not know positions of atoms prior to structure determination. To sample the density within unitcell, the closest approximation in the above relation is to let \( j \) range over the discrete grid points. Again we note that eq. (5) is the best possible approximation for Parseval relation when we are dealing with discrete grid to sample the unitcell. We substitute Rayleigh expansion\textsuperscript{13,14} given by,

\[
e^{ikr} = 4\pi \sum_{lm} (-i)^l j_l(kr) Y^m_l(\hat{k}) Y^m_l(\hat{r}) \quad (6)
\]
in the inverse \( FT \) in eq. (1) and derive the partial wave Parseval relation given in the appendix as,

\[
\sum_j |u(r_j)|^2 = \sum_k |F(k)|^2 = \sum_{k,j,lm} |F_{r_j}^{lm}(k)|^2 \quad (7)
\]

for the discrete grid within the unitcell. Derivation follows the full-amplitude version of Parseval relation using Dirac \( \delta \) function in spherical polar coordinates. Partial wave analysis permits to subdivide the full-amplitudes into partial wave sub-amplitudes.

Localized sub-amplitudes as amplitudes of wave packets for probability interpretation. The Fourier basis functions can be viewed as eigen solutions to position and momentum operators as
well as Helmholtz equation. In three dimensions, the \( FT \) kernel can be viewed as a three dimensional generalization of an infinite plane wave. Hence in the traditional full-amplitude \( FT \) relation \( \rho(r_j) \overset{FT}{\rightarrow} F(k) \), the full-amplitude \( |F(k)| \) from the experiment becomes the amplitude of an infinite plane wave. A plane wave is non-localized with zero absolute probability at any given space point. With fractional coordinates, the \( FT \) kernel becomes an infinite plane wave delimited to within the unitcell. A delimited plane wave too is still a plane wave and describes a particle that is equally likely to be found everywhere within the unitcell without absolute probability for any localized space point within. Hence, the delimited infinite plane wave also is an unphysical object as a probability measure\(^1\) even if delimited to within unitcell by fractional coordinates. For exact and complete description, we need a localized wave packet with absolute probability as a probability measure. The next immediate alternative is spherical coordinate description\(^7\) where a spherical wave as a probability measure becomes a localized wave packet and offers exact probability description.

Spherical polar coordinate description is in terms of spherical waves. Substitution of Rayleigh expansion in inverse \( FT \) relation in eq. (1) gives the expression for partial wave sub-amplitudes and their phases in terms of precision angle data as\(^{11}\),

\[
F_{l,m}^{r_j}(k) = |F(k)|e^{im\phi(k)}(2l + 1)\frac{(l - m)!}{(l + 1)!}(-i)^lP_l^m(\cos \theta_{r_j})j_l(2\pi kr_j)P_l^m(\cos \theta_k)e^{-im(\phi_{r_j} - \phi_k)} \tag{8}
\]

where we may drop \((-i)^l = e^{-il\pi/2}\) as a constant unitary phase factor that leaves the physical system invariant. The sub-amplitudes in eq. (8) become the amplitudes of the spherical waves. The subscript on a sub-amplitude corresponds to localization within the unitcell and hence the spherical waves become the localized wave packets. Thus, the sub-amplitudes as amplitudes of
wave packets become the localized sub-amplitudes.

The subscript on a sub-amplitude represents localization such that the sub-amplitude becomes the amplitude of a localized wave packet. We note that subdivision of full-amplitudes into sub-amplitudes is not possible without using Rayleigh expansion. We may think of extracting a localized sub-amplitude \( F_{r_j}(k) \) by simply removing the summation in the traditional full-amplitude \( FT \) relation and write,

\[
F_{r_j}(k) = \frac{1}{\sqrt{V}} |F(k)| e^{i\alpha} e^{-i2\pi k \cdot r_j}
\]

with subscript \( r_j \) and without indices \( l \) and \( m \). Then, Parseval relation as the probability conservation law becomes,

\[
\sum_j |u(r_j)|^2 = \sum_k |F(k)|^2 = \sum_k \sum_j |F_{r_j}(k)|^2
\]

But modulus squaring eq. (9) shows that \( |F_{r_j}(k)| \) becomes equal to the average \( |F(k)|/V \) without the subscript \( r_j \). Which means the sub-amplitude becomes the same for all \( r_j \) and the subdivision of the full-amplitude into localized sub-amplitudes without Rayleigh expansion becomes invalid. In other words, the partial wave sub-amplitude \( FT \) relation without the indices \( l \) and \( m \) becomes the full-amplitude \( FT \) relation averaged over unitcell volume. Hence, the only way to derive the partial wave sub-amplitude \( FT \) relation in terms of localized spherical wave wave packets is by using Rayleigh expansion.
Local scaling of the partial wave sub-amplitudes. Using eq. (8), we subdivide the experimental full-amplitudes $|F(k)|$ into partial wave sub-amplitudes $|F_{lm}^{r}(k)|$ given by,

$$|F_{lm}^{r}(k)| = \left| |F(k)| (2l + 1) \frac{(l - m)!}{(l + 1)!} (-i)^l P_l^m(\cos \theta_r j_l(2\pi kr_j) P_l^m(\cos \theta_k) \right|$$

which depend on precision angles data from the experiment. For $l = 0$, only the zero order spherical Bessel function sub-divides the full-amplitude into sub-amplitudes without the necessity for precision angles data. The sub-amplitudes in eq. (11) are unscaled and hence we must subject sub-amplitudes to scaling so as not to violate Parseval relation as the probability conservation law. Each $k$th full-amplitude sub-divides into a set of $k$th sub-amplitudes and hence the scaling is necessary for each diffraction spot. The relation for spot-wise scaling of all the $k$th sub-amplitudes to the $k$th full-amplitude is given by,

$$|F(k)|^2 = c \sum_{j,lm} |F_{lm}^{r}(k)|_{\text{unscaled}}^2$$

$$|F_{lm}^{r}(k)|_{\text{scaled}} = \sqrt{c} |F_{lm}^{r}(k)|_{\text{unscaled}}$$

where $c$ is the scaling constant. We call the diffraction spot-wise scaling of sub-amplitudes to full-amplitudes as the local scaling.

5 The partial wave sub-amplitude Fourier transform relation for crystallography.

The modulus square summation in the scaling relation in eq. (12) defines an orthonormal Hilbert subspace at each momentum lattice point. Similar modulus square summation in the scaling relation in position domain defines an orthonormal Hilbert subspace at each grid point within unitcell also. We note that eq. (1) is in terms of full-amplitudes from the experiment. An integration vari-
able in an integral transform is always the variable in the transforming domain. Hence, we remove
the summation over \( l \) and \( m \) and convert the transformed full-amplitude into transformed \( l, m \) sub-
amplitude in the \( FT \) relation. Thus, we retain summation over only \( k \) and define the inverse \( FT \) relation between the \( l, m \) sub-amplitudes as,

\[
u_{lm}(r_j) = \frac{1}{\sqrt{V}} \sum_k |F_{r_j}^{lm}(k)|_{\text{scaled}} e^{i\alpha[F(k)]} e^{-i2\pi k \cdot r_j} \left( e^{-im(\phi_{r_j} - \phi_k)} \left( e^{i\alpha[P^m_l(\cos \theta_{r_j})]} + i\alpha[jm(2\pi k r_j)] + i\alpha[P^m_l(\cos \theta_k)] \right) \right)
\]

(14)
The full-amplitude phase \( \alpha[F(k)] \) and the \( FT \) kernel are essential to preserve the Fourier transform
characteristic of crystal diffraction. We call the factor in the first parentheses as the phase factor
and in the second parenthesis as the sign factor. The phase factor contains the azimuthal angles and
the sign factor contains polar angles from the precision angles data. Both Legendre polynomials
and spherical Bessel function are purely real-valued. Thus the sign factor in each term can only be
either \( e^{i0} \) or \( e^{i\pi} \) which means sign factor carries sign of the sub-amplitude. For the same reason as
in the traditional map calculation, we calculate the Born map also by modulus squaring only the
real-part of \( \nu_{lm}(r_j) \). Born interpretation gives electron density as the modulus square summation
of \( \nu_{lm}(r_j) \) given by,

\[
R(r_j) = |\text{Re}(\nu(r_j))|^2 = \sum_{lm} |\text{Re}(\nu_{lm}(r_j))|_{\text{scaled}}^2 (15)
\]

Thus, we may use notations \( \rho(r_j) \) for the traditional electron density and \( R(r_j) \) for the Born elec-
tron density obtained by the modulus square summation of partial wave unitcell function.

In tracing the orbital structures, the \( m = -l, \cdots, +l \) corresponds to different orientations of
the orbitals of atoms. To preserve the orientations, we must preserve the orbitals given by differ-
ent $m$ values by modulus squaring the electron density obtained from individual $lm$ partial wave sub-amplitude $FT$s\textsuperscript{11}. This is where Born probability rule defined modulus square summation as probability becomes important in extracting the orbital structures of individual atoms.

We call eq. (14) as the partial wave sub-amplitude $FT$ relation for quantum crystallography. We note that the currently existing full-amplitude $FT$ is the $FT$ of amplitude of a non-localized plane wave. Whereas the partial wave sub-amplitude $FT$ is the $FT$ of amplitude of a localized wave packet. In crystal diffraction, we may state that the full-amplitude $FT$ relation offers description as the far-field Fraunhofer diffraction and the partial wave sub-amplitude $FT$ relation offers description as the near-field Fresnel diffraction. Angle dependence and thus the precision angles data correspond to near-field Fresnel diffraction.

The full-amplitude $FT$ relation gives the $FT$ between all orbitals of all atoms in the whole unitcell. The partial wave sub-amplitude $FT$ relation gives the $FT$ of only $lm$ orbitals of all atoms in the whole unitcell. Thus the partial wave sub-amplitude $FT$ describes diffraction from a hypothetical or a theoretical crystal consisting of only $lm$ orbital on each atom within the unitcell\textsuperscript{11}.

Among the two $FT$ relations given by eq. (1) and eq. (14), the one which follows Born’s probability interpretation alone is exact and complete and hence is acceptable in quantum mechanics. Thus, we claim that it is the proposed partial wave sub-amplitude $FT$ relation in eq. (14) that defines the description of crystal diffraction in quantum crystallography.

The full-amplitudes $|F(k)|$ and their phases $\alpha[F(k)]$ are independent of precision angles
data. Whereas the sub-amplitudes $|F_{lm}^{rj}(k)|$ and their phases $\alpha[F_{lm}^{rj}(k)]$ are dependent on precision angles data only for $l > 0$. And only for $l = 0$, the partial wave sub-amplitudes and their phases in eq. (8) become independent of precision angles data.

**The reduced partial wave sub-amplitude $FT$ relation.** We note that the precision angles data from the experiment is not required for $l = 0$ calculation and thus the $l = 0$ Born map is independent of the precision angles data. The traditional electron density map calculated from eq. (1) also is independent of the precision angles data. For $l = 0$, eq. (8) gives $l = 0$ sub-amplitudes $F_{rj}^{00}(k)$ which are devoid of precision angles data. Hence, we call $l = 0$ partial wave sub-amplitudes as the reduced partial wave sub-amplitudes. Accordingly for $l = 0$, eq. (14) gives the $FT$ relation,

$$u^{00}(r_j) = \frac{1}{V} \sum_k |F_{rj}^{00}(k)|_{\text{scaled}} e^{i\alpha[F(k)]} e^{-i2\pi k \cdot r_j} e^{i\alpha[j_0(2\pi kr_j)]}$$

which is independent of the precision angles data with reduced partial wave sub-amplitudes. We call eq. (16) as the reduced partial wave sub-amplitude $FT$ relation. Born probability rule dictates that we calculate the Born map by modulus squaring. In Born map too, we note that we calculate the Born map using only the real-part, i.e., $R(r_j) = |\text{Re}(u^{00}(r_j))|^2$ for the same reason as in the traditional map. In eq. (16), $e^{i\alpha[j_0(2\pi kr_j)]} = e^{i0}$ for positive $j_0(2\pi kr_j)$ and $e^{i\alpha[j_0(2\pi kr_j)]} = e^{i\pi}$ for negative $j_0(2\pi kr_j)$. We may calculate the $l = 0$ Born map with and without the sign factor to visualize the effect of the sign factor. We note that the only difference between with and without the sign factor is little extension of the density towards neighboring atoms while the position atoms remain the same.

**Importance in the direct method solution to phase problem.** The triple phase tangent formula\textsuperscript{15}
works for small molecules and fails for macromolecules. Hence, the only reason for the failure is simply a bigger unitcell giving rise to more number of diffraction spots. And we lack theoretical explanation for such a failure. Hence, it is necessary to investigate whether the non-localized full-amplitudes as input data and hence the traditional full-amplitude Fourier transform relation may reason the failure of triple phase tangent formula for macromolecular crystallography.

Both full-amplitudes and reduced sub-amplitudes are devoid of precision angles data and thus devoid of angle dependence. Hence, we can expect only spherical atom structure with both full-amplitudes and reduced sub-amplitudes. As \( l = 0 \) partial wave sub-amplitudes too are devoid of angle dependence, eq. (14) shows that the phases are given by \( \alpha[F^{lm}_{ij}(k)] = \alpha[F(k)] \) for spherical atom structure which corresponds to \( l = 0 \). Hence, the phases \( \alpha[F(k)] \) give the spherical atom structure and the precision angles data as additional data can only give the orbital structure of atoms.

In all the heretofore \textit{ab initio} phasing methods for direct method solution deployed in the past, the input data was exclusively and solely only the experimental full-amplitudes. If a phasing method does not work, only alternative is to change the input data. We now have the provision in our partial wave analysis to change the input data from the experimental full-amplitudes to the reduced sub-amplitudes. The reduced partial wave sub-amplitude Fourier transform relation does just that. Hence, all the heretofore unsuccessful multivariate optimization methods may prove successful in extracting the phases using the reduced partial wave sub-amplitude Fourier transform relation in place of the traditional full-amplitude Fourier transform relation.
6 Discussion and conclusions.

The Maxwell-Schrödinger equation in the form of Helmholtz equation becomes the governing partial differential equation. The unitcell function as solution becomes equivalent to position wave function in the viewpoint of $\mathcal{F}$ relation between position and momentum wave functions. Following Born probability rule, the probability density and thus the electron density becomes proportional to modulus square of the unitcell function. Hence, Born probability rule summarily proscribes electron density as directly the inverse Fourier transform of structure factors.

We derive the partial wave Parseval relation as the probability conservation law to subdivide the experimental full-amplitudes into partial wave sub-amplitudes. The phase set of full-amplitudes is essential to preserve the Fourier transform nature of crystal diffraction. Hence, the phase determination of the full-amplitudes follows the already existing methods.

In three dimensional Fourier transform, the kernel can be viewed as a three dimensional generalization of an infinite plane wave and hence a full-amplitude can be viewed as the amplitude of an infinite plane wave. A plane wave is non-localized and hence is an unphysical object as a probability measure. A full-amplitude is independent of localization and a sub-amplitude alone expressly carries a subscript that represents localization at a specific location within the unitcell. A partial wave sub-amplitude is the amplitude of a spherical wave and hence a spherical wave becomes a wave packet. A localized wave becomes a wave packet that serves as an exact probability measure. Which means, the localized sub-amplitudes merit over the full-amplitudes. In other words, the partial wave sub-amplitude Fourier transform relation tightens the precision in
probability interpretation and thus merits over the full-amplitude Fourier transform.

The precision angles data carries angle dependence and constitute a huge part of experimental data which is being grossly ignored in the traditional full-amplitude Fourier transform description. For the first time in all the history of crystallography, the partial wave sub-amplitude Fourier transform relation alone has provision to incorporate the precision angles data from the experiment to access orbital structures, coordination numbers and bonding schemes of individual atoms. Among all the currently existing structure reconstruction technologies, the partial wave $FT$ relation alone can reach out to the highest resolution enough to mapping the orbital structures.

The partial wave sub-amplitude Fourier transform relation alone obeys Born probability interpretation. Hence, we state that it is the partial wave sub-amplitude Fourier transform relation that defines quantum crystallography.

**Author contributions :** P. Bhanumoorthy conceptualized the work, formulated the theory and the partial wave sub-amplitude Fourier Transform relation and wrote and reviewed the manuscript.

**Data availability :** The current study requires no additional data from the experiment and hence no datasets were generated or analyzed.

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Appendix: partial wave Parseval relation.

Born probability rule replaces the electron density by the unitcell function and hence the full-amplitude inverse $FT$ relation becomes $u(r_j) \stackrel{FT}{\equiv} F(k)$. Then the unitcell function is given by,

$$u(r_j) = \frac{1}{\sqrt{V}} \sum_k F(k)e^{-i2\pi kr_j} \quad (17)$$

where unitarity property of $FT$ requires symmetric constant $1/\sqrt{V}$ in forward and inverse $FT$
relations. Then the full-wave Parseval relation in terms of the unitcell function \(u(r_j)\) is given by,

\[
\int_V |u(r)|^2 \, dr = \int_V u^*(r_j)u(r_j) \, dr = \sum_{k} F^*(k)F(k') \frac{1}{V} \int_V e^{+i2\pi(k-k')r_j} \, \delta(k - k') = \sum_k |F(k)|^2
\]

where \(V\) is the volume of the unitcell and,

\[
\delta(k - k') = \frac{1}{V} \int_V e^{i2\pi(k-k')r} \, dr \tag{19}
\]

is the \(\delta\)-function. We note that the full-wave Parseval relation is in terms of full-amplitude modulus squares. We have the relation for integration over volume \(V\),

\[
dr = r^2 \, dr \sin \theta \, d\theta \, d\phi_r \tag{20}
\]

From Rayleigh expansion and eq. (19),

\[
\delta(k - k') = \frac{1}{V} \int_V e^{i2\pi(k-k')r} \, dr \tag{21}
\]

\[
= \frac{1}{V} \int_V (e^{i2\pi kr}) (e^{-i2\pi k'r}) \, dr \tag{22}
\]

\[
= \frac{1}{V} \int_V \sum_{lm'm'} (i)^l (-i)^{l'} (2l + 1) (l - m)! (2l' + 1) (l' - m')! (l + m)! (l' + m')! \\
\]

\[
j_l(2\pi kr)j_{l'}(2\pi k'r)P^m_l(\cos \theta_r)P^{m'}_{l'}(\cos \theta_{r'}) \frac{1}{r^2} \, e^{-im\phi_r}e^{-im'\phi_{r'}} \, \sin \theta_r \, d\theta_r \, d\phi_r \tag{23}
\]
When we integrate, we can introduce $\delta_{ll'}$ and $\delta_{mm'}$ such that,

\[
\int e^{-i2\pi(k-k') \cdot r} \, dr = \sum_{lm'm'} (i)^l(-i)^{l'} (2l+1)(l-m)! \frac{(l-m)!}{(l+m)!} (2l'+1)(l'-m')! \frac{(l'-m')!}{(l'+m')!} P^m_l (\cos \theta_k) P^{m'}_{l'} (\cos \theta_{k'}) e^{-im\phi_k} e^{im'\phi_{k'}}
\]

\[
\int j_l (2\pi kr) j_{l'} (2\pi k'r) r^2 \, dr \int P^m_l (\cos \theta_k) P^{m'}_{l'} (\cos \theta_{k'}) \sin \theta_r d\theta_r
\]

\[
\int e^{-i(m-m')\phi_r} d\phi_r \delta_{ll'} \delta_{mm'}
\]

(24)

We remove $\delta_{ll'} \delta_{mm'}$ such that the factor with $(m-m')$ disappears and we have,

\[
\int e^{-i2\pi(k-k') \cdot r} \, dr = \sum_{lm} \left( (2l+1) \frac{(l-m)!}{(l+m)!} \right)^2 P^m_l (\cos \theta_k) P^m_{l'} (\cos \theta_{k'}) e^{-im(\phi_k-\phi_{k'})}
\]

\[
\int j_l (2\pi kr) j_{l'} (2\pi k'r) r^2 \, dr \int |P^m_l (\cos \theta_r)|^2 \sin \theta_r d\theta_r
\]

(25)

and we note that it is the same if we replace $+i$ by $-i$ in the exponential. For numerical integration using precision angles data, we replace integral by summation over discrete grid points such that,

\[
\sum_j e^{-i2\pi(k-k') \cdot r_j} = \sum_{lm} \left( (2l+1) \frac{(l-m)!}{(l+m)!} \right)^2 P^m_l (\cos \theta_k) P^m_{l'} (\cos \theta_{k'}) e^{-im(\phi_k-\phi_{k'})}
\]

\[
\sum_j j_l (2\pi kr_j) j_{l'} (2\pi k'r_j) |P^m_l (\cos \theta_r)|^2
\]

(26)

For the factor in eq. (18) with $\sum_{k'}$ summation,

\[
\sum_{k'} F(k') \delta(k-k') = \sum_{k'} F(k') \frac{1}{V} \sum_j e^{-i2\pi(k-k') \cdot r_j} = F(k)
\]

(27)

\[
= \sum_{k'} F(k') \frac{1}{V} \sum_{lm} \left( (2l+1) \frac{(l-m)!}{(l+m)!} \right)^2 P^m_l (\cos \theta_k) P^m_{l'} (\cos \theta_{k'}) e^{-im(\phi_k-\phi_{k'})}
\]

\[
\sum_j j_l (2\pi kr_j) j_{l'} (2\pi k'r_j) |P^m_l (\cos \theta_r)|^2
\]

(28)

\[
= F(k) \frac{1}{V} \sum_{lm} \left( (2l+1) \frac{(l-m)!}{(l+m)!} \right)^2 |P^m_l (\cos \theta_k)|^2 \sum_j |j_l (2\pi kr_j)|^2 |P^m_l (\cos \theta_r)|^2
\]

(29)
From eq. (18) with both $\sum_k$ and $\sum_{k'}$ summation,

\[
\int_V |u(r)|^2 dr = \sum_k F^* (k) \sum_{k'} F (k') \frac{1}{V} \sum_j e^{-i2\pi(k-k') r_j} \\
= \sum_{k,lm,j} |F(k)|^2 \frac{1}{V} \left( \frac{(l + 1)(l - m)!}{(l + m)!} \right)^2 |P^m_l (\cos \theta_k)|^2 |j_i (2\pi kr_j)|^2 |P^m_l (\cos \theta_{r_j})|^2 \\
= \sum_{k,lm,j} |F^l_{lm} (k)|^2
\]

which is the partial wave Parseval relation.