The Algebraic Approach to the Phase Problem for Neutron Scattering

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Abstract

The algebraic approach to the phase problem for the case of X-ray scattering from an ideal crystal is extended to the case of the neutron scattering, overcoming the difficulty related to the non-positivity of the scattering density. In this way, it is proven that the atomicity is the crucial assumption while the positiveness of the scattering density only affects the method for searching the basic sets of reflections. We also report the algebraic expression of the determinants of the Karle-Hauptman matrices generated by the basic sets with the most elongated shape along one of the reciprocal crystallographic axes.

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1 Introduction

The main crystallographic problem, namely: to determine the electron density of an ideal crystal with known chemical composition from its X-ray diffraction pattern, is brought to its essence when the atoms are assumed to be point-like because the positions of the atoms present in the unit cell are the only unknown quantities to be determined. The unknowns' number being finite, it appears reasonable that the knowledge of the peak intensities relevant to a sufficiently large portion of the reciprocal lattice is sufficient to determine the atomic positions. In fact, Ott (1927) and Avrami (1938) first showed that the atomic positions are the roots of a set of polynomial equations determined by an appropriate set of reflection intensities. This method of inversion of scattering data is known as the algebraic approach to the phase problem [Buerger (1960), Hauptman (1991)]. Actually, the correct formulation of the algebraic approach is slightly more involved [Navaza & Silva (1979), Silva & Navaza (1981), Rothbauer (1994)] for two reasons. Firstly, the unimodular roots of the system of polynomial equations, referred to in the following as resolvent system, are the positions of the peaks of the infinitely resolved Patterson map [Patterson (1939)]. Secondly, for the general case where some of the aforesaid peaks have the same projections along one of the three crystallographic axes, the resolvent system has to be determined by a more involved procedure than Avrami’s. These points have been fully clarified in two recent papers [Cervellino & Ciccariello, (1996) and (2001)], referred to as I and II in the following. These papers showed the existence of many resolvent systems. In particular, the determination of resolvent systems is made possible by the positivity of the scattering density, ensured by
the fact that we are dealing with X-ray scattering. Very briefly, according to the
basic paper by Goedkoop (1950), the positivity condition allows us to associate
to each point of the reciprocal space lattice $\mathbb{Z}^3$ a vector of a finite-dimensional
Hilbert space $\mathcal{H}(\mathcal{N})$. The scalar products of these vectors reproduce the intensities
of the full diffraction pattern. Each resolvent system is determined by a basic set
of reflections denoted by $\mathcal{B}(\mathcal{N})$, i.e. by a simply connected set of $\mathcal{N}$ reflections such
that the associated vectors are linearly independent and form a basis of $\mathcal{H}(\mathcal{N})$. The coefficients of the polynomial equations of the resolvent system require the
knowledge of the peak intensities relevant to all the reflections obtained as difference
of any two reflections of $\mathcal{B}(\mathcal{N})$. Hence, it is important to select $\mathcal{B}(\mathcal{N})$ in such a
way that it is centred on $0$ (the origin of reciprocal space) and that its points lie
as close as possible to the origin. Only when the limiting sphere is large enough
to contain one of these sets, a resolvent system is known and, after solving it, the
atomic positions can be determined. The procedure to be followed in order to select
a basic minimal set of reflections was reported in ref. II, where it was also shown
how to convert each resolvent system of polynomial equations in three variables
into a resolvent system of polynomial equations in a single variable.

The algebraic approach has been successfully applied to solve the structure of
some real crystals [Fischer & Pilz (1997) and Pilz & Fischer (2000)] and it can be
implemented to account for experimental errors on reflex intensities (Cervellino &
Ciccariello, 1999). As a matter of fact, its practical usefulness is severely limited
by the fact that the degree of the polynomial equations sharply increases with the
number of the atoms present in the unit cell (Hauptman, 1991). On a theoretical
ground, the approach looks however quite interesting for its rigorous conclusions
and its far reaching implications since the algebraic approach is intimately related
to other classical issues of mathematical-physics (see the introductory section of
II).

The aim of this paper is to report on the extension of the algebraic approach
to the case of neutron scattering. As already mentioned, the presently known
formulations exploit the positiveness of the scattering density, a condition generally
not fulfilled in the case of neutron scattering due to the fact that some atomic
species have negative scattering lengths. On this basis, one rightly wonders whether
the mentioned results - in particular the property that the full diffraction pattern
can be reconstructed from the knowledge of the intensities relevant to a finite
set of reflections, i.e. the ”difference” set generated by a basic set of reflections
- do apply to neutron scattering or not. We shall show that the answer to this
question is affirmative\(^1\). In order to prove this statement, it is necessary to relax
the positiveness condition. Hence, the plan of the paper is as follows. In §2 we
report the basic equations of the algebraic approach and the finite vectorial space
\( \mathcal{H}(N) \) will be introduced on the basis of simple quantum mechanical notions. Based
on the results proven in Appendices A and B, in §3 we generalize the algebraic
approach to neutron scattering in the case of two-dimensional crystals and in §4 we

\(^1\)To the authors’ knowledge, Navaza & Navaza (1992) already gave a positive answer to this
question. However, these authors explicitly recognized to see no rigorous way for demonstrating
the reconstruction procedure in three dimensions, that is the most interesting point. This difficulty
is related to that of singling out a basic set of reflections from the set of the observed ones. In
this paper we overcome this difficulty by showing how the isolation of a basic set of reflections can
be carried out also in presence of a non-positive scattering density. By so doing, we generalize
the results obtained in papers I and II and based on the positiveness of the scattering density.
It should also be remarked that the aforesaid proof of the reconstruction property requires no
probabilistic assumption. Therefore, our conclusions are more general than those obtained by
Hauptman (1976) with the probabilistic approach that, for practical aplications, is by far the
most useful one (see, e.g., Hauptman and Langs (2003)).
sketch the generalization to the three-dimensional case and report our conclusions. Appendix A illustrates a new procedure, not requiring the positivity assumption, for singling out a principal basic set of reflections, where principal means that the basic set has the most elongated shape along one axis of reciprocal space. Appendix B deals with the derivation of the algebraic expression of the determinant of the Karle-Hauptman matrix associated to a principal basic set of reflection.

2 Basic results of the algebraic approach

The formulation of the algebraic approach, reported in I and II, assumed positivity. We will now retrace our steps through the theory in order to make the necessary changes to allow for non-positive scattering densities, as it happens with neutrons. We continue to assume that the unit cell contains \( N \) point-like atoms. Its scattering density has the following expression

\[
\rho_{\text{cell}}(r) = \sum_{j=1}^{N} \hat{Z}_j \delta(r - r_j)
\]  

(1)

where \( \delta(\cdot) \) is the three-dimensional (3D) Dirac function, \( r_j \) the position of the \( j \)th atom and \( \hat{Z}_j \) the atomic number or the scattering-length of the \( j \)th atom, depending on whether one considers X-ray or neutron scattering. The two cases differ because the \( \hat{Z}_j \)'s are positive integers in the case of X-rays and only real numbers in the case of neutrons\(^2\). Thus, the positiveness of the scattering density is generally not ensured in the neutron case. But \( I_{\text{obs},h} \) - the intensity observed at reflection \( h \) - is

\(^2\)It is understood that absorption and other experimental effects are either absent or corrected for.
in both cases the square modulus of the Fourier transform of (1), \( i.e. \)

\[
I_{\text{obs}, \mathbf{h}} = \left| \sum_{j=1}^{N} \hat{Z}_j e^{i2\pi\mathbf{h} \cdot \mathbf{r}_j} \right|^2 = \sum_{j=1}^{N} \hat{Z}_j^2 + \sum_{1 \leq j \neq k \leq N} \hat{Z}_j \hat{Z}_k e^{i2\pi\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_k)}. \tag{2}
\]

Each vector \( \mathbf{r}_j - \mathbf{r}_k \) can be brought within the unit cell by adding to it a vector \( \mathbf{m}_{j,k} \) with components equal to 0 or -1, so as to write

\[
\mathbf{r}_j - \mathbf{r}_k + \mathbf{m}_{j,k} = \mathbf{\delta}. \tag{3}
\]

As \( (j, k) \) runs over its \( N(N-1) \) values, we label the different \( \mathbf{\delta} \)'s, defined by (3), by \( j \) and we denote by \( \mathcal{N}' \) the number of the different \( \mathbf{\delta}_j \)'s. Moreover, we denote by \( \mathcal{L}_j \) the set of pairs \( (j, k) \) such that \( \mathbf{r}_j - \mathbf{r}_k \) defines the same \( \mathbf{\delta}_j \) after applying (3). Then, the second sum on the right hand side (rhs) of (2) becomes

\[
\sum_{j=1}^{\mathcal{N}'} e^{i2\pi\mathbf{h} \cdot \mathbf{\delta}_j} \sum_{(j, k) \in \mathcal{L}_j} \hat{Z}_j \hat{Z}_k \tag{4}
\]

After setting

\[
\nu_j \equiv \sum_{(j, k) \in \mathcal{L}_j} \hat{Z}_j \hat{Z}_k, \tag{5}
\]

and

\[
I_{\mathbf{h}} \equiv I_{\text{obs}, \mathbf{h}} - \sum_{j=1}^{N} \hat{Z}_j^2, \tag{6}
\]

Eq.(2) reads

\[
I_{\mathbf{h}} = \sum_{j=1}^{\mathcal{N}} \nu_j e^{i2\pi\mathbf{h} \cdot \mathbf{\delta}_j}, \tag{7}
\]

where \( \mathcal{N} \) is the number of the \( \nu_j \)'s different from zero. [In the case of neutron scattering, \( \mathcal{N} \) can be smaller than \( \mathcal{N}' \) because the negativeness of some \( \hat{Z}_j \)'s can make some \( \nu_j \)'s equal to zero.] Eq.(7) shows that the \( I_{\mathbf{h}} \)'s, the "subtracted" peak intensities defined by Eq. (6), are the Fourier transforms of the scattering density...
relevant to the Patterson map

\[ \rho_{\text{Pat}}(\mathbf{r}) = \sum_{j=1}^{N} \nu_j \delta(\mathbf{r} - \mathbf{\delta}_j). \]  

(8)

This consists of \(N\) scattering centres located at \(\mathbf{\delta}_1, \ldots, \mathbf{\delta}_N\) with weights or "charges" equal to \(\nu_1, \ldots, \nu_N\), and the positiveness of the weights is ensured only in the case of X-ray scattering. Moreover, Eqs. (6), (7) and (8) make it evident that the knowledge of all the observed intensities \(I_{\text{obs},h}\) only determines quantities \(\mathbf{\delta}_j\)'s and \(\nu_j\)'s, \(i.e.\) the scattering density of the Patterson map. Assuming the latter quantities known, Eqs (3) and (5) can be inverted to determine the atoms’ positions \(\mathbf{r}_1, \ldots, \mathbf{r}_N\) by the procedure reported in §3.2 of I. This deconvolution of the Patterson map involves a finite number of operations. In this way, all the atomic configurations that reproduce the observed diffraction pattern are determined. Hence, the difficult problem to be solved is to find out the set of Eq.s (7) that uniquely determine \(N, \mathbf{\delta}_j\) and \(\nu_j\) for \(j = 1, \ldots, N\). The solution of this problem requires, firstly, the choice of an appropriate set of \(h\) values that determine the equations to be solved and, secondly, a procedure able to solve the resulting set of non-linear equations.

For X-ray scattering, the solution of the first problem is achieved by introducing the Goedkoop (1950) lattice of vectors, which is a subset of a finite-dimensional Hilbert space. Unfortunately, this step requires that all the \(\nu_j\)'s are positive and, therefore, it cannot be extended to the case of neutrons. However, by using some notions of elementary Quantum Mechanics, we show now that in both cases it is possible to introduce a finite-dimensional Hilbert space and, within the latter, a lattice of vectors in such a way that the scattering density (8) and the "subtracted" intensities (7) are two different representations of a single hermitian operator.
To this aim we recall that the position and momentum operator, respectively denoted by $\vec{R}$ and $\vec{P}$, have eigenvectors $|r\rangle$ and $|p\rangle$ whose eigenvalues $r$ and $p$ span the full 3D space $\mathbb{R}^3$. Consider now the eigenvalues $p$ equal to $-2\pi h$, $h$ being a triple of integers, and put $|h\rangle \equiv |2\pi h\rangle$. As $h$ ranges over the 3D lattice $\mathbb{Z}^3$, the set of $|h\rangle$’s defines a lattice of vectors lying within the infinite-dimensional Hilbert space $\mathcal{H}$ spanned by the eigenvectors $|p\rangle$ or $|r\rangle$. Introduce now the linear operator

$$Q \equiv \sum_{j=1}^{N} |\delta_j\rangle\langle\delta_j|,$$  

(9)

where $|\delta_j\rangle$ is the eigenvector of $\vec{R}$ with eigenvalue $\delta_j$ equal to the position vector of the $j$th scattering centre. Due to the property $\langle r| r' \rangle = \delta(r - r')$, the matrix elements of $Q$ with respect to the eigenvectors of $\vec{R}$ are

$$\langle r|Q|r' \rangle = \delta(r - r') \sum_{j=1}^{N} \nu_j \delta(r - \delta_j),$$  

(10)

At the same time, the matrix elements of $Q$ with respect to the lattice vectors $|h\rangle$ are

$$(h|Q|h') = (2\pi)^{-3} \sum_{j=1}^{N} \nu_j e^{i2\pi \delta_j \cdot (h - h')},$$  

(11)

where we used the property that $\langle p| r \rangle = e^{i p \cdot r} / (2\pi)^{3/2}$ and units such that $\hbar = 1$ (Messiah, 1959). Comparison of (10) with (8) shows that the scattering density (8) coincides with the diagonal matrix elements of $Q$ (leaving aside the divergent factor related to the value $\delta(0)$ of the 1st Dirac function). On the other hand, the comparison of (11) with (7) shows that all the subtracted intensities (7) are $(2\pi)^3$ times the matrix elements of $Q$ with respect to the lattice vectors $|h\rangle$. Moreover, Eq.(9) shows that the ”charge density” operator $Q$ is determined only by the $N$ eigenvectors $|\delta_1\rangle, \ldots, |\delta_N\rangle$ of $\vec{R}$ with eigenvalues equal to the positions of the $N$
scattering centres, and by the $N$ real numbers $\nu_1, \ldots, \nu_N$ equal to the weights of the scattering centres. Hence, we can restrict ourselves to the finite-dimensional Hilbert space $\mathcal{H}(N)$ spanned by the vectors $|\vec{\delta}_1\rangle, \ldots, |\vec{\delta}_N\rangle$ and defined as

$$\mathcal{H}(N) \equiv \{ |v\rangle = \sum_{j=1}^{N} \alpha_j |\vec{\delta}_j\rangle \mid \alpha_1, \ldots, \alpha_N \in C \}.$$ 

Vectors $|\vec{\delta}_1\rangle, \ldots, |\vec{\delta}_N\rangle$ obey the orthonormality condition

$$\langle \vec{\delta}_{j'} | \vec{\delta}_j \rangle = \delta_{j,j'}, \quad j, j' = 1, \ldots, N, \quad (12)$$

$\delta_{j,j'}$ being the Kronecker symbol, as well as the completeness relation

$$\sum_{j=1}^{N} |\vec{\delta}_j\rangle \langle \vec{\delta}_j| = 1. \quad (13)$$

In order to preserve the validity of (11), we still need to assume that $\mathcal{H}(N)$ contains a lattice of vectors $|h\rangle$ [not to be confused with $|\vec{\delta}\rangle$] or with the eigenvectors of $\vec{P}$, see the following Eq. (17). To this aim, it is sufficient to put

$$|h\rangle \equiv \sum_{j=1}^{N} e^{-i2\pi h \cdot \vec{\delta}_j} |\vec{\delta}_j\rangle, \quad \forall h \in \mathbb{Z}^3. \quad (14)$$

After taking the scalar product with $\langle \vec{\delta}_{j'} |$ one gets

$$\langle \vec{\delta}_{j'} | h \rangle = e^{-i2\pi h \cdot \vec{\delta}_{j'}}, \quad \forall h \in \mathbb{Z}^3, \quad j' = 1, 2, \ldots, N. \quad (15)$$

From the above two relations it follows that vectors $|h\rangle$ are no longer orthogonal since from (14) and (12) one gets

$$\langle h | h' \rangle = \sum_{j=1}^{N} e^{i2\pi \delta_{j} (h-h')} = \langle h + m| h' + m \rangle, \quad \forall h, h', m \in \mathbb{Z}^3, \quad (16)$$

\footnote{By so doing, the previous normalization $\langle \vec{\delta}_{j'} | \vec{\delta}_j \rangle = \delta(\vec{\delta}_{j'} - \vec{\delta}_j)$ has been scaled to $\langle \vec{\delta}_{j'} | \vec{\delta}_j \rangle = \delta_{j,j'}.$}
with $\langle h|h \rangle = \bar{N}$. This property is not surprising if one observes that $|h\rangle$ and $|h\rangle$ are related as follows

$$|h\rangle = (2\pi)^{3/2} \sum_{j=1}^{\bar{N}} |\vec{\delta}_j\rangle \langle \vec{\delta}_j| |h\rangle$$

(17)

so that $|h\rangle$ is the projection of $|h\rangle(\in \mathcal{H})$ into $\mathcal{H}(\bar{N})$ and, therefore, it is no longer an eigenvector of $\bar{P}$. Now it is important to note that

$$\langle h'|Q|h \rangle = \sum_{j=1}^{\bar{N}} \nu_j e^{i2\pi \vec{\delta}_j \cdot (h'-h)} = I_{h'-h}.$$  

(18)

Thus, on the one hand, all the matrix elements of $Q$ with respect to the lattice of vectors $|h\rangle$ reproduce the full diffraction pattern. On the other hand, the diagonal matrix elements of $Q$ with respect to the basis vectors $|\vec{\delta}_j\rangle$ are the weights of the scattering density (8). In this way, it has been shown that: i) both for X-ray and for neutron scattering it can be introduced a finite-dimensional Hilbert space $\mathcal{H}(\bar{N})$ spanned by the $\bar{N}$ eigenvectors of $\bar{R}$ associated to the position vectors of the $\bar{N}$ scattering centres, ii) within $\mathcal{H}(\bar{N})$ it exists a lattice of vectors $\mathcal{Z}_v^3 = \{|h\rangle | h \in \mathbb{Z}^3\}$ with $|h\rangle$ defined by Eq. (14), iii) it exists a hermitian linear operator $Q$ whose matrix elements with respect to the basis vectors $|\vec{\delta}_j\rangle$ and to the vectors of the vectorial lattice $\mathcal{Z}_v^3$ yield all the weights of the scattering density and all the subtracted intensities $I_h$, respectively.

We are now left with the problem of determining $\bar{N}$, the $|\vec{\delta}_j\rangle$’s and the $\nu_j$’s knowing an appropriate number of $I_h$ values. Before tackling with this problem in the following sections, we report some interesting consequences of the aforesaid vectorial structure underlying the phase problem for an ideal crystal. The first, related to Eq. (16), shows that $\langle h'|h \rangle = \langle h' + m|h + m \rangle$, $\forall h, h', m \in \mathbb{Z}^3$. Thus, the scalar product of any two vectors of $\mathcal{Z}_v^3$ does not change if the associated lattice
points are translated by an arbitrary vector \( \mathbf{m} \in \mathbb{Z}^3 \). The same property applies to \( \langle \mathbf{h}'|\mathcal{Q}|\mathbf{h} \rangle \) because by Eq. (18) one gets

\[
I_{\mathbf{h}'-\mathbf{h}} = \langle \mathbf{h}'|\mathcal{Q}|\mathbf{h} \rangle = \langle \mathbf{h}' + \mathbf{m}|\mathcal{Q}|\mathbf{h} + \mathbf{m} \rangle = \langle \mathbf{h}' - \mathbf{h}|\mathcal{Q}|0 \rangle, \quad \forall \, \mathbf{h}, \mathbf{h}', \mathbf{m} \in \mathbb{Z}^3. \tag{19}
\]

Second, \( \mathbb{Z}_v^3 \) cannot contain more than \( \bar{N} \) linearly independent vectors because it is a subset of \( \mathcal{H}(\bar{N}) \). In Appendix A it will be shown that \( \mathbb{Z}_v^3 \) exactly contains \( \bar{N} \) linearly independent vectors. Thus, if we denote one set of these vectors by \( |k_1\rangle, |k_2\rangle, \ldots, |k_{\bar{N}}\rangle \), we can write

\[
|h\rangle = \sum_{j=1}^{\bar{N}} A_{h,j} |k_j\rangle, \quad \forall \, h \in \mathbb{Z}^3. \tag{20}
\]

Taking the scalar product of the adjoint of this equation with vector \( |0\rangle \) and using Eq. (19) one obtains

\[
I_h = \sum_{j=1}^{\bar{N}} \bar{A}_{h,j} \langle k_j|\mathcal{Q}|0 \rangle = \sum_{j=1}^{\bar{N}} \bar{A}_{h,j} I_{k_j} \quad \forall \, h \in \mathbb{Z}^3, \tag{21}
\]

where the overbar denotes the complex conjugate. Eq. (21) shows that any subtracted intensity \( I_h \) is a linear combination of the \( \bar{N} \) intensities \( I_{k_1}, \ldots, I_{k_{\bar{N}}} \). The matrix elements \( A_{h,j} \) obey to a set of relations. The first is obtained by taking the scalar product of (20) with \( \langle \bar{\delta}_j \rangle \) and reads

\[
e^{-i2\pi h \cdot \bar{\delta}_j} = \sum_{\ell=1}^{\bar{N}} A_{h,\ell} e^{-i2\pi k_{\ell} \cdot \bar{\delta}_j}, \quad \forall \, h \in \mathbb{Z}^3, \quad j = 1, 2, \ldots, \bar{N}. \tag{22}
\]

After introducing an \( \bar{N} \times \bar{N} \) matrix \( \mathcal{V} \) with \( \mathcal{V}_{j,\ell} \equiv e^{-i2\pi k_{\ell} \cdot \bar{\delta}_j} \), the previous equations becomes

\[
\sum_{\ell=1}^{\bar{N}} \mathcal{V}_{j,\ell} A_{h,\ell} = e^{-i2\pi h \cdot \bar{\delta}_j}, \tag{23}
\]

which, as it will be shown later, can formally be solved as

\[
A_{h,\ell} = \sum_{j=1}^{\bar{N}} (\mathcal{V}^{-1})_{\ell,j} e^{-i2\pi h \cdot \bar{\delta}_j} \tag{24}
\]
The second is obtained by substituting Eq. (20) in Eq. (19), using Eq. (21) and the linear independence of $|k_1⟩, \ldots, |k_N⟩$. One finds

$$\tilde{A}_{h-h',l} = \sum_{j=1}^{N} \sum_{j'=1}^{N} \tilde{A}_{h,j} A_{h',j'} \tilde{A}_{k_j-k_{j'},l} \quad \forall h, h' \in \mathbb{Z}^3, \ l = 1, 2, \ldots, \bar{N}.$$  \hspace{1cm} (25)

### 3 Neutron scattering

Given their lengthy nature, we report in Appendix A the proof of the existence of the principal basic set of vectors $|h⟩$ along a crystallographic axis, and in Appendix B the analytic expression of the determinant of the Karle-Hauptman matrix associated to this principal basic set of vectors. It is stressed that these results, worked out in the two-dimensional case ($D = 2$), apply both for X-ray and for neutron scattering, because we never require the positivity in proving them. Moreover, they easily generalize to the three-dimensional case. In this section we show how to single out a basic set of reflections in the case of neutron scattering, knowing an appropriate number of subtracted intensities $I_h$. [For simplicity we shall still confine ourselves to the case $D = 2$.] Firstly, we recall that the results, obtained in the previous section as well as in Appendices A and B independently of the positiveness, show that: i) it is possible to introduce a Hilbert space $\mathcal{H}(\bar{N})$ having as an orthonormal basis the set of the (scaled) eigenvectors $|\tilde{\delta}_j⟩$ of $\tilde{R}$ with eigenvalues equal to the position vectors $\tilde{\delta}_j$ of the $N$ scattering centres of the (infinitely resolved) Patterson map determined by the full diffraction pattern, ii) within $\mathcal{H}(\bar{N})$ it is possible to extract a lattice $\mathbb{Z}_v^2$ of vectors $|h⟩$ defined by (14), iii) the (subtracted) intensities defined by (6) are the matrix elements of the charge density operator $Q$ [defined by
with respect to vectors of $\mathcal{Z}^2_\nu$, while the charges $\nu_j$ are the eigenvalues of the eigenvectors $|\vec{\delta}_j\rangle$ of $\mathcal{Q}$, iv) the knowledge of the eigenvalues $\vec{\delta}_j$ allows us to determine the subset $\mathcal{I}$ [defined by (39)] of $\mathcal{Z}^2$ and the translation of $\mathcal{I}$ by $(-1, -1)$ yields the principal basic set $\mathcal{B}(a^*)$ of $\mathcal{H}(N)$ along the reciprocal crystallographic direction $a^*$ and, finally, v) the algebraic expression of the determinant of the KH matrix associated to $\mathcal{B}(a^*)$ is given by Eq. (69). Even though results i)-iv) were essentially obtained in papers I and II, it is stressed that they are now extended to the case of neutrons. Moreover, the above presentation makes the introduction of $\mathcal{H}(N)$ clearer and shows that the $\nu_j$'s and the $I_n$'s are the matrix elements of a single operator ($\mathcal{Q}$) with respect to two different sets of vectors. As yet, however, the aforesaid generalization is practically useless, because we do not know the $\vec{\delta}_j$'s and $\bar{N}$. Since the only known quantities are the subtracted intensities $I_n$, the determination of the $\vec{\delta}_j$'s, $\nu_j$'s and $\bar{N}$ must be carried out in terms of the $I_n$'s. Hence, the search of a basic set must be performed in terms of these quantities. In papers I and II, we reported the procedures for carrying through such a search. Unfortunately, they only apply to the case of X-ray scattering because they exploit the positiveness of the charge density operator $\mathcal{Q}$, a condition fulfilled only in the case of X-rays. Very briefly, as shown in I and II, the simplest search of a basic set proceeds as follows. One starts from the set of reflections $\mathcal{B}_2 = \{(0,0),(1,0)\}$ and one evaluates the determinant of the associated KH matrix $\left(\mathcal{D}[\mathcal{B}_2]\right)$. If $\det\left(\mathcal{D}[\mathcal{B}_2]\right) \neq 0$, one "enlarges" $\mathcal{B}_2$ by "adding" to it the next reflection $(2,0)$ so as to have the new set $\mathcal{B}_3 = \{(0,0),(1,0),(2,0)\}$. Then one evaluates $\det\left(\mathcal{D}[\mathcal{B}_3]\right)$ and if this value is different from zero one adds the next reflection $(3,0)$ to $\mathcal{B}_3$ so to have the enlarged set $\mathcal{B}_4$. As far as the vectors associated to the reflections of the considered
set are linearly independent, the positiveness of $Q$ ensures that the corresponding KH matrix has a strictly positive determinant. On the contrary, if the vectors are linearly dependent the determinant is equal to zero. This property is easily shown as follows. Assume that $\mathcal{B}_m = \{h_1, h_2, \ldots, h_m\}$ and consider the $m \times m$ matrix $(Q_m)$ having its $(r, s)$ element given by

$$
\langle h_r | Q | h_s \rangle = I_{h_r - h_s} = \sum_{j=1}^N \langle h_r | \delta_j \rangle \nu_j \langle \delta_j | h_s \rangle = \sum_{j=1}^N \nu_j \nu_j \nu_{j,s} \quad r, s = 1, \ldots, m
$$

(26)

where Eq. (15) and the definition of $V_{j,l}$ reported below Eq. (22) have been used. Eqs. (26) can be written in matricial form as

$$
\left( Q_m \right) = \left( V^\dagger \right) \cdot (v) \cdot (v)
$$

(27)

where $(v)$ is now an $\bar{N} \times m$ matrix (with $m < \bar{N}$), $(v^\dagger)$ its hermitian conjugate and $(v)$ an $\bar{N} \times \bar{N}$ diagonal matrix with its $(j, j')$ element equal to $\nu_j \delta_{j,j'}$. The determinant of matrix $(Q_m)$, evaluated by Bezout’s theorem (Gantmacher, 1966), yields

$$
\det(Q_m) = \sum_{1 \leq j_1 < j_2 < \cdots < j_m \leq \bar{N}} \left[ \nu_{j_1} \cdots \nu_{j_m} \right] \left| \det(V_{j_1, \cdots, j_m}) \right|^2,
$$

(28)

where $(V_{j_1, \cdots, j_m})$ denotes the $m \times m$ minor formed with the $j_1$th, $\cdots$, $j_m$th row of $(v)$. In the case of X-rays the non-negativeness of the addends present in the above sum implies that $\det(Q_m) \neq 0$ unless all the quantities $\det(V_{j_1, \cdots, j_m})$ are equal to zero for $1 \leq j_1 < j_2 < \cdots < j_m \leq \bar{N}$. The latter conditions are verified if and only if the considered vectors $|h_1\rangle, \ldots, |h_m\rangle$ are linearly dependent. In fact, when this condition is fulfilled, the generic vector

$$
|a\rangle = \sum_{r=1}^m \alpha_r |h_r\rangle, \quad \alpha_1, \ldots, \alpha_m \in \mathbb{C}
$$
can be equal to zero with some $\alpha_j$’s different from zero. Then, the scalar products with $\langle \vec{\delta}_j \rangle$ yields

$$
\langle \vec{\delta}_j | a \rangle = \sum_{r=1}^{m} \alpha_r \langle \vec{\delta}_j | h_r \rangle = \sum_{r=1}^{m} \alpha_r \nu_{j,r} = 0, \quad j = 1, \ldots, \bar{N}.
$$

This being a set of $\bar{N}$ linear homogeneous equations in the unknown $\alpha_1, \ldots, \alpha_m$, the Rouchè-Capelli theorem ensures that a non-trivial solution exists if and only if the rank of the $\bar{N} \times m$ matrix $(V)$ is smaller than $m$, i.e. if the determinants of all the $m \times m$ matrices contained in $(V)$ are equal to zero. In this case, one finds that $\det(Q_m) = 0$ and the vectors of the considered set $B_m$ are linearly dependent. On the contrary, if one of the $m \times m$ matrix contained in $(V)$ is non singular, all the $\alpha_m$’s are equal to zero, the vectors $|h_1\rangle, \ldots, |h_m\rangle$ are linearly independent and $\det(Q_m) \neq 0$. Coming back to the search procedure of a basic set, the aforesaid property makes it clear that the enlargement procedure comes to a halt when $\det(D[B_{\bar{m}}]) = 0$, i.e. when one finds a ”KH zero”. This condition must certainly occur because the number of the linearly independent vectors cannot exceed $\bar{N}$. Hence, according to the analysis reported in Appendix A, we find that $\bar{m} = \mu_1 = M$ and the vectors associated to the set $B_{\mu_1} = \{(0,0), \ldots, (M-1,0)\}$ are linearly independent. Then, we enlarge the previous set by adding to it, step by step, the reflections lying on the next upper row starting with $(0,1)$. The next KH zero is found when we ”add” the reflection $(\mu_2,1)$. We move now to the next upper row and we start by adding the reflection $(0,2)$ to the set $B_{\mu_1,\mu_2} = \{(0,0), \ldots, (\mu_1-1,0), (0,1), \ldots, (\mu_2-1,1)\}$. The search of the basis set is accomplished when we arrive at the point where the inclusion of the reflection $(0,m_1)$ leads to a KH zero. By construction, the resulting basis set is simply connected.
In the case of neutron scattering, this analysis is no longer possible because the finding of a KH zero (i.e. \( \det(\mathbf{Q}_m) = 0 \)), during the enlargement procedure, does not allow us to infer that the associated vectors are linearly dependent. This appears evident from Eq. (28): here, each factor related to the charge product is not ensured to be positive so that the condition \( \det(\mathbf{Q}_m) = 0 \) does not imply that all the quantities \( |\det(\mathbf{V}_{j_1,\ldots,j_m})|^2 \) are equal to zero. Thus, in order to extend the search procedure of a basic set to the case of neutron scattering, we must introduce a positive definite operator whose matrix elements with respect to the vectorial lattice \( \mathbf{Z}_v^2 \) are known in terms of the observed scaled intensities \( I_\mathbf{h} \). To this aim, denote by \( S_{\text{obs}} \) the set of the observed reflections and denote by \( S_1 \) the largest subset of \( S_{\text{obs}} \) such that for any two reflections \( \mathbf{h}_r \) and \( \mathbf{h}_{r'} \) in \( S_1 \) it results \( (\mathbf{h}_r - \mathbf{h}_{r'}) \in S_{\text{obs}} \). We denote by \( \mathcal{N}_1 \) the number of reflections contained in \( S_1 \) and we assume first that \( S_1 \) is large enough to contain at least one basic set so that \( \mathcal{N}_1 > \mathcal{N} \). Consider now the linear operator\(^4\)

\[
\mathbf{Q}_{S_1} \equiv \mathbf{Q} \sum_{r=1}^{\mathcal{N}_1} \left| \mathbf{h}_r \right\rangle \left\langle \mathbf{h}_r \right| \mathbf{Q}.
\]

This operator is hermitian and positive definite. The first property is evident. To show the second, we consider the expectation value of \( \mathbf{Q}_{S_1} \) with respect to an arbitrary vector \( |\mathbf{a}\rangle \in \mathcal{H}(\mathcal{N}) \). One finds that

\[
\left\langle \mathbf{a}|\mathbf{Q}_{S_1}|\mathbf{a}\right\rangle = \sum_{r=1}^{\mathcal{N}_1} \left| \left\langle \mathbf{a}|\mathbf{Q}|\mathbf{h}_r \right\rangle \right|^2
\]

This expectation value can be equal to zero either if \( \mathbf{Q}|\mathbf{a}\rangle \) is perpendicular to all the \( |\mathbf{h}_r\rangle \)'s for \( r = 1, \ldots, \mathcal{N}_1 \) or if \( \mathbf{Q}|\mathbf{a}\rangle = 0 \). The first condition is impossible unless

\(^4\)The introduction of this quantity is suggested by the procedure followed by Silva & Navaza (1981) and Navaza & Navaza (1992).
\( Q|a\rangle = 0 \) because \( S_1 \) is assumed to contain a basic set of vectors. We are left with the condition \( Q|a\rangle = 0 \). This implies that \( |a\rangle \) is eigenvector of \( Q \) with eigenvalue 0. But this condition is impossible because the eigenvalues of \( Q \) are all different from zero as it appears evident from Eq. (9). Hence, \( \langle a|Q_{S_1}|a\rangle > 0 \ \forall|a\rangle \neq 0 \) and the positivity of \( Q_{S_1} \) is proven. The matrix elements of \( Q_{S_1} \) with respect to the vectors of the lattice \( Z_v^2 \) are

\[
\langle h|Q_{S_1}|k\rangle = \sum_{r=1}^{N_1} I_{h-h_r} I_{h_r-k}.
\]

If \( h, k \in S_1 \), the matrix elements of \( Q_{S_1} \) are fully known and will be denoted as

\[
J_{h_l,h_m} \equiv \langle h_l|Q_{S_1}|h_m\rangle = \sum_{r=1}^{N_1} I_{h_l-h_r} I_{h_r-h_m}, \ l, m = 1, \ldots, N_1.
\]

(30)

[It is noted that the \( J_{h_l,h_m} \)'s are symmetric since they obey the relation \( J_{h_l,h_m} = J_{h_m,h_l} \) that follows from the Friedel property valid for the subtracted intensities, i.e. \( I_h = I_{-h} \).] At this point, the search of a basic set becomes possible acting as follows. We start from the set of reflections \( B_2 = \{(0,0),(0,1)\} \) and we evaluate the determinant of the matrix whose elements are the matrix elements of \( Q_{S_1} \) between the vectors associated to \( B_2 \). These matrix elements are known owing to (30). For simplicity, this matrix also will be called a Karle-Hauptman matrix, even though its matrix elements are the \( I_{h_l,h_m} \)'s instead of the \( I_{h_l,h_m} \)'s. If the determinant of this KH matrix is different from zero, we enlarge \( B_2 \) by adding to it a further reflection chosen either by the procedure described above or by one of the other procedures reported in II. Assume that \( B_m \) is the first set, found during the enlargement procedure, such that the determinant of the KH matrix (with elements \( I_{h_l,h_m} \)) is equal to zero. Since \( Q_{S_1} \) is a positive definite operator, the vectors \( |h_1\rangle, \ldots, |h_m\rangle \) associated to the reflections of \( B_m \) are linearly dependent.
Moreover, the vectors $|h\rangle$ considered in this paper do not depend on the charges $\nu_j$ [see Eq. (14)]. Actually, as explained in footnote 6, they refer to positive charges. Thus, property 1 proven in sect. 4 of II applies. Therefore, in the subsequent enlargement procedure, we must discard all the reflections relevant to the quadrant defined in property 1. The search of a basic set will be accomplished once the resulting set cannot further be enlarged by the adopted procedure of enlargement. If this happens, one concludes that the considered $S_1$ set and, consequently, the underlying limiting sphere are large enough to contain a basic set. Before discussing the consequences of this result, we need to say what happens when $S_1$ is not large enough to contain a basic set of vectors. In this case, we can always denote by $|h_1\rangle, \ldots, |h_M\rangle$ the $M(<N_1)$ linearly independent vectors contained in $S_1$ that are closer to the origin of reciprocal space. The remaining vectors $|h_{M+1}\rangle, \ldots, |h_{N_1}\rangle$ of $S_1$ take the form

$$ |h_r\rangle = \sum_{j=1}^{M} \alpha_{r,j} |h_j\rangle, \quad r = (M + 1), \ldots, N_1. $$

The aforesaid linearly independent vectors can be singled out by the centred square procedure reported in §5 of II because $Q_{S_1}$ is positive definite in the subspace spanned by $|h_1\rangle, \ldots, |h_M\rangle$. By so doing we shall find some KH zeros, but the KH matrix (with elements $T_{h_i, h_m}$) relevant to the set of vectors $B_M = \{|h_1\rangle, \ldots, |h_M\rangle\}$ certainly is non-singular. On the contrary, the KH matrices relevant to the $(N_1 - M)$ sets of vectors $B_M \cup |h_r\rangle$, with $r = (M + 1), \ldots, N_1$, are singular and all the $h_r$, with $r = (M + 1), \ldots, N_1$ are KH zeros. However, the locations of these zeros must be such that the configuration of $B_M$ is not that of a basic set, in the sense that the locations of the KH zeros is such that an "enlargement" of $B_M$ by the centred
square procedure is possible whenever one could dispose of a set $\mathcal{S}_1' \supset \mathcal{S}_1$ (as it would happen with a larger limiting sphere). One concludes that the configuration of the KH zeros associated to $\mathcal{B}_M$ is alike to that found in the previous case, *i.e.* when $\mathcal{S}_1$ contains $\mathcal{N}$ linearly independent vectors and a basic set is not found. Hence, only two cases are possible: either $\mathcal{S}_1$ is large enough to contain a basic set or it is not. In the second case, the observed diffraction pattern does not allow to solve the phase problem. In the first case, it does. In fact, as already stressed, the singled-out basic set is also a basic set for the substracted intensities $I_h$ and we can use all the results found in papers I and II for the case of X-ray scattering\(^5\). In particular, the knowledge of the basic set and of the further reflections where we have found a KH zero allow us to determine the associated *complete set* ($\mathcal{C}$) and *complementary set* ($\mathcal{F}$) of reflections. The first consists of the reflections differences of any two reflections of the basic set $\mathcal{B}_N$, and the second of the reflections (not contained in the complete set) that are differences of the reflections associated to the KH zeros with the reflections of the basic set. The recursive determination of the intensities relevant to the reflections not contained in $\mathcal{C} \cup \mathcal{F}$ proceeds along the lines described in I and one finds that also in the case of neutron scattering the full diffraction pattern is determined by the knowledge of the intensities associated to the finite set of reflections $\mathcal{C} \cup \mathcal{F}$. Moreover, each KH zero states that the added vector to $\mathcal{B}_m$ is a linear combination of the vectors of $\mathcal{B}_m$. The coefficients of the linear combination are obtained by solving the associated linear equations \(^5\)Strictly speaking, the determination of matrix ($T$) as reported in Appendix D of I is not possible in the case of neutron scattering. Hence, the matrix ($R$), instead of being evaluated by Eq. (I.2.41), must be evaluated by the first equality in Eq. (I.2.45), *i.e.* by inverting the KH matrix (with elements $I_{h_h, h_m}$) associated to the basic set of reflections.
whose matrix of coefficients is the KH matrix associated to $B_m$. The scalar product with $|\delta_j|$ yields a polynomial equations in the variables $e^{-i2\pi x_j}$ and $e^{-i2\pi y_j}$ (we recall that we are considering the case $D = 2$). The system of these polynomial equations has $2\tilde{N}$ common unimodular roots that are related to the positions of the $\tilde{N}$ scattering centres as it is just specified. It is interesting to note that, by following the procedure reported in sect. 6 of II, the aforesaid system of polynomial equations in two variables can be converted into a set of polynomial equations in a single variable, so as to make the solution of the problem simpler.

4 Conclusion

The results reported in §3 and appendices A and B refer to the two-dimensional case. Their extension to the case $D = 3$ is rather straightforward by following the lines illustrated in paper II. In particular, we write now $\delta_j$ as $(x_1, y_1, z_1, j, \ell)$ where index $i$ labels the different projections of all the $\tilde{\delta}_j$’s along $a = \hat{x}$, $j$ the different projections of the $\tilde{\delta}_j$’s that have the same $\hat{x}$ projection along $b = \hat{y}$, and $\ell$ the different projections along $c = \hat{z}$ of the $\tilde{\delta}_j$’s that have the same $\hat{x}$ and $\hat{y}$ projections. Then the set $I$ becomes

$$I \equiv \{(i, j, \ell) \mid 1 \leq \ell \leq q_{i,j}, \quad 1 \leq j \leq p_i, \quad 1 \leq i \leq M\}, \quad (31)$$

with $\tilde{N} = \sum_{i=1}^{M} \sum_{j=1}^{p_i} q_{i,j}$. Here label $i$ is assigned in such a way that $p_1 \geq p_2 \geq \cdots \geq p_M$. Then, for each $i$, label $j$ is defined in such a way that $q_{i,1} \geq \cdots \geq q_{i,p_i}$, and similarly for $\ell$. After putting

$$\xi_i \equiv e^{-i2\pi x_i}, \quad \eta_{i,j} \equiv e^{-i2\pi y_{i,j}}, \quad \text{and} \quad \zeta_{i,j,\ell} \equiv e^{-i2\pi z_{i,j,\ell}} \quad (32)$$
a generic vector $|h\rangle$ with $h = (h, k, l)$ takes the form

$$|h, k, l\rangle = \sum_{i=1}^{M} \sum_{j=1}^{p_i} \sum_{\ell=1}^{q_{i,j}} \xi_i^h \eta_{i,j}^k \zeta_{i,j,\ell}^l |x_i, y_{i,j}, z_{i,j,\ell}\rangle. \quad (33)$$

By the same analysis carried out in Appendix A, one finds that the basic set of reflections consists of the reflections $(h, k, l)$ determined by the conditions: $0 \leq l \leq (q_{h+1,k+1}-1)$, $0 \leq k \leq (p_{i+1}-1)$ and $0 \leq h \leq (M-1)$, so that $\mathcal{B}(a^*)$ coincides with $\mathcal{I}$ shifted by $(-1,-1,-1)$. The generic element $V_{h,j}$ of the associated $\bar{N} \times \bar{N}$ matrix $(\mathcal{V})$ now reads $\xi_i^h \eta_{i,j}^k \zeta_{i,j,\ell}^l$ and, generalizing the procedure followed for obtaining Eq (66), one finds that its determinant is

$$\det(\mathcal{V}) = \left[ \prod_{i=1}^{M} \prod_{j=1}^{p_i} \prod_{1 \leq s_1 < s_2 \leq q_{i,j}} \left( \xi_{i,j,s_2} - \xi_{i,j,s_1} \right) \right] \cdot \left[ \prod_{1 \leq t_1 < t_2 \leq M} \left( \xi_{t_2} - \xi_{t_1} \right)^{\min(P_{t_2},P_{t_1})} \right] \cdot \left[ \prod_{i=1}^{M} \prod_{1 \leq r_1 < r_2 \leq p_i} \left( \eta_{i,r_2} - \eta_{i,r_1} \right)^{\min(q_{i,r_2},q_{i,r_2})} \right], \quad (34)$$

where it has been put $P_i = \sum_{j=1}^{p_i} q_{i,j}$ for $i = 1, \ldots, M$. Since Eq. (68) holds also true in the 3D case, one concludes that the determinant of the KH matrix associated to the 3D principal basic set of reflections defined above has the following algebraic expression

$$\det\left(D[\mathcal{B}(a^*)]\right) = \left[ \prod_{i=1}^{M} \prod_{j=1}^{p_i} \prod_{1 \leq s_1 < s_2 \leq q_{i,j}} \left| \xi_{i,j,s_2} - \xi_{i,j,s_1} \right|^2 \right] \cdot \left[ \prod_{1 \leq t_1 < t_2 \leq M} \left| \xi_{t_2} - \xi_{t_1} \right|^{2\min(P_{t_2},P_{t_1})} \right] \cdot \left[ \prod_{i=1}^{M} \prod_{1 \leq r_1 < r_2 \leq p_i} \left| \eta_{i,r_2} - \eta_{i,r_1} \right|^{2\min(q_{i,r_2},q_{i,r_2})} \right] \cdot \prod_{j=1}^{N} \nu_j. \quad (35)$$

In conclusion, it has been shown that the algebraic approach applies both to X-ray and to neutron scattering. In this way it appears clear that the atomicity is the crucial assumption, while the positiveness of the scattering density is from a theoretical point of view not important. It only makes the search of the basic set...
faster, because the search can be carried through with the subtracted intensities $I_h$.
On the contrary, in the case of neutrons, the procedure is slightly more involved, because one must first select the largest $S_1$ subset within the observed diffraction pattern and by these intensities to evaluate the $J_{h_r,h_s}$’s for all the $h_r$ and $h_s$ of $S_1$. Then, the search of a basic set is performed, as in the case of X-ray scattering, using the $J_{h_r,h_s}$’s. Finally, after finding a basic set, one proceeds with the $I_h$’s and with the found basic set to reconstruct the full diffraction pattern and to determine the atomic positions as in the case of X-ray scattering.
A Principal basic sets for the 2-D case

We show now that $Z^3$ contains different sets of $\bar{N}$ linearly independent vectors and we report the procedure for selecting one of these sets. Actually, this proof is immediately achieved by the procedures illustrated in I and II if we assume to know the quantities

$$\tilde{I}_{h,k} \equiv \langle h|k \rangle = \sum_{j=1}^{\bar{N}} e^{i2\pi(h-k)\cdot \vec{\delta}_j} = I_{h-k}$$  \hspace{1cm} (36)

[where the rhs follows from Eq. (16)], because the involved vectors belong to $Z^3$ and, therefore, belong to a Hilbert space so that the assumptions, made in I and II, are obeyed\(^6\). We prefer however to proceed differently in order to make it evident that the geometry of the scattering centres determines the principal basic set of reflections. To this aim, we first observe that all the equations reported in §2 hold also true if we restrict ourselves, for greater notational simplicity, to the case of a 2D space. We remark that, even though the locations of the $\bar{N}$ scattering centres are different from each other, it can happen that the distinct projections of the $\vec{\delta}_j$’s along one of the crystal axes are only $M$ with $M < \bar{N}$. Hence, we shall denote the distinct projections along $\hat{x} = a$ by $x_1, \ldots, x_M$. Consider now those $\vec{\delta}_j$’s that have $x$-projections equal to, say, $x_1$. Since these $\vec{\delta}_j$’s are different, their projections along axis $y$ must differ among themselves and we shall denote their number by $m_1 \geq 1$. In this way, the considered $\vec{\delta}_j$’s can be written as $[(x_1,y_1), (x_1,y_2), \ldots, (x_1,y_{m_1})]$ and, in general, we have

$$\left\{ \vec{\delta}_1, \ldots, \vec{\delta}_N \right\} = \left\{ (x_r,y_{r,s}) \mid s = 1, 2, \ldots, m_r, \ r = 1, \ldots, M, \right\} \hspace{1cm} (37)$$

\(^6\)The comparison of (36) with (7) shows that the $\tilde{I}_{h-k}$’s can be considered as the scattering intensities relevant to a set of $\bar{N}$ scattering centres, located at $\vec{\delta}_1, \ldots, \vec{\delta}_N$, with positive charges all equal to one.

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Further, in labeling the different \( x_r \), we choose the label in such a way that \( m_1 \geq m_2 \geq \cdots \geq m_M \). It is observed that points \((x_r, y_{rs})\) can be mapped into a subset \( \mathcal{I} \) of the \( \mathbb{Z}^2 \) lattice defined either as

\[
\mathcal{I} \equiv \{(r, s) \mid s - 1, \ldots, m_r, \ r = 1, \ldots, M\}
\]

(38)

or as

\[
\mathcal{I} \equiv \{(r, s) \mid r = 1, \ldots, \mu_s, \ s = 1, \ldots, m_1\}
\]

(39)

In the first case, \( m_r \) is the number of points lying on the \( r \)th column, while in the second \( \mu_s \) is the number of points lying on the \( s \)th row. In both cases, we have \( \sum_{r=1}^{M} m_r = \sum_{s=1}^{m_1} \mu_s = \bar{N} \). Writing \(|h\rangle\) as \(|h, k\rangle\) with \( h \) and \( k \) integers, Eq. (14) reads

\[
|h, k\rangle = \sum_{r=1}^{M} \sum_{s=1}^{m_r} e^{-i2\pi x_r} e^{-i2\pi y_{rs}} |x_r, y_{rs}\rangle,
\]

or, after putting

\[
\xi_r \equiv e^{-i2\pi x_r} \quad \text{and} \quad \eta_{r,s} \equiv e^{-i2\pi y_{rs}},
\]

(40)

as

\[
|h, k\rangle = \sum_{r=1}^{M} \sum_{s=1}^{m_r} \xi_r^h \eta_{r,s}^k |x_r, y_{rs}\rangle.
\]

(41)

Consider now the polynomial

\[
P_M(z) = \prod_{r=1}^{M} (z - \xi_r) = \sum_{s=0}^{M} \alpha_{M,s} z^s
\]

(42)

with

\[
\alpha_{M,s} = (-1)^{M-s} \sum_{1 \leq s_1 < s_2 < \cdots < s_{M-s} \leq M} \xi_{s_1} \xi_{s_2} \cdots \xi_{s_{M-s}}, \quad s = 0, \ldots, (M - 1),
\]

(43)
and $\alpha_{M,M} = 1$. Eq. (42) implies that $P_M(\xi_r) = 0$ for $r = 1, \ldots, M$. From Eq. (42) one gets
\begin{equation}
\xi_r^M = - \sum_{s=0}^{M-1} \alpha_{M,s} \xi_{r}^s \equiv \sum_{s=0}^{M-1} \beta_{M,M,s} \xi_{r}^s, \quad r = 1, \ldots, M
\end{equation}
and substituting these relations in $|M, k\rangle$ one obtains
\begin{equation}
|M, k\rangle = - \sum_{p=0}^{M-1} \alpha_{M,p} \sum_{r=1}^{M} m_r \xi_{r}^p \eta_{r,s}^{k} |x_r, y_{r,s}\rangle = \sum_{s=0}^{M-1} \beta_{M,M,s} |s, k\rangle,
\end{equation}
which shows that $|M, k\rangle$ is a linear combination of vectors $|s, k\rangle$ defined as
\begin{equation}
|s, k\rangle \equiv \sum_{r=1}^{M} \sum_{p=1}^{m_r} \xi_{r}^{s} \eta_{r,p}^{k} |x_r, y_{r,p}\rangle, \quad s = 0, \ldots, (M - 1).
\end{equation}
Moreover, after multiplying both sides of Eq. (44) by $\xi_r$ and using again Eq. (44), one gets
\begin{equation}
\xi_r^{M+1} = - \sum_{s=0}^{M-2} \alpha_{M,s} \xi_r^{s+1} - \alpha_{M,(M-1)} \xi_r^M \equiv \sum_{s=0}^{M-1} \beta_{M,(M+1),s} \xi_r^s, \quad r = 1, \ldots, M,
\end{equation}
with
\begin{equation}
\beta_{M,(M+1),s} = \begin{cases}
\alpha_{M,(M-1)} \alpha_{M,s}, & \text{if } s = 0, \\
-\alpha_{M,s-1} + \alpha_{M,(M-1)} \alpha_{M,s}, & \text{if } s = 1, \ldots, (M-1).
\end{cases}
\end{equation}
Eq. (47) shows that $\xi_r^{M+1}$ also is a linear combination of $\xi_r^0, \ldots, \xi_r^{M-1}$ with coefficients $\beta_{M,(M+1),s}$ specified by Eq. (48) and obtained by a recursive application of Eq. (44). After dividing the equation $P_M(\xi_r) = 0$ by $\xi_r^{-1}$, one obtains that
\begin{equation}
\xi_r^{-1} = - \alpha_{M,0}^{-1} \sum_{s=0}^{M-1} \alpha_{M,s+1} \xi_r^s \equiv \sum_{s=0}^{M-1} \beta_{M,-1,s} \xi_r^s, \quad r = 1, \ldots, M.
\end{equation}
Iterating the procedure one finds that
\begin{equation}
\xi_r^k = \sum_{s=0}^{M-1} \beta_{M,k,s} \xi_r^s, \quad r = 1, \ldots, M, \quad \forall k \geq M, \quad \forall k \leq -1.
\end{equation}
From these relations it follows that

$$|h, k⟩ = \sum_{s=0}^{M-1} \beta_{M,h,s}|s, k⟩, \quad \forall h \geq M, \quad \forall h \leq -1. \quad (50)$$

Consider now the polynomials

$$P_{mr}(z) = \prod_{s=1}^{m_r} (z - \eta_{r,s}), \quad \text{for} \quad r = 1, \ldots, M. \quad (51)$$

By the same procedure, one proves that

$$\eta_{r,s}^k = \sum_{q=0}^{m_r-1} \beta_{m_r,k,q} \eta_{r,q}^q, \quad r = 1, \ldots, M, \quad s = 1, \ldots, m_r, \quad \forall k \geq m_r, \quad \forall k \leq -1 \quad (52)$$

where coefficients $\beta_{m_r,k,q}$ are iteratively determined in terms of the coefficients that define the polynomials (51). We put now

$$|x_{r,k}⟩ \equiv \sum_{s=1}^{m_r} \eta_{r,s}^k |x_{r,r,s}⟩, \quad k = 0, 1, \ldots. \quad (53)$$

From Eqs (12) and (40) it follows that

$$\langle x_{s,k'}|x_{r,k}⟩ = \delta_{s,r} \sum_{s=1}^{M} \eta_{r,s}^{k-k'} \quad (54)$$

and one concludes that vectors $|x_{r,k}⟩$ and $|x_{s,k'}⟩$ are linearly independent if $r \neq s$. The same happens for the vectors $|x_{r,0}, \ldots, x_{r,(m_r - 1)}⟩$. This property immediately follows from Eq. (53), because the rhs of the equation involves $m_r$ linearly independent vectors at fixed $r$ and the matrix of coefficients $\eta_{r,s}^k$, with $k = 0, \ldots, (m_r - 1)$ and $s = 1, \ldots, m_r$, is a Vandermonde matrix with determinant equal to $\prod_{1 \leq p < q \leq m_r} (\eta_{r,q} - \eta_{r,p})$, which is certainly different from zero because the $\eta_{r,q}$’s are all different among themselves. Combining Eqs (41) and (53) one finds that

$$|h, k⟩ = \sum_{r=1}^{M} \xi_r^h |x_{r,k}⟩. \quad (55)$$
If $k = 0$, all the vectors on the rhs are linearly independent as $r$ ranges from 1 to $M$.

If we let $h$ range in $[0, \ldots, (M-1)]$, we have $M$ linear relations and the coefficient matrix is a Vandermonde matrix with determinant equal to $\prod_{1 \leq t < \ell \leq M} (\xi_j - \xi_t) \neq 0$.

Thus, the linear independence of $|x_1, 0\rangle, \ldots, |x_M, 0\rangle$ ensures the linear independence of the vectors $|0, 0\rangle, \ldots, |(M-1), 0\rangle$. If $m_M > 1$, by the same procedure and using the linear independence of the sets of vectors $[|x_1, k\rangle, \ldots, |x_M, k\rangle]$ for $k = 0, \ldots, (m_M - 1)$, one finds that each of the following sets of vectors $[[0, \ell], \ldots, |(M-1), \ell\rangle]$, with $\ell = 0, \ldots, (m_M - 1)$, is a set of $M$ linearly independent vectors. Moreover, the vectors $[[0, \ell], \ldots, |(M-1), \ell\rangle]$ are linearly independent from the vectors $[|0, j\rangle, \ldots, |(M-1), j\rangle]$ if $0 \leq \ell \neq j \leq (m_M - 1)$ due to Eq. (54). Consider now the $m \times m$ Vandermonde matrix $\left(\mathcal{V}(m, \xi)\right)$ with elements

$$\mathcal{V}_{j,k}(m, \xi) = \xi_j^{k-1}, \quad 1 \leq j, k \leq m. \quad (56)$$

As far as $m \leq M$, the aforesaid matrix is non-singular and endowed of an inverse denoted by $\left(\mathcal{V}^{-1}(m, \xi)\right)$. Then, one can write

$$|x_r, q\rangle = \sum_{s=1}^{M} \mathcal{V}^{-1}_{r,s}(M, \xi)(|s-1\rangle, q\rangle), \quad 1 \leq r \leq M, \quad 0 \leq q \leq (m_M - 1). \quad (57)$$

Assume now that $m_{M-1} > m_M$ and consider those values of $k$ such that $m_M \leq k < m_{M-1}$. Eq. (41) can be written by (52) as

$$|h, k\rangle = \sum_{r=1}^{M-1} \sum_{s=1}^{m_r} \xi_r^h \eta_{r,s} |x_r, y_{r,s}\rangle + \sum_{q=0}^{m_{M-1}} \xi^h \beta_{m_M, k,q} |x_M, q\rangle$$

$$= \sum_{r=1}^{M-1} \xi_r^h |x_r, k\rangle + \sum_{q=0}^{m_{M-1}} \xi_M^h \beta_{m_M, k,q} |x_M, q\rangle$$
that by Eq. (57) becomes

\[ |h, k\rangle = \sum_{q=0}^{m_M-1} \xi_M^h \beta_{m_M,k,q} \sum_{s=1}^{M} \mathcal{V}^{-1}_{r,s}(M, \xi)((s-1), q) \]

\[ = \sum_{r=1}^{M-1} \mathcal{V}_{r,(h+1)}(M-1, \xi)|x_r, k\rangle, \quad m_M \leq k \leq (m_{M-1} - 1). \quad (58) \]

The vectors \(|x_r, k\rangle\) present on the rhs of (58) are linearly independent for \(k = 0, \ldots, (M - 1)\) and the matrix \(\mathcal{V}(M - 1, \xi)\) is non singular. Thus, the vectors on the lhs are also linearly independent for \(0 \leq h \leq (M - 1)\) and \(m_M \leq k \leq (m_{M-1} - 1)\). The vectors within the sum present on the lhs of (58) were already shown to be linearly independent because they are characterized by \(q\) values ranging in \([0, (m_M - 1)]\). One concludes that the vectors \(|h, k\rangle\) with \(0 \leq h \leq (M - 1)\) and \(m_M \leq k \leq (m_{M-1} - 1)\) are linearly independent. In this way, we have proven that the vectors \(|h, k\rangle\) with \(0 \leq k \leq (m_{M-1} - 1)\) are linearly independent if \(0 \leq h \leq (\mu_k - 1)\), the integers \(\mu_k\) being defined by Eq. (39). If \(m_{M-1} = m_M\), the inequality \(m_M \leq k < m_{M-1}\) is never verified and it must be substituted with \(m_{M-1} \leq k < m_{M-2}\) provided \(m_{M-2} > m_{M-1}(= m_M)\). In this way, step by step, by the procedure just reported one shows that the vectors linearly independent are

\[ \mathcal{B}(a^*) \equiv \left\{ |h, k\rangle \mid h = 0, \ldots, (\mu_k - 1), \quad k = 0, \ldots, (m_1 - 1) \right\} \]

\[ = \left\{ |h, k\rangle \mid k = 0, \ldots, (m_h - 1), \quad h = 0, \ldots, (M - 1) \right\}. \quad (59) \]

The corresponding set of \((h, k)\) is nothing else that set \(\mathcal{I}\), specified by Eq. (39) and shifted by \((-1, -1)\). Hence it is fully specified by the geometry of the \(\tilde{\delta}_j\) values, once these values are mapped into \(\mathcal{I}\). The set \(\mathcal{B}(a^*)\) consists of \(\bar{N}\) points. It will be referred to as the principal basic set of vectors along reciprocal crystallographic axis \(a^*\): basic because \(\mathcal{B}(a^*)\) determines a complete basis of \(\mathcal{H}(\bar{N})\), linearly related
to that formed by $|\tilde{\delta}_1,..,|\tilde{\delta}_X\rangle$ and used to define $\mathcal{H}(\mathcal{N})$, and principal (along $a^*$) because $\mathcal{B}(a^*)$ has the largest extension along $a^*$ since, at each step of the procedure, we tried to include the largest number of reflections $(h, k)$ lying on the rows parallel to $a^*$. Any possible confusion being avoided by the context, the set of reflections $(h, q)$ with $h$ an $k$ obeying to the constraints specified in Eq.(59) will also be denoted by $\mathcal{B}(a^*)$ and named principal basic set of reflections. Papers I and II showed the existence of less elongated basic sets as well as the procedures for singling them out. These procedures are based on an "enlargement" method dictated by the Karle-Hauptman zeros found during the basic set search. On the contrary, the procedure illustrated above only bases on the geometry of the locations of the scattering centres.

B Generalized Vandermonde determinant

In Appendix A we showed that the vectors $|h, k\rangle$, with $h$ and $k$ obeying Eq. (59), are linearly independent because they form the principal basic set of vectors along $a^*$. Then, the associated matrix $(V)$ with its elements defined by Eq. (41) must be non-singular. The analytical expression of the determinant of this matrix $(V)$ is remarkably simple. To get this expression, we note that the full expression of $(V)$
The rows of \((\mathcal{V})\) correspond to \((r, s)\) with \(s = 1, \ldots, m_r\) and \(r = 1, \ldots, M\) and the columns to \((p, q)\) with \(q = 0, \ldots, (m_{p+1} - 1)\) and \(p = 0, \ldots, (M - 1)\). The determinant of \((\mathcal{V})\) is a homogeneous polynomial in variables \(\{\xi\}\) and \(\{\eta\}\), because each term of \(\det(\mathcal{V})\) has degree \(Q\) with respect to variables \(\{\eta\}\) and degree \(P\) in the \(\{\xi\}\)'s. \(Q\) and \(P\) respectively are

\[
Q = [0 + 1 + \cdots + (m_1 - 1)] + [0 + 1 + \cdots + (m_2 - 1)] + \cdots + [0 + 1 + \cdots + (m_M - 1)] = \sum_{k=1}^{M} m_k^2/2 - \bar{N}/2, \tag{61}
\]

and

\[
P \equiv 0 \cdot m_1 + 1 \cdot m_2 + \cdots + (M - 1) \cdot m_M \tag{62}
\]

If, whatever \(i, \eta_{i,j} = \eta_{i,l}\) with \(j \neq l\), two rows of \((\mathcal{V})\) are equal and the determinant will be equal to zero. Thus, one can write

\[
\det(\mathcal{V}) = \left[ \prod_{i=1}^{M} \prod_{1 \leq j_1 < j_2 \leq m_i} (\eta_{i,j_2} - \eta_{i,j_1}) \right] \cdot \mathcal{R}(\{\xi\}, \{\eta\}). \tag{63}
\]

Since the total degree of the expression inside the square brackets in (63) is \(Q\), one concludes that \(\mathcal{R}\) does not depend on variables \(\{\eta\}\) so that \(\mathcal{R}(\{\xi\}, \{\eta\}) = \mathcal{R}(\{\xi\})\),
and \( R(\{\xi\}) \) must be a polynomial of degree \( P \). Evaluate now \( \det(V) \) by considering the \((m_1 \times m_1)\) minors contained in the first \( m_1 \) rows of \((V)\). From each column of the considered minor one first factorizes \( \xi_1 \) to an appropriate power. In this way we are left with an \((m_1 \times m_1)\) Vandermonde-like matrix with elements equal to \( \eta_{i,j}^p \). It is remarked that, whenever \( m_1 > m_2 \), a minor is non singular only if it contains the \((m_2 + 1), (m_2 + 2), \ldots, m_1\)th columns of \((V)\) and, therefore, each complementary minor will not present terms \( \eta_{r,j}^p \) with \( 2 \leq r \leq M \) and \( m_2 \leq j \leq (m_1 - 1) \).

Assume now that \( \xi_1 = \xi_j \), \( j \) being a particular value such that \( 1 < j \leq M \). We have \( m_1 \geq m_j \). We can evaluate \( \det(V) \) by considering all the minors containing the rows \((1, r)\) with \( 1 \leq r \leq m_1 \) and the rows \((j, s)\) with \( 1 \leq s \leq m_j \). Having assumed that \( \xi_1 = \xi_j \), each column of one of these minors factorizes \( \xi_j^p \) with \( p \) in \([0, \ldots, (M - 1)]\) depending on the considered column. Thus, we are left with an \((m_1 + m_j) \times (m_1 + m_j)\) Vandermonde matrix whose elements are \( \eta_{1,p}^r \) or \( \eta_{j,q}^s \) with \( 1 \leq p \leq m_1 \), \( 1 \leq q \leq m_j \), while \( r \) and \( s \) belong to \([0, \ldots, (m_1 - 1)]\). The rank of this matrix at most is equal to \( m_1 \) and, therefore, its determinant will have a zero of order \( m_j = \min(m_1, m_j) \). Hence, \( \det(V) \) evaluated by this procedure will have a zero, related to the fact that \( \xi_1 = \xi_j \), of order \( m_j \). Assume now that \( \xi_2 = \xi_j \) for a particular \( j \) such that \( 2 < j \leq M \). Before repeating the reasoning made in the case \( \xi_1 = \xi_j \), we imagine of having developed \( \det(V) \) with respect to the minors contained in the first \( m_1 \) rows. As noted above, each complementary minor will no longer contain the columns with exponents \( m_2, \ldots, (m_1 - 1) \). Each of these complementary minor can be developed by considering its \((m_2 + m_j) \times (m_2 + m_j)\) minors contained in the rows presenting the factors \( \xi_2 \) and \( \xi_j \). By the same reasoning made above for the case \( \xi_1 = \xi_j \), one concludes that each \((m_2 + m_j) \times (m_2 + m_j)\) minor has a
rank at most equal to $m_2$ and, therefore $\det(\mathcal{V})$ must have a zero of order at least equal to $m_j = \min(m_2, m_j)$ when $\xi_2 = \xi_j$. One concludes that the zero of $\det(\mathcal{V})$ is at least of the order $\min(m, m_j)$ when $\xi_i = \xi_j$ and one can write that
\[
\det(\mathcal{V}) = \left[ \prod_{1 \leq l_1 < l_2 \leq M} (\xi_{l_2} - \xi_{l_1})^\min(m_{l_2}, m_{l_1}) \right] \cdot \mathcal{R}_1(\{\xi\}, \{\eta\}). \tag{64}
\]
The degree of the $\xi$-polynomial inside square brackets is equal to $P$, so that $\mathcal{R}_1$ is a polynomial of the only variables $\{\eta\}$. Thus, combining Eq.(63) with (64), one finds that
\[
\det(\mathcal{V}) = \mathcal{R}_0 \left[ \prod_{1 \leq l_1 < l_2 \leq M} (\xi_{l_2} - \xi_{l_1})^\min(m_{l_2}, m_{l_1}) \right] \prod_{i=1}^M \prod_{1 \leq j_1 < j_2 \leq m_i} (\eta_{i,j_2} - \eta_{i,j_1}), \tag{65}
\]
where $\mathcal{R}_0$ is a simple constant, eventually dependent on the dimensionality of $\mathcal{V}$. Comparing the ”diagonal” term $\prod_{i=1}^M (\xi_i^{l_i-1}) m_i \prod_{i=1}^M \prod_{j=1}^{m_i} \eta_{ij}^{j-1}$ resulting from the calculation of $\det(\mathcal{V})$, starting from the explicit expression of $\mathcal{V}$, with the corresponding term obtained developing the products present in (65), one finds that $\mathcal{R}_0 = 1$. Thus, the determinant of matrix $\mathcal{V}$ is
\[
\det(\mathcal{V}) = \left[ \prod_{1 \leq l_1 < l_2 \leq M} (\xi_{l_2} - \xi_{l_1})^\min(m_{l_2}, m_{l_1}) \right] \prod_{i=1}^M \prod_{1 \leq j_1 < j_2 \leq m_i} (\eta_{i,j_2} - \eta_{i,j_1}). \tag{66}
\]
By this result it is possible to get the algebraic expression of the determinant of the Karle-Hauptman matrix $\left[ \mathcal{D}[\mathcal{B}(a^*)] \right]$ associated to the principal basic set of vectors $\mathcal{B}(a^*)$. To this aim, we denote the vectors $|h\rangle \in \mathcal{B}(a^*)$ as $|h_\ell\rangle$ with $\ell = 1, \ldots, \bar{N}$. The $(i, \ell)$ element of $\left[ \mathcal{D}[\mathcal{B}(a^*)] \right]$ is defined as $D_{i,\ell}[\mathcal{B}(a^*)] = I_{h_i, h_\ell}$. Then, by Eq. (18), one finds that
\[
D_{i,\ell}[\mathcal{B}(a^*)] = I_{h_i, h_\ell} = \langle h_i | Q[h_\ell] \rangle = \sum_{j=1}^{\bar{N}} e^{i2\pi \delta_{j,i}^\ell h_i} e^{-i2\pi \delta_{j,i}^\ell h_\ell}, \quad i, \ell = 1, \ldots, \bar{N}. \tag{67}
\]
These can be written, using Eq.s (26) and (27), as

\[
\left( D[B(a^*)] \right) = \left( \mathcal{V}^\dagger \right) \cdot \left( v \right) \cdot \left( \mathcal{V} \right)
\]  

(68)

It follows that the determinant of the matrix on the lhs is the product of the determinants of the matrices present in the rhs. Hence, by Eq. (66), the determinant of the KH matrix associated to \( B(a^*) \) is

\[
\det \left( D[B(a^*)] \right) = \left[ \prod_{j=1}^{\bar{N}} \nu_j \right] \left[ \prod_{1 \leq j < l \leq M} \left| \xi_j - \xi_l \right|^{2 \min(m_j, m_d)} \right] \left[ \prod_{l=1}^{M} \prod_{1 \leq j < l \leq m_l} \left| \eta_{l,l} - \eta_{l,j} \right|^2 \right].
\]  

(69)

This expression applies both to X-ray and to neutrons. Its value is certainly different from zero. It is strictly positive in the first case while, in the second case, its sign depends on the sign of the first factor related to the product of the charges of the \( \bar{N} \) scattering centres.

References

Avrami, M. *Phys. Rev.* **50**, 300, (1938).

Buerger, M.J. *Crystal-Structure analysis*, New York: Wiley, (1960).

Cervellino, A. and Ciccarello, S. *J. Phys. A: Math. Gen.* **34**, 731, (2001).

Cervellino, A. and Ciccarello, S. *Z. Kristall.* **214**, 739, (1999).

Cervellino, A. and Ciccarello, S. *Riv. Nuovo Cimento* **19/8**, 1, (1996).

Fischer, K.F. and Pilz, K. *Acta Cryst.* A **53**, 475, (1997).

Gantmacher, F.R. *Théorie des matrices*, Paris: Dunod. Vol. I, (1966).

Goedkoop, J.B. *Acta Cryst.* **3**, 374, (1950).

Hauptman, H.A. *Rep. Prog. Phys.* **54**, 1427, (1991).

Hauptman, H.A. *Acta Cryst.* A **32**, 877, (1976).
Hauptman, H.A. and Langs, D.A. *Acta Cryst.* A59, 250, (2003).

Karle, J. and Hauptman, H.A. *Acta Cryst.* 3, 181, (1950).

Messiah, A. *Mécanique quantique*, Paris: Dunod. Vol. I, (1959).

Navaza, A. and Navaza, J. *Acta Cryst.* A 48, 695, (1992).

Navaza, J. and Silva, A.M. *Acta Cryst.* A 35, 266, (1979).

Ott, H. *Z. Kristall.* 66, 136, (1927).

Patterson, A.L. *Phys. Rev.* 55, 682, (1939).

Pilz, K. and Fischer, K.F. *Z. Kristall.* 215, 640, (2000).

Rothbauer, R. *Z. Kristall.* 209, 578, (1994).

Silva, A.M. and Navaza, J. *Acta Cryst.* A 37, 658, (1981).