On the Use of Eigenvalues and Eigenvectors in the Phase Problem

J. L. van der Plas,* R. A. G. de Graaff and H. Schenk

Gorlaeus Laboratories, Leiden Institute of Chemistry, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: jaco@chemb0b.leidenuniv.nl

Abstract

Karle–Hauptman matrices may be used in an algebraic approach to the phase problem. When eigenvalues and eigenvectors are used, it is possible to obtain structural information from Karle–Hauptman matrices of orders greater than N, despite the fact that the determinants are zero. In this paper, the properties of large Karle–Hauptman matrices are examined in the infinite and non-infinite cases. The characteristics of electron densities corresponding to separate eigenvectors are examined.

1. Introduction

The nomenclature used in this paper is given in Table 1.

A serious investigation into the possible use of matrix algebraic methods was performed by Main in 1975. He rewrites

$$E_{\mathbf{h}} = \Theta \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}, \qquad (1)$$

the Sayre equation, as

$$\mathbf{E} = \mathbf{E}\mathbf{B}, \qquad (2)$$

in which he defines $\mathbf{B}$ as a matrix with elements b_{ij} equal to $\Theta E_{\mathbf{H}_{ij}}$. The reciprocal-lattice vector $\mathbf{H}_{ij}$ is obtained by subtracting the vectors $\mathbf{h}(j)$ and $\mathbf{h}(i)$. $\mathbf{E}$ is a vector of normalized structure factors $E_{\mathbf{h}(i)}$. The resulting matrix $\mathbf{B}$ is a Karle–Hauptman matrix multiplied by a scale factor Θ. Equation (2) indicates the close relation between Karle–Hauptman matrices and the Sayre equation. In his paper, Main discusses the algebraic properties of the matrix $\mathbf{B}$. It should be noted that $\mathbf{E}$ determines $\mathbf{B}$, as can be readily seen from its definition, but given a matrix $\mathbf{B}$ an infinite number of $\mathbf{E}$ satisfying (2) can be found, as the elements b_{ij} are defined by the differences between $\mathbf{h}(j)$ and $\mathbf{h}(i)$. An alternative vector $\mathbf{E}'$ may be generated using the reflections $E_{\mathbf{h}(i)+\mathbf{l}}$ instead of $E_{\mathbf{h}(i)}$, where $\mathbf{l}$ can be any reciprocal-lattice vector.

When the spectrum of eigenvalues of $\mathbf{B}$ is studied, one finds restrictions on the values of λ_i. It was shown by Main that, under the condition of (2), one finds the following restrictions on λ_i:

Theorem 1. (Main.) λ_i equals 1 or $\mathbf{e}_i$ does not contribute to $\mathbf{E}$.

Table 1. *Nomenclature*

N	Number of atoms in the unit cell
n	Order of a matrix
$\mathbf{A}, \mathbf{B}$	Hermitian matrices
$\lambda_j, \mathbf{e}_j$	The jth eigenvalue and corresponding eigenvector
$\mathbf{h}$	Index array for generating Karle–Hauptman matrices: $A_{ij} = E_{\mathbf{h}(j)-\mathbf{h}(i)}$
Θ	Scale factor for very large matrices
θ	Scale factor in the Sayre equation

The proof follows from the fact that $\mathbf{E}$ is spanned by the eigenvectors of $\mathbf{B}$ ($\mathbf{e}_j$) and $\mathbf{B}$ equals $\mathbf{B}\mathbf{E}$.

$$\mathbf{E} = \sum_{j=1}^{n} a_j \mathbf{e}_j \qquad (3)$$

$$\mathbf{B}\mathbf{E} = \sum_{j=1}^{n} a_j \mathbf{B}\mathbf{e}_j \qquad (4)$$

$$a_j \lambda_j \mathbf{e}_j = a_j \mathbf{e}_j, \qquad (5)$$

where a_j is the length of the projection of the eigenvector $\mathbf{e}_j$ along $\mathbf{E}$. The sum over n can be left out of (5) as the eigenvectors $\mathbf{e}_j$ are orthonormal.

In this paper, an alternative derivation for restrictions on the eigenvalue spectrum will be given because the formulae previously given hold in the infinite case only, losing their validity in practice. The reason is that formula (2) only holds exactly when $n = \infty$, *i.e.* when the sum over all possible reflections is taken.

Furthermore, even if $\mathbf{E}$ is an eigenvector of a Karle–Hauptman matrix with an eigenvalue 1, all formulae presented by Main can be simplified by taking $a_1 = 1$ for $\mathbf{e}_1 = \mathbf{E}$ and $a_j = 0$ for all other $\mathbf{e}_j$. In this case, all formulae reduce to standard crystallographic equations or equations with both sides equal to zero. Writing $\mathbf{E}$ as a linear combination of other $\mathbf{e}_j$'s with eigenvalue 1 is nothing more than a change of basis and has little crystallographic relevance.

Finally, for very large matrices, the eigenvalues do become nearly equal to 1, but never exactly so. Therefore, using (2) in the finite case is incorrect, even in the first approximation.

An important restriction that holds for both the approach in this paper and the methods described by

Main is that all formulae are valid only for equal atoms, since this is an implicit condition when the Sayre equation is used.

2. The infinite case

An alternative way of regarding the problem is to investigate the entire eigenvalue spectrum of **B**. It will be shown that for equal atoms, when the dimension of the matrix reaches infinity, all eigenvalues become either 0 or 1. This differs from Theorem 1, as Main states that while some eigenvalues have a value of 1 the remaining eigenvalues are undetermined.

The proof follows from the non-negativity of a Karle–Hauptman matrix. The non-negativity implies that all eigenvalues are larger than or equal to 0. When a Karle–Hauptman matrix has a dimension $n \leq N$, the determinant of a Karle–Hauptman matrix is greater than 0 (Karle & Hauptman, 1950; Goedkoop, 1950). If $n > N$, the determinant of **B** becomes 0, implying that at least one eigenvalue must be 0. Navaza & da Silva (1979) and earlier von Eller (1955) have shown that the elements of a Karle–Hauptman matrix can be written as the variance and covariance factors of an N-dimensional basis **V** for vectors **V(k)** defined as

$$\mathbf{V(k)} = \sum_{j=1}^{N} \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_j)\mathbf{e}_j. \qquad (6)$$

Each element $E_{\mathbf{h}(j)-\mathbf{h}(i)}$ in a Karle–Hauptman matrix can be written as $\mathbf{V(h(}i)) \cdot \mathbf{V(h(}j))$; all vectors **V(k)** can be written as linear combinations of the basis **V**. If Karle–Hauptman matrices of orders greater than N are considered, clearly the elements in the additional rows and columns can be written as the in-product of a linear combination of vectors in the original basis. The maximum rank of the Karle–Hauptman matrix is therefore N and no more than N eigenvalues can be different from 0. If the dimension is larger than N, the rank is also at least N since the N vectors **V(k)** are spanned by an N-dimensional basis. From these conditions, it follows that the rank of a Karle–Hauptman matrix of order $n \geq N$ equals N.

Two interesting observations can be made. First, the sum of eigenvalues of a Karle–Hauptman matrix equals the sum of the diagonal elements (this is an algebraic property which holds for any square matrix) and is therefore independent of the phases in the matrix. Second, the variance of the eigenvalues of a Karle–Hauptman matrix is also independent of the phases in the matrix, which can be verified by calculating the square of a Karle–Hauptman matrix and calculating its trace.

These observations enable one to estimate the eigenvalue spectrum for large n if the Karle–Hauptman matrix contains the calculated and scaled E factors. The average over all eigenvalues is

$$\langle \lambda \rangle = \sum_{i=1}^{n} \lambda_i/n$$
$$= \sum_{j=1}^{n} b_{jj}/n$$
$$= \Theta E_{000} \qquad (7)$$

and because $n - N$ eigenvalues are zero, the average of the remaining N eigenvalues is

$$\langle \lambda | \lambda \in \sigma(\mathbf{B}), \lambda > 0 \rangle = \Theta E_{000} n/N, \qquad (8)$$

where $\sigma(\mathbf{B})$ is the spectrum of the eigenvalues of matrix **B**. Now it is useful to investigate the value of Θ. If (1) is rewritten as

$$E_{\mathbf{h}} = \Theta \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$$
$$= \theta \langle E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}}, \qquad (9)$$

clearly the relation between Θ and θ is

$$\Theta = \theta/n \qquad (10)$$

since (9) is the Sayre–Hughes equation. Since the equal-atom case is considered, we may substitute $N^{1/2}$ for E_{000}, θ becomes $N^{1/2}$ and (8) becomes

$$\langle \lambda | \lambda \in \sigma(\mathbf{B}), \lambda > 0 \rangle = \Theta E_{000}(n/N)$$
$$= (N^{1/2}/n)N^{1/2}(n/N)$$
$$= 1, \qquad (11)$$

thus obtaining the average value of those λ's greater than zero.

The sum of the squared eigenvalues (which is equal to the trace of the square of the Karle–Hauptman matrix) is

$$\text{trace}(\mathbf{B}^2) = \Theta^2 \sum_{i=1}^{n} \sum_{j=1}^{n} |E_{\mathbf{h}(j)-\mathbf{h}(i)}|^2. \qquad (12)$$

For infinitely large matrices, we can substitute the average value for $|E_{\mathbf{h}(j)-\mathbf{h}(i)}|^2$, which is 1, from which follows that the sum of the square of all non-zero eigenvalues equals N when n goes to ∞. This leads to two equations:

$$\sum_{i=1}^{N} \lambda_i = N \qquad (13)$$

$$\sum_{i=1}^{N} \lambda_i^2 = N. \qquad (14)$$

Clearly this system of equations is satisfied if and only if all eigenvalues greater than zero are one (for real eigenvalues).

This conclusion has two interesting consequences: as was shown earlier, $\mathbf{B}^2$ has the same eigenvectors and the squared eigenvalues of **B**, and since $1^2 = 1$ and $0^2 = 0$,

the eigenvalues are identical as well. This is only possible when $\mathbf{B}^2 = \mathbf{B}$, which implies that

Theorem 2. An n-dimensional Karle–Hauptman matrix equals its own square for $\lim_{n \to \infty}$ in the equal-atom case.

This results in a relation between the elements in $\mathbf{B}$ and $\mathbf{B}^2$. Comparing two elements b_{ij} and b_{ij}^2, we find

$$b_{ij} = b_{ij}^2$$

$$\Theta E_{\mathbf{h}(j)-\mathbf{h}(i)} = \sum_{k=1}^{\infty} b_{ik} b_{kj}$$

$$= \Theta^2 \sum_{k=1}^{\infty} E_{\mathbf{h}(k)-\mathbf{h}(i)} E_{\mathbf{h}(j)-\mathbf{h}(k)}. \qquad (15)$$

Equation (15) becomes clearer when we substitute $\mathbf{K}$ for $\mathbf{h}(j) - \mathbf{h}(i)$ and $\mathbf{L}$ for $\mathbf{h}(k) - \mathbf{h}(i)$. Equation (15) now becomes

$$E_{\mathbf{K}} = \Theta \sum_{\mathbf{L}} E_{\mathbf{L}} E_{\mathbf{K}-\mathbf{L}}, \qquad (16)$$

where the sum over $\mathbf{L}$ can be taken instead of the sum over $\mathbf{k}$ since the vectors only differ by a constant vector $\mathbf{h}(i)$ and the sum is over an infinite number of terms, the terms in the total sum are the same.

Equation (16) is the Sayre equation, indicating that taking the square of an infinitely large Karle–Hauptman matrix results in a Hermitian matrix with entries obtained by applying the Sayre equation to the original elements. It should be noted that the sum in (16) for one reflection is only over the product of one row and one column in the Karle–Hauptman matrix.

Concluding this section, we summarize the properties of a Karle–Hauptman matrix $\mathbf{B}$ of infinite order corresponding to an equal-atom structure:

(i) The eigenvalues of $\mathbf{B}$ are either 0 or 1.
(ii) There are only N eigenvalues not equal to 0.
(iii) $\mathbf{B}$ equals its own square.

These properties indicate that $\mathbf{B}$ is a projection matrix. A random vector would be projected on the space spanned by the N eigenvectors with eigenvalue 1.

3. The finite case

When n is no longer very much larger than N, several results obtained in the previous paragraphs no longer hold, except in a first approximation. Perhaps the most important change is in the spectrum of the eigenvalues: No longer are they restricted to zero or one, and only their average value remains the same. Theorem 2 is also no longer valid. As is customary in the literature on Karle–Hauptman matrices, unitary structure factors will be used in the following discussion.

$$b_{ij} = U_{\mathbf{h}(j)-\mathbf{h}(i)}, \qquad (17)$$

where

$$U_{\mathbf{H}} = E_{\mathbf{H}}/E_{000}$$

$$= \left(1 \Big/ \sum_{j=1}^{N} Z_j\right) \sum_{j=1}^{N} Z_j \exp[2\pi i(\mathbf{H} \cdot \mathbf{r}_j)], \qquad (18)$$

leading to the following expressions for the average and the sum of the eigenvalues. Note that U_{000} equals 1 and therefore all the diagonal elements are equal to 1.

$$\sum_{i=1}^{n} \lambda_i = n \qquad (19)$$

$$\sum_{i=1}^{n} \lambda_i^2 = \sum_{i=1}^{n} \sum_{j=1}^{n} |U_{\mathbf{h}(j)-\mathbf{h}(i)}|^2. \qquad (20)$$

Of course, the restriction that only N eigenvalues can be non-zero still holds. With calculations similar to the ones in the previous section, one can show that the eigenvalues are restricted to 1 and 0 only if all terms $|U_{\mathbf{h}(j)-\mathbf{h}(i)}|^2$ are equal to their expected values of 1.

Only a few properties of the eigenvalue spectrum can be calculated *a priori* in the non-infinite case. It has been shown that the variance and the average of the eigenvalues are independent of the choice of phases and may be calculated without knowledge of the structure. Furthermore, the correct phase set has an eigenvalue spectrum containing $n - N$ zeros and N eigenvalues greater than zero.

4. Eigendensities

In the original paper by Main (1975), the concept of 'eigendensities', associated with the eigenvectors of a Karle–Hauptman matrix was introduced, defined as:

$$\rho(x)_j = \sum_h e_{jh} \exp[2\pi i \mathbf{H}(h) \cdot \mathbf{x}], \qquad (21)$$

where e_{jh} corresponds to the hth element of the jth eigenvector (note: the original notation has been adapted slightly to be consistent with the rest of this paper). When the eigenvectors and eigenvalues of a matrix $\mathbf{B}$ are known, $\mathbf{B}$ can be written as

$$\mathbf{B} = \sum_{j=1}^{n} \mathbf{e}_j \lambda_j \mathbf{e}_j^*, \qquad (22)$$

where $\mathbf{e}_j^*$ is the complex conjugate of the transpose of $\mathbf{e}_j$. Therefore, the element at position kl in a matrix $\mathbf{B}$ can be written as a sum of contributions of the eigenvector elements:

$$b_{kl} = \sum_{j=1}^{n} e_{jk} \lambda_j \bar{e}_{jl}. \qquad (23)$$

If the electron density is defined as

$$\rho(x) = \sum_{\mathbf{H}} E(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) \qquad (24)$$

and the following assumptions are made: (a) the reflections present in a Karle–Hauptman matrix are sufficient to describe the electron density; (b) all reflections occur once and only once in the Karle–Hauptman matrix, the electron density may be written as

$$\rho(x) = \sum_{k=1,l=1}^{n}\sum_{j=1}^{n} \lambda_j e_{jk}\bar{e}_{jl} \exp\{-2\pi i[\mathbf{h}(l) - \mathbf{h}(k)] \cdot \mathbf{x}\}.$$

(25)

If every reflection occurs only once in the Karle–Hauptman matrix, the first assumption can always be met by increasing the order of the matrix. The validity of the second assumption depends on the choice of the index array $\mathbf{h}$. In practice, the problem of choosing $\mathbf{h}$ is not a trivial one. This problem will be discussed further in the following paper, dealing with the application of the the theory discussed here. From (25), it is possible to define an eigendensity different from (21), e.g.

$$\rho(x)_j = \sum_{k=1,l=1}^{n} \lambda_j e_{jk}\bar{e}_{jl} \exp\{-2\pi i[\mathbf{h}(l) - \mathbf{h}(k)] \cdot \mathbf{x}\}. \quad (26)$$

The main difference between the definitions (21) and (26) is that in (21) the Fourier transform of the eigenvectors is considered, whereas in (26) the Fourier transform of the contributions of the eigenvectors to the reflections in the matrix are taken. Equation (26) is more complex, but the sum over j of (26) is always equal to the electron density corresponding to the Fourier transform of the reflections in the Karle–Hauptman matrix, irrespective whether infinite or non-infinite matrices are being considered. This is not true for (21).

The properties of the eigendensities defined by (26) will now be examined. First of all, it is expected that, since the eigenvectors are orthogonal, the eigendensities are also orthogonal. Thus one would expect

$$\int_V \rho(x)_i \rho(x)_j^* \, dx = 0 \quad (27)$$

when $i \neq j$. Equation (27) must still be verified, since the product $\rho(x)_i \rho(x)_j$ is not a normal in-product but a quadruple sum. Verifying (27) is simple when the product $\rho(x)_i \rho(x)_j$ is written as

$$\int_V \rho(x)_i \rho(x)_j^* \, dx$$

$$= \sum_{h=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n}\sum_{m=1}^{n} e_{ih}\bar{e}_{ik}\bar{e}_{jl}e_{jm}$$

$$\times \exp\{2\pi i[\mathbf{h}(h) - \mathbf{h}(k) - \mathbf{h}(l) + \mathbf{h}(m)] \cdot \mathbf{x}\}, \quad (28)$$

remembering that the integral over one period of a sine or cosine function is zero. The exponential part of (28) is a sum of a cosine and a sine, periodic with a period equal to $2\pi/n_i$ in the directions x_1, x_2 and x_3, respectively. Since the first part of (28) is independent

of $\mathbf{x}$, the total integral in (28) is zero unless the second part has a phase of zero and thus becomes independent of $\mathbf{x}$. So only those terms in (28) for which $\mathbf{h}(h) - \mathbf{h}(k) - \mathbf{h}(l) + \mathbf{h}(m) = 0$ holds need to be considered.

When all possible combinations of $\mathbf{h}(h) - \mathbf{h}(k) - \mathbf{h}(l) + \mathbf{h}(m)$ are examined clearly only for $(h = k \wedge l = m) \vee (h = l \wedge k = m)$ is the second part of (28) zero. However, the sum of these terms is *not* equal to zero. They can be written as

$$\int_V \rho(x)_i \rho(x)_j^* \, dx = \sum_{k=1}^{n}\sum_{l=1}^{n} e_{ik}\bar{e}_{ik}\bar{e}_{jl}e_{jl} + \sum_{k=1}^{n}\sum_{m=1}^{n} e_{ik}\bar{e}_{jk}\bar{e}_{im}e_{jm}$$

$$- \sum_{k=1}^{n} e_{jk}\bar{e}_{jk}\bar{e}_{ik}e_{ik}$$

$$= 1 + 0 - \sum_{k=1}^{n} e_{jk}\bar{e}_{jk}\bar{e}_{ik}e_{ik} \quad (29)$$

[note that the final part in (29) contains the terms present in both the first and second sums]. Therefore *not* all eigendensities are orthogonal. The first term in (29) consists of elements corresponding to reflections on the diagonal only, thus with index (000). Further investigation shows that, even if every reflection occurs at most once in the Karle–Hauptman matrix, the diagonal elements are all equal to E_{000}. Thus, if the reflections used to calculate the eigendensities are to be the same as the ones used to calculate the conventional electron density, only one diagonal element should be used in the summation. This leads to a definition of an alternative eigendensity,

$$\rho(x)_j = \sum_{k=1,l=1,k \neq l}^{n} \lambda_j(e_{jk}\bar{e}_{jl} + \varepsilon_j)$$

$$\times \exp\{-2\pi i[\mathbf{h}(l) - \mathbf{h}(k)] \cdot \mathbf{x}\}, \quad (30)$$

in which ε_j is the average value of the diagonal elements in the matrix $\mathbf{B_j} = e_j\lambda e_j^*$, namely $\langle e_{jk}\bar{e}_{jk}\rangle_k$. This changes (29) to

$$\int_V \rho(x)_i \rho(x)_j^* \, dx$$

$$= \left[\left(\sum_{h=1}^{n}\sum_{k=1,k \neq h}^{n} e_{ih}\bar{e}_{ik}\right) + \varepsilon_i\right]\left[\left(\sum_{l=1}^{n}\sum_{m=1,m \neq l}^{n} \bar{e}_{jl}e_{jm}\right)\right.$$

$$\left. + \varepsilon_j\right] \exp\{2\pi i[\mathbf{h}(h) - \mathbf{h}(k) - \mathbf{h}(l) + \mathbf{h}(m)] \cdot \mathbf{x}\}$$

$$= \varepsilon_i\varepsilon_j + \sum_{k=1}^{n}\sum_{m=1}^{n} e_{ik}\bar{e}_{jk}\bar{e}_{im}e_{jm} - \sum_{k=1}^{n} e_{jk}\bar{e}_{jk}\bar{e}_{ik}e_{ik}$$

$$= \varepsilon_i\varepsilon_j + 0 - \sum_{k=1}^{n} e_{jk}\bar{e}_{jk}\bar{e}_{ik}e_{ik}. \quad (31)$$

An estimate of the value of expression (31) can be made by substituting the average values for $e_{jk}\bar{e}_{jk}$. The sum of all elements $\sum_j e_{jk}\bar{e}_{jk}$ equals B_{kk}. Since $B_{kk} = \Theta E_{000} = \theta E_{000}/n$, the product $e_{jk}\bar{e}_{jk}$ averages

$\theta E_{000}/nN$. Equation (31) can be estimated by

$$\int_V \rho(x)_i \rho(x)_j^* \, dx = (\theta E_{000}/Nn)^2 - n(\theta E_{000}/Nn)^2$$

$$= (N^{1/2}N^{1/2}/nN)^2 - (N^{1/2}N^{1/2})^2/nN^2$$

$$= 1/n^2 - 1/n$$

$$= (1-n)/n^2, \tag{32}$$

indicating that: the average overlap between eigen-densities defined by (30) is negative; and for large values of n the overlap approaches zero.

5. The meaning of semipositivity

An important question is: What is the physical meaning of the semipositivity property? In 1977, the Slater determinants proposed by Lajzérowicz & Lajzérowicz (1966) were used to prove that that the forbidden region for an $N \times N$ Karle–Hauptman matrix is the entire space, with the exception of the atomic positions (Knossow et al., 1977). On the other hand, in a recent paper it was demonstrated that if there is no redundancy or symmetry present in a Karle–Hauptman matrix there is an infinite number of alternative phase sets with identical determinants and eigenvalues (de Gelder, Elout, de Graaff & Schenk, 1993). The eigenvectors, however, differ and the Fourier transform of the reflections in the Karle–Hauptman matrix does not necessarily correspond to a positive electron density. In fact, if it does correspond, this electron density must also be constituted by N equal atoms, since it shares the eigenvalue spectrum of the original structure. The Patterson map must be identical also. The proof of the existence of phase sets with equal eigenvalues presented by de Gelder et al. is given below: If **A** is a semipositive Karle–Hauptman matrix, there is a similar matrix **B** defined by:

$$\mathbf{B} = \mathbf{C}^{-1}\mathbf{AC}, \tag{33}$$

where **C** is a diagonal matrix with elements $\exp(i\phi_i)$, ϕ_i are random phases between 0 and 2π. It can also be shown by squaring equation (33) that the square of **B** is also similar to the square of **A** and thus the 'reflections' in **B** also obey the Sayre equation for large orders.

Combining the fact that only the atomic positions are outside the forbidden space and the existence of an infinite number of phase sets that correspond to a semipositive Karle–Hauptman matrix, it follows that if a phase set corresponds to a Karle–Hauptman matrix that has no negative eigenvalues there is no guarantee that this phase set is the correct one. However, the phase set must be related to the correct phase set by (33). If there are negative eigenvalues, it can be

concluded immediately that the phase set is incorrect (note that this only true when calculated $|E|$'s or $|U|$'s are used!). It is important to realise that (33) only holds exactly in space group $P1$ since the phase transformation does not preserve the phase restrictions imposed by symmetry. Furthermore, if certain reflections (or symmetry-related reflections) occur more than once in a Karle–Hauptman matrix, their phase values are no longer related after the transformation. These two properties result in a reduced importance of this problem in practice.

6. Conclusions

Large Karle–Hauptman matrices containing the correctly phased structure factors have N eigenvectors with an eigenvalue greater than zero and $n - N$ eigenvectors with an eigenvalue equal to zero. For very large matrices, the Karle–Hauptman matrix becomes a projection matrix with N eigenvalues equal to one.

The new definition of the eigendensities enables the electron density to be written as the sum of contributions from the individual eigenvectors. These eigendensities are approximately orthogonal for large matrices.

There is only one phase set (disregarding a change of origin and homometric structures) whose Fourier transform is non-negative and whose eigenvalues are greater than or equal to zero when the eigenvalue spectrum of the corresponding Karle–Hauptman matrix is calculated. There are phase sets corresponding to Karle–Hauptman matrices with semipositive eigenvalues and a nonpositive Fourier transform.

The information obtained in this article has been used to generate phase-refinement routines that have been tested on several organic molecules. The techniques and the results will be discussed in the following article (van der Plas et al., 1998).

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