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On the Trace of the Correlation Rigid-Body Tensor

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It is shown that if the eigenvalues of the **TLS** matrix $\mathbf{C}_{66}$ are all positive, then the trace of **S** must lie within an open interval, which is effectively determined. Further Scheringer's equation for the estimate of the trace of **S** is shown to have in this interval exactly one root which is simultaneously the point of the maximum of the determinant of the **TLS** matrix $\mathbf{C}_{66}$.

1. Introduction*

Schomaker & Trueblood (1968) showed that the external vibrations of almost rigid molecules can be described by three tensors **T**, **L** and **S**. However, trace (**S**) cannot be determined from diffraction data since only the differences $S^i_i - S^j_j$ enter into the calculation. The condition, trace (**S**) = 0, was chosen by them for practical purposes. But this condition does not remove the indeterminacy of trace (**S**).

Scheringer (1973 – hereafter SCHE) pointed out that we should know trace (**S**), at least approximately, for a lattice-dynamical interpretation of the **TLS** tensor. He found that the limits for trace (**S**) follow from the fact that the matrix $\mathbf{C}_{66}$ must be positive definite. He gave also an estimate for the trace (**S**) originating in the lattice dynamics of molecular crystals. We quote his equation (4.15):

$$\{\mathbf{C}_{66}^{-1}(K)\}_{14} + \{\mathbf{C}_{66}^{-1}(K)\}_{25} + \{\mathbf{C}_{66}^{-1}(K)\}_{36} = 0\ . \quad (1.1)$$

The principal purpose of this paper is to show that an estimate of the trace (**S**), for which matrix $\mathbf{C}_{66}(K)$ is positive definite, follows uniquely from (1.1). This supports the lattice-dynamical interpretation of the **TLS** tensors indicated by SCHE. Therefore we shall try to answer the following questions:

(i) What is the shape of the set M of all K for which the **TLS** matrix $\mathbf{C}_{66}(K)$ is positive definite?

(ii) How many roots has (1.1) in the set M?

Mathematical analysis of these questions will also show an effective way of finding the limits and an estimate of trace (**S**). It is obvious that the limits for trace (**S**) found by mathematical analysis are not narrower than those previously established [SCHE (4.5)] but about the same.

2. Mathematical analysis*

Theorem 1: The set M is an open interval.

Proof: The matrix **C** is positive definite (see SCHE Appendix) and therefore at least one K must exist for which the matrix $\mathbf{C}_{66}(K)$ is also positive definite. Thus M is not void. Let $K_1 \in M$. According to Lemma 1 of Appendix I the principal minor determinants $\Delta_1, \Delta_2, \Delta_3, \Delta_4(K_1), \Delta_5(K_1), \Delta_6(K_1)$ are positive. However, these determinants are continuous functions of K, the

$$\Delta_1, \Delta_2, \Delta_3 \quad (2.1)$$

being constants and the

$$\Delta_4(K), \Delta_5(K), \Delta_6(K) \quad (2.2)$$

being polynomials of second, fourth and sixth orders respectively. Consequently, a region for this point K_1 may be found where the determinants (2.1) and (2.2) are positive and therefore the matrix $\mathbf{C}_{66}(K)$ positive definite. This means that M is an open set.

Further let $K_1, K_2 \in M$. According to SCHE (Appendix) the matrix $\mathbf{C}_{66}(K_1) + \mathbf{C}_{66}(K_2)$ is positive definite and hence the matrix $[\mathbf{C}_{66}(K_1) + \mathbf{C}_{66}(K_2)]/2 = \mathbf{C}_{66}[(K_1 + K_2)/2]$ is positive definite as well. Thus $(K_1 + K_2)/2 \in M$. This means that M must be an open interval and Theorem 1 is proved.

Theorem 2: The roots of equations (E_4), (E_5) and (E_6) fulfil the inequalities:

$$^4K_1 \le {}^5K_2 \le {}^6K_3 < {}^6K_4 \le {}^5K_3 \le {}^4K_2 \quad (2.3)$$

and the set M is the interval:

$$({}^6K_3, {}^6K_4)\ . \quad (2.4)$$

Proof: The determinants (2.1) being independent of K and positive (see Lemma 1 of Appendix I), only the polynomials (2.2) will be investigated. For the matrix $\mathbf{C}_{66}(K)$ to be positive definite it is necessary that (2.2) be simultaneously positive. This condition implies the form (2.4) of the set M. The behaviour of the polynomials (2.2) for $K \to \pm\infty$ is governed by the coefficients of the highest-order terms. Writing:

$$\Delta_4(K) = -[T^{22}T^{33} - (T^{23})^2]K^2 + \sum_{n=0}^{1} a_n K^n$$

$$\Delta_5(K) = T^{33}K^4 + \sum_{n=0}^{3} b_n K^n$$

$$\Delta_6(K) = -K^6 + \sum_{n=0}^{5} c_n K^n\ ,$$

we see that the expression $T^{22}T^{33} - (T^{23})^2$, being a principle minor determinant of the matrix $\mathbf{C}_{66}(K)$ independent of K, is positive in view of Note 1 of Appendix I. For the same reason $T^{33} > 0$. Thus:

* Symbols are summarized in Appendix III.

$$K \to \pm\infty \Rightarrow \Delta_4(K) \to -\infty \quad (2.5a)$$

$$K \to \pm\infty \Rightarrow \Delta_5(K) \to +\infty \quad (2.5b)$$

$$K \to \pm\infty \Rightarrow \Delta_6(K) \to -\infty\,. \quad (2.5c)$$

From Theorem 1, Lemma 1 of Appendix I and (2.5a) it follows that the equation (E_4) has two roots ${}^4K_1 < {}^4K_2$ and:

$$K \in ({}^4K_1, {}^4K_2) \Rightarrow \Delta_4(K) > 0 \quad (2.6)$$

$$K \notin \langle {}^4K_1, {}^4K_2 \rangle \Rightarrow \Delta_4(K) < 0\,.$$

Since the numbers (2.1) are positive and $\Delta_4({}^4K_1) = \Delta_4({}^4K_2) = 0$ the rank of matrix $\mathbf{C}_{44}(K)$ at the points ${}^4K_1, {}^4K_2$ is equal to 3. According to Lemma 2 of Appendix I, $\mathbf{C}_{44}(K)$ has at these two points three positive eigenvalues and one equal to zero. Applying the Lemma of Appendix II we get:

$$\Delta_5({}^4K_1) \le 0 \quad \Delta_5({}^4K_2) \le 0\,. \quad (2.7)$$

The roots of equation (E_5) fulfil then the following inequalities [see Theorem 1, Lemma 1 of Appendix I and (2.5b), (2.6), (2.7)]:

$${}^5K_1 \le {}^4K_1 \le {}^5K_2 < {}^5K_3 \le {}^4K_2 \le {}^5K_4\,. \quad (2.8)$$

Further we shall confine ourselves to the case when all roots of equation (E_5) are simple. Though the remaining cases are more complicated, they give the same results.† Under our assumption we have:

$$K \in (-\infty, {}^5K_1) \Rightarrow \Delta_5(K) > 0$$

$$K \in ({}^5K_1, {}^5K_2) \Rightarrow \Delta_5(K) < 0$$

$$K \in ({}^5K_2, {}^5K_3) \Rightarrow \Delta_5(K) > 0$$

$$K \in ({}^5K_3, {}^5K_4) \Rightarrow \Delta_5(K) < 0$$

$$K \in ({}^5K_4, +\infty) \Rightarrow \Delta_5(K) > 0\,. \quad (2.9)$$

From (2.6), (2.8) and (2.9) it follows:

$$\Delta_4(K) > 0 \;\&\; \Delta_5(K) > 0 \Leftrightarrow K \in ({}^5K_2, {}^5K_3)\,. \quad (2.10)$$

The numbers (2.1) are positive and $\Delta_4({}^5K_1) \le 0$, $\Delta_4({}^5K_2) \ge 0$, $\Delta_5({}^5K_1) = \Delta_5({}^5K_2) = 0$. The following four cases have been considered separately.

(i) $\Delta_4({}^5K_1) < 0 \;\&\; \Delta_4({}^5K_2) > 0$

Here the rank of matrix $\mathbf{C}_{55}(K)$ at the points ${}^5K_1, {}^5K_2$ is equal to 4. Lemma 2 of Appendix I implies that the matrix $\mathbf{C}_{55}({}^5K_1)$ has three positive, one negative and one zero eigenvalues and the matrix $\mathbf{C}_{55}({}^5K_2)$ four positive and one zero eigenvalues. Applying the Lemma of Appendix II we get:

$$\Delta_6({}^5K_1) \ge 0 \quad \Delta_6({}^5K_2) \le 0\,. \quad (2.11a)$$

(ii) $\Delta_4({}^5K_1) = 0 \;\&\; \Delta_4({}^5K_2) > 0$

At the point ${}^5K_{\_}$ the situation is similar to that of the previous case. However, at ${}^5K_1$ the sequence $\Delta_1, \Delta_2, \Delta_3, \Delta_4(K), \Delta_5(K), \Delta_6(K)$ cannot be used for determining the signs of eigenvalues, since the rank of $\mathbf{C}_{55}({}^5K_1)$ is equal to four (see Note 2 of Appendix I). The last statement follows from the assumption that the roots of (E_5) are simple. Then $\mathrm{d}[\Delta_5(K)]/\mathrm{d}K$ is different from zero for $K = {}^5K_1$. But $\mathrm{d}[\Delta_5(K)]/\mathrm{d}K$ is a sum of minors of order four, so that at least one of them must be different from zero and the rank of $\mathbf{C}_{55}({}^5K_1)$ is four as stated above. Thus the signs of eigenvalues may be determined from the continuity of the eigenvalues of $\mathbf{C}_{55}(K)$ as functions of K and the behaviour of $\Delta_4(K)$ and $\Delta_5(K)$ in the neighbourhood of ${}^5K_1$. We find that $\mathbf{C}_{55}({}^5K_1)$ has three positive, one negative and one zero eigenvalues and get in view of the lemma of Appendix II again the inequalities (2.11a).

(iii) $\Delta_4({}^5K_1) < 0 \;\&\; \Delta_4({}^5K_2) = 0$

The discussion is quite analogous to the previous one.

(iv) $\Delta_4({}^5K_1) = 0 \;\&\; \Delta_4({}^5K_2) = 0$

The eventuality cannot occur since the roots of (E_5) are simple and (2.8) holds. Thus the inequalities (2.11a) are true in all cases. Performing a similar analysis at the points ${}^5K_3, {}^5K_4$ we obtain:

$$\Delta_6({}^5K_3) \le 0 \quad \Delta_6({}^5K_4) \ge 0\,. \quad (2.11b)$$

The roots of equation (E_6) fulfil [see Theorem 1, Lemma 1 of Appendix I and (2.5c), (2.10), (2.11)]:

$${}^6K_1 \le {}^5K_1 \le {}^6K_2 \le {}^5K_2 \le {}^6K_3 < {}^6K_4 \le {}^5K_3 \le {}^6K_5 \le {}^5K_4 \le {}^6K_6\,. \quad (2.12)$$

Further:

$$K \in ({}^6K_3, {}^6K_4) \Rightarrow \Delta_6(K) > 0\,. \quad (2.13)$$

From (2.10), (2.12) and (2.13) it follows:

$$\Delta_4(K) > 0 \;\&\; \Delta_5(K) > 0 \;\&\; \Delta_6(K) > 0 \Leftrightarrow K \in ({}^6K_3, {}^6K_4)\,. \quad (2.14)$$

This means that the set M is the interval (2.4). The inequalities (2.3) follow from (2.8) and (2.12) and the proof of Theorem 2 is completed.

Theorem 3: (1.1) has in the set M exactly one solution, say K_0, fulfilling the maximum condition:

$$\Delta_6(K_0) = \operatorname*{Max}_{K \in M} \Delta_6(K)\,.$$

Proof: Writing (1.1) in the form:

$$\frac{A_{14}(K) + A_{25}(K) + A_{36}(K)}{\Delta_6(K)} = 0 \quad (2.15)$$

and having in mind that:

$$\frac{\mathrm{d}}{\mathrm{d}K}[\Delta_6(K)] = 2[A_{14}(K) + A_{25}(K) + A_{36}(K)] \quad (2.16)$$

[since $\mathbf{C}_{66}(K)$ is symmetric], we can see that (1.1) is equivalent to the following condition in the set M:

$$\frac{\mathrm{d}}{\mathrm{d}K}[\Delta_6(K)] = 0\,. \quad (2.17)$$

Considering the behaviour of the function $\Delta_6(K)$ [see (2.12), (2.13)] we get Theorem 3.

* See Appendix III.

† The detailed discussion is available from the author.

3. Conclusions

The above theorems enable us to put limits on trace (S) [trace (S) = 3K] and to estimate its value in the following simple way.

We find first the coefficients of polynomials $\Delta_4(K)$, $\Delta_5(K), \Delta_6(K)$. The knowledge of these makes it possible to determine subsequently such roots of (E_4), (E_5) and (E_6) which fulfil inequalities (2.3). In this way we get the limits for trace (S). The next step is to find the derivative $\mathrm{d}[\Delta_6(K)]/\mathrm{d}K$ and to determine its root lying in the interval M. In this way we get an estimate for trace (S).

This method presents a direct and simpler approach of determining the limits of and the estimate for trace (S) than the numerical methods described earlier (SCHE).

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APPENDIX I

For the convenience of the reader we quote two well-known propositions concerning matrix theory [see *e.g.* Gantmacher (1953)]. Supposing **A** is a symmetric matrix of order n we denote:

$$D_1 = A_{11}, D_2 = \det\begin{pmatrix} A_{11} A_{12} \\ A_{12} A_{22} \end{pmatrix}, \ldots, D_n = \det\begin{pmatrix} A_{11} A_{12} \ldots A_{1n} \\ A_{12} A_{22} \ldots A_{2n} \\ \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \\ A_{1n} A_{2n} \ldots A_{nn} \end{pmatrix}.$$

Lemma 1: The matrix **A** is positive definite (*i.e.* its eigenvalues are positive) if and only if:

$$D_1 > 0, D_2 > 0, \ldots, D_n > 0 .$$

Note 1: It follows that all principal minor determinants of a positive definite matrix are positive.

Lemma 2: Let r be the rank of matrix **A**, let $D_k \neq 0$ for $k = 1, \ldots, r$. Then the number of zero eigenvalues is equal to $n - r$. The number of the negative eigenvalues is equal to the number of changes of signs in the sequence $1, D_1, \ldots, D_r$.

Note 2: The sequence $1, D_1, D_2, \ldots, D_r$ cannot be used to determine the number of negative eigenvalues if, in particular, $D_r = 0$.

APPENDIX II

Lemma: Let **A** be a symmetric square matrix of order n which has one zero eigenvalue and an odd (or even) number of negative eigenvalues. Let the matrix **B** originate from **A** in the following way:

$$\mathbf{B} = \begin{pmatrix} A_{11} A_{12} \ldots A_{1n} B_1 \\ A_{12} A_{22} \ldots A_{2n} B_2 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \quad \cdot \\ A_{1n} A_{2n} \ldots A_{nn} B_n \\ B_1 \; B_2 \; \ldots B_n \; B_{n+1} \end{pmatrix}.$$

Then $\det(\mathbf{B}) \geq 0$ [or $\det(\mathbf{B}) \leq 0$, respectively].

Proof: Certainly an orthogonal matrix **R** may be found in such a way that:

$$\mathbf{R}^T\mathbf{A}\mathbf{R} = \mathbf{\Lambda} .$$

Where $\mathbf{\Lambda}$ is a diagonal matrix with $\lambda_{nn} = 0$ and $\mathbf{R}^T$ denotes the transpose of **R**. Let **D** be the row matrix $(B_1, B_2, \ldots, B_n)$ and **O** the row matrix consisting of n zero elements. Taking the auxiliary orthogonal matrix **Q**:

$$\mathbf{Q} = \begin{pmatrix} \mathbf{R} & \mathbf{O}^T \\ \mathbf{O} & 1 \end{pmatrix}$$

we get

$$\mathbf{Q}^T\mathbf{B}\mathbf{Q} = \begin{pmatrix} \mathbf{\Lambda} & \mathbf{R}^T\mathbf{D}^T \\ \mathbf{DR} & B_{n+1} \end{pmatrix} \Rightarrow \det(\mathbf{Q}^T\mathbf{B}\mathbf{Q}) = \det(\mathbf{B}) = -\lambda_{11}\lambda_{22}\ldots\lambda_{n-1n-1}[(DR)_n]^2$$

which makes the Lemma clear.

APPENDIX III
Symbols for quantities

C = the mean-square-amplitude matrix
T = the translation tensor
L = the libration tensor
S = the correlation tensor with trace (S) = 0
S(K) = the correlation tensor whose trace is equal to 3 K.

$S^j_j(K) = S^j_j + K$; $S^j_i(K) = S^j_i$ for $(i \neq j)$
where S^i_j $(i,j = 1,2,3)$ are the components of **S**.

$\mathbf{C}_{66}(K)$ = the matrix $\begin{pmatrix} \mathbf{T} & \mathbf{S}^T(K) \\ \mathbf{S}(K) & \mathbf{L} \end{pmatrix}$
where $\mathbf{S}^T(K)$ denotes the transpose of $\mathbf{S}(K)$

$A_{ij}(K)$ = the cofactor of $\{\mathbf{C}_{66}(K)\}_{ij}$ $i,j = 1,2,\ldots,6$

$\mathbf{C}_{44}(K)$ = the matrix which arises from $\mathbf{C}_{66}(K)$ by deleting the fifth and sixth rows and columns

$\mathbf{C}_{55}(K)$ = the matrix which arises from $\mathbf{C}_{66}(K)$ by deleting the 6th row and column

$\Delta_1 = T^{11}$, $\Delta_2 = \det\begin{pmatrix} T^{11} T^{12} \\ T^{12} T^{22} \end{pmatrix}, \ldots, \Delta_6(K) = \det[\mathbf{C}_{66}(K)]$
= the sequence of principal minor determinants of the matrix $\mathbf{C}_{66}(K)$

(E_i) = the equation $\Delta_i(K) = 0$ $(i = 4,5,6)$

${}^iK_1 \leq {}^iK_2 \ldots \leq {}^iK_j$ = the real roots of the equation (E_i) $(i = 4,5,6)$.

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