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APPLICATIONS OF A GROUP THEORETICAL THEOREM.
GENERALIZATION OF THE EQUATIONS OF CRYSTALLINE
AND MOLECULAR VIBRATIONS IN THEIR GENERAL RECTILINEAR
COORDINATE AXES. PARTICULAR CASE OF MoS$_2$.
APPLICATION TO THE SHELL MODEL

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Résumé. — Un théorème sur la nature tensorielle des coefficients du développement en série de
Taylor d’une fonction permet d’obtenir les relations entre les éléments de matrice apparaissant dans
les problèmes de vibration.
Les équations de la dynamique du réseau peuvent s’écrire facilement dans le repère cristallogra-
phique naturel.
La méthode est expérimentée avec succès dans le cas particulier du cristal lamellaire de MoS$_2$,
dans l’approximation des forces centrales.
Finalement, on montre comment il est possible d’obtenir quelques relations utiles dans le modèle
de la coquille.

Abstract. — A theorem on the tensorial nature of the Taylor expansion coefficients of a function
allows the relations between the elements of the matrices occurring in the vibrational problems to be
obtained.
The dynamical equations can be easily written in oblique natural coordinates taking into account
the crystal symmetries.
The method is tested with success on the particular case of the lamellar crystal, MoS$_2$, in the central
force approximation.
Finally, it is shown how to get some useful relations in shell model theory.

1. General introduction. — Before applying group
theory, it is often desirable to substitute the operators
of the treated problem by other equivalent operators
which are easier to handle [1]. In particular, this is
the case of the derivative operators, which appear
in the expansion of the molecular or crystalline
potential energy as a Taylor series of the displacement
variables.

More generally, let us assume that the physical
properties of a system derive from a potential func-
tion $V$ which can be expanded in a Taylor (or Cauchy)
series, and that the system remains invariant with
respect to linear operators $S$ belonging to a group $L$.

The linearity of the derivative operators allows [2]
one to substitute the coefficients of the Taylor expan-
sion by tensor products which are constructed from
the variables, and the transformation law of which
with respect to $S$ is known.

We intend to apply this method to the simplifi-
cation of the potential energy of the crystals and
molecules referred to their own rectilinear coordinate
axis.

For simplicity, we will consider the harmonic
approximation and tensorial interactions [3].

It is customary to treat the crystalline and molecular
dynamical problems in a rectilinear orthogonal coor-
dinate system. This choice is evidently justified for
the objects which possess a cubic, quadratic, etc...
symmetry. However, it seems more judicious to
operate in an oblique coordinate system, in order to take advantage of
the symmetry of the studied system. In particular,
it is often easier to construct the force tensor $c$
in an oblique coordinate system than in an ortho-
gonal one. In other respects, the symmetry coordinates
are simplified in oblique coordinate system because
in the general case the use of orthogonal axes can
introduce undesirable cross terms.

It is desirable to choose the frame of reference
which makes this derivation the easiest, even at the

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price of using afterwards transformation formulas to express \([c]\) in the chosen reference. The use of oblique axes thus constitutes a very flexible method.

Now, it is necessary to generalize the dynamical equations [4]. Consequently, the formulas are made longer, but in exchange the formalism is considerably simplified. This is well illustrated, for example, in the case of the central force approximation.

The application of the Lagrange equations in oblique axes requires contravariant expressions of the kinetic \((T)\) and potential \((V)\) energies, which will be simplified by taking into account the symmetry operations of the system.

Only the more general case of crystalline vibrations, which contains the particular case of the molecules, will be treated here.

The obtained results will be applied to the case of the lamellar MoS\(_2\) crystal.

Finally, the method yields easily the relations between the dynamical matrix elements in the case of the crystal shell models.

2. General group theoretical theorem. — Let \(V(x^1, x^2, \ldots, x^k)\) be any function of the variables \(x^1, x^2, \ldots, x^k\) of \(\mathbb{R}^3\), which fulfils the so-called Taylor's conditions, namely:

1) The function \(V\) and its \(n\)-th order derivatives exist and are continuous on the interval \([a, b]\).
2) The \((n + 1)\)-th order derivatives exist on the open interval \((a, b)\).

**Theorem.** — The \(n\)-th order coefficients of the Taylor's series expansion of any function \(V(x^1, \ldots, x^k)\) are the components of a tensor product of \(n\) vectors \(v\) whose components are \(x^1, x^2, \ldots, x^k\).

**Proof.** — The \(n\)-th order terms of the Taylor series of \(V\) are written generally as:

\[
V = \frac{1}{n!} \sum \frac{\partial^{(n)} V}{\partial (x^1)^{i_1} \cdots \partial (x^k)^{i_k}} \times (x^1)^{j_1} \cdots (x^k)^{j_n}; \sum_j = n. \tag{2.1}
\]

But, according to the Leibnitz theorem, the products \((x^1)^{i_1} \cdots (x^k)^{i_k}\) are multilinear forms constructed on the linear forms \(x^1, x^2, \ldots, x^k\). As \(V\) is a constant, the general tensor criterion [5] shows that the quantities

\[
\frac{\partial^{(n)} V}{\partial (x^1)^{i_1} \cdots \partial (x^k)^{i_k}}
\]

are necessarily the components (co- or contravariant or mixed) of the tensor \([c]\) constructed on the vector \(v\):

\[
\left[ \frac{\partial^{(n)} V}{\partial (x^1)^{i_1} \cdots \partial (x^k)^{i_k}} \right] = v \otimes \cdots \otimes v \tag{2.2}
\]

where : \(\otimes\) is the symbol of the tensor product.

**Consequence:** General relations between the coefficients of the Taylor expansion of the function \(V\).

Let \(S\) be any linear operator belonging to a group which leaves \(V\) invariant.

Let us represent by \(\cong\) the symbol which means that two expressions (at right and at left of \(\cong\)) have the same behaviour with respect to \(S\).

If \(S\) leaves invariant the function \(V\), then the \(n\)-th order coefficients of the Taylor expansion are necessarily connected by:

\[
\frac{v \otimes \cdots \otimes v}{n \times n} = \frac{(Sy) \otimes \cdots \otimes (Sy)}{n \times n}. \tag{2.3}
\]

These relations provide conditions on the components of the tensor \([c]\), and then on the coefficients of the series expansion of \(V\).

In particular, it should be observed that \(S\) can be considered as a change of vector basis, and that \([c]\) can be expressed in terms of covariant, contravariant or mixed components.

This theorem will be applied to the simplification of the crystalline or molecular potential energy expressed in oblique axis.

**Remarks.** — 1) This theorem is to be compared with the so-called direct inspection method [1, 6] which constitutes a particular case of the general theorem.

Because, in this case, \(V\) is an \(n\)-th degree polynomial, the demonstration is the same as above.

2) The same results are valid if operators are substituted for the \(V\) function [2].

3. Dynamical equations in oblique rectilinear axes. —

3.1 The Reference Axes and the Transformations Matrices. – a) Transformation matrix of the set \(e_i\) to the set \(e'_j\) in the general case. — Let \(e_1, e_2, e_3\) be three orthonormal vectors. Subsequently, \(e_3\) will be identified with the principal symmetry axis of the system. Let \(e'_1, e'_2, e'_3\) be three vectors defining the oblique natural axis of the system; \(e'_3\) and \(e'_3\) are then superposed and by construction \(e'_2\) is located in the plane \((e'_1, e'_3)\) (Fig. 1).

Let us put:

\[
e'_j = (A) e_i = (a_{ij}) e_i \tag{3.1.1}
\]

**Fig. 1.** General oblique coordinate axis \(e'_1, e'_2, e'_3\) positioned in an orthogonal reference.
where \((A)\) represents the 3 \(\times\) 3 transformation matrix from \(e_i\) to \(e_j\):

\[
(A) = \begin{pmatrix}
\cos (e_1, e'_1) & -\cos (e_2, e'_1) & \cos \beta \\
\sin \gamma & 0 & \cos \gamma \\
0 & 0 & 1
\end{pmatrix}.
\]

\((3.1.2)\)

Remarks. — The components \((x'_1)\) in the orthonormal system are deduced from the contravariant \((q^\text{contra})\) one by:

\[
x'_1 = (A)q^\text{contra}.
\]

\((3.1.3)\)

In the calculations, one often needs the fundamental tensor \([g]\) to which is associated the matrix

\[
(g) = (g_{ij}) = (e'_i, e'_j) = (A)(\bar{A})
\]

where the superscript \(^\top\) denotes the transpose

\[
(g) = \begin{pmatrix}
1 & \cos \alpha & \cos \beta \\
\cos \alpha & 1 & \cos \gamma \\
\cos \beta & \cos \gamma & 1
\end{pmatrix}.
\]

\((3.1.4)\)

Important particular cases. — In practice, the studied systems possess at least one axis of symmetry which is taken as \(e_3\). Then (Fig. 2):

\[
(e'_1, e'_2) = (e'_2, e'_3) = \beta
\]

\((3.1.5)\)

\[
(A) = \begin{pmatrix}
\cos (e_1, e'_1) & -\cos (e_2, e'_1) & \cos \beta \\
\sin \beta & 0 & \cos \beta \\
0 & 0 & 1
\end{pmatrix}
\]

\((3.1.6)\)

\[
\cos (e_1, e'_1) = \pm \frac{\cos \alpha - \cos^2 \beta}{\sin \beta}
\]

\((3.1.7a)\)

\[
\cos^2 (e_2, e'_1) = \frac{4 \cos^2 \frac{\alpha}{2} \cos \left(\frac{\alpha + 2 \beta}{2}\right) \cos \left(\frac{\alpha - 2 \beta}{2}\right)}{\sin^2 \beta}.
\]

\((3.1.7b)\)

In this case, \((g)\) becomes:

\[
(G) = (A)(\bar{A}) = \begin{pmatrix}
1 & \cos \alpha & \cos \beta \\
\cos \alpha & 1 & \cos \beta \\
\cos \beta & \cos \beta & 1
\end{pmatrix}.
\]

\((3.1.8)\)

Remark. — For the rhombic and hexagonal crystals [7], for example:

\[
\beta = \gamma = \frac{\pi}{2}
\]

\((3.1.9)\)

\[
(A) = \begin{pmatrix}
\cos \alpha & -\sin \alpha & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
(G) = (A)(\bar{A}) = \begin{pmatrix}
1 & \cos \alpha & 0 \\
\cos \alpha & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]

\((3.1.10)\)

b) The co- and contravariant components of a vector. — It is well known that the covariant components \(q_i\) of a vector transform like the base vectors under a transformation of coordinates [5, 8].

Let \(q^j\) be the contravariant components of the vector. The fundamental tensor \([g]^j_i\) allows the transformation of the covariant components \(q_j\) to the contravariant ones by the formula:

\[
q^j = [g]^j_i q_i.
\]

\((3.1.11a)\)
Let \((g^{-1}) = (g^i)\) be the inverse matrix of \((g)\). Then:

\[
q_{\text{contra}} = (g)^{-1} q_{\text{cov}}. \tag{3.1.11b}
\]

c) The rotational matrices. — \(x\) Molecular case. — Consider the change of the basic vectors \(e'_1, e'_2, e'_3\) to a new set \(e''_1, e''_2, e''_3\) under a rotation through an angle \(\alpha\) about the axis \(e''_3\) (Fig. 2).

It is easy to show, if \(\sigma\) represents the angle \((e'_1, e'_2)\), that:

\[
\cos \sigma = \frac{2 \cos^2 \alpha - 4 \cos \alpha \cos^2 \beta + 3 \cos^2 \beta - 1}{\sin^2 \beta}. \tag{3.1.12}
\]

If \((R)\) designates the transfer matrix from \(e'_i\) to \(e''_j\):

\[
e''_j = (R) e'_i. \tag{3.1.13}
\]

After calculations, it is found that:

\[
(R) = \left( \begin{array}{ccc}
\frac{2(\cos \alpha - \cos^2 \beta)}{\sin^2 \beta} - 1 & 2 \cos \beta(1 - \cos \alpha) \\
\sin^2 \beta & 1 & 0 \\
0 & 0 & 1
\end{array} \right). \tag{3.1.14}
\]

\(\beta\) Crystalline case. — The formula (3.1.14) is valid only for the rotations which lead \(e'_1\) to coincide with \(e'_3\).

For the crystals (where \(\beta = \pi/2\)), it is necessary to consider the case of more general rotations through an angle \(\theta \neq \alpha\) about the axis \(e''_3\) (Fig. 3).

The \((R)\) matrix gives the covariant components of the transformed vector \(Q_i\) of a vector \(q_j\) under the rotation \((e'_3, \theta)\):

\[
Q_i = (R) q_j. \tag{3.1.15a}
\]

Similarly, the contravariant components of the transformed vector \(Q^i\) of a vector \(q^j\) under the rotation \((e'_3, \theta)\) are given by:

\[
Q^i = (R^{-1}) q^j \tag{3.1.15b}
\]

with:

\[
(R^{-1}) = \frac{1}{\sin \alpha} \begin{pmatrix}
\sin (\alpha - \theta) & -\sin \theta & 0 \\
\sin \theta & \sin (\alpha + \theta) & 0 \\
0 & 0 & \sin \alpha
\end{pmatrix}. \tag{3.1.16}
\]

3.2 Kinetic Energy. — \(T\) is the kinetic energy of the system:

\[
2T = \sum_{ij} M_i \left( \begin{pmatrix} \tilde{u}_{\text{rec}}(l) \\ \tilde{u}_{\text{rec}}(l') \end{pmatrix} \right) \left( \begin{pmatrix} \tilde{u}_{\text{rec}}(l') \\ \tilde{u}_{\text{rec}}(l) \end{pmatrix} \right). \tag{3.2.1}
\]
where \( \mathbf{u}_{\text{rect}}(l) \) represents the displacement off the normal equilibrium position of the \( s \)-th atom (mass \( M_s \)) in the \( l \)-th cell. The time derivative is symbolized by : \( \dot{\cdot} \).

In the basis \( e'_i \), \( 2T \) is:

\[
2T = \sum_{s l} M_s \dot{\mathbf{u}}_{\text{contra}}(A A) \dot{\mathbf{u}}_{\text{contra}}(l) = \sum_{s l} M_s \dot{\mathbf{u}}_{\text{contra}}(l)(G(x, \beta, \gamma)) \dot{\mathbf{u}}_{\text{contra}}(l) .
\]

(3.2.2)

3.3 Potential energy. — Generalities. — In the classical theory of the vibrations \([3, 9]\), it is assumed that the forces derive from a potential \( V \) which is expanded in a series of small displacements off the equilibrium position. All terms of higher order than the second one are neglected (harmonic approximation):

\[
2V = \sum_{i l} \frac{\partial^2 V}{\partial^2 \mathbf{u}_{\text{contra}}(l) \partial^2 \mathbf{u}_{\text{contra}}(l')} u_i(l) u_i(l') .
\]

(3.3.1)

The general theorem (form. 2. 3) shows that the coefficients of the expansion have the same behaviour with respect to the symmetry operators \( S = (\beta, \tau) \) of a group \( L \) (where \( \beta \) denotes a rotation operator and \( \tau \) a translation one) as do the components of the tensor product:

\[
\begin{bmatrix}
\partial^2 V \\
\partial^2 \mathbf{u}_{\text{contra}}(l) \partial^2 \mathbf{u}_{\text{contra}}(l')
\end{bmatrix} \approx u_{\text{cov}}(l) \otimes u_{\text{cov}}(l') = \mathbf{C}_{\text{cov}}(l) .
\]

(3.3.2)

If operator \( S \) transforms the atoms \( (l) \) and \( (l') \) respectively to the atoms \( (L) \) and \( (L') \) and if \( V \) remains invariant, we have:

\[
\begin{bmatrix}
\mathbf{C}_{\text{cov}}(l) \\
\mathbf{C}_{\text{cov}}(l')
\end{bmatrix} = \begin{bmatrix}
\mathbf{C}_{\text{cov}}(l) \\
\mathbf{C}_{\text{cov}}(l')
\end{bmatrix}.
\]

or:

\[
\begin{bmatrix}
\mathbf{u}_{\text{cov}}(l) \\
\mathbf{u}_{\text{cov}}(l')
\end{bmatrix} = \begin{bmatrix}
S \mathbf{u}_{\text{cov}}(l) \\
S \mathbf{u}_{\text{cov}}(l')
\end{bmatrix} .
\]

(3.3.3)

This relation gives conditions on the components of the tensor \( \mathbf{C} \).

Basis transformation for the \( \mathbf{C} \) components. — \( u_{\text{rect}}(l) \) and \( u_{\text{cov}}(l) \) and \( u_{\text{contra}}(l) \) represent the components of a vector \( u \) in the basis \( e_i \) and \( e'_i \), respectively. But:

\[
\mathbf{C}_{\text{rect}} \equiv u_{\text{rect}} \otimes u_{\text{rect}} .
\]

The relation (3.1.3) shows that:

\[
\begin{align*}
\mathbf{C}_{\text{rect}} & \equiv [(A^{-1}) u_{\text{cov}}] \otimes [(A^{-1}) u_{\text{cov}}] \\
& \equiv [(A^{-1}) u_{\text{cov}}] [(A^{-1}) u_{\text{cov}}] = (A^{-1}) (u_{\text{cov}}) (u_{\text{cov}}) (A^{-1}) .
\end{align*}
\]

From which:

\[
\begin{align*}
\mathbf{C}_{\text{rect}} &= (A^{-1}) (\mathbf{C}_{\text{cov}} (\mathbf{A}^{-1})) \\
\mathbf{C}_{\text{rect}} &= (\mathbf{A}^{-1}) (\mathbf{C}_{\text{contra}}) (\mathbf{A}) .
\end{align*}
\]

(3.3.4a)

(3.3.4b)

These formulae give the components of \( \mathbf{C} \) in rectangular coordinates when the oblique ones are known, and conversely.

Potential energy in oblique axis.

\[
2V = \sum_{s l s' l'} \mathbf{u}_{\text{rect}}(l) \mathbf{C}_{\text{rect}}(l) \mathbf{u}_{\text{rect}}(l') .
\]

(3.3.5)
where \((C_{\text{rect}})\) is the matrix associated with \([C]\) in rectangular coordinates. Now:

\[
\begin{bmatrix} C_{\text{rect}}(l_{s}^{'s}) \end{bmatrix} = (A) \begin{bmatrix} C_{\text{contra}}(l_{s}^{'s}) \end{bmatrix} (A) = A^{-1} C_{\text{cov}}(l_{s}^{'s}) A^{-1}.
\]

The fundamental theorem of tensor analysis [5] requires that \(C_{\text{cov}}\) has to be chosen when \(u\) is expressed with contravariant coordinates:

\[
2 V = \sum_{s l} \bar{u}_{\text{contra}}(l_{s}^{'}) (A) (A^{-1}) \begin{bmatrix} C_{\text{cov}}(l_{s}^{'s}) \end{bmatrix} (A^{-1}) (A) \begin{bmatrix} u_{\text{contra}}(l_{s}^{'}) \end{bmatrix}
\]

\[
= \sum_{s l} \bar{u}_{\text{contra}}(l_{s}^{'}) \begin{bmatrix} C_{\text{cov}}(l_{s}^{'s}) \end{bmatrix} u_{\text{contra}}(l_{s}^{'}). \tag{3.3.6}
\]

**Rotational transform of the tensor \([C]\).** — Let us seek the components \(C_{ij}\) of the tensor \([C]\) at a point \(M\) which are related to the components \(C_{ij}^{'}\) for an homologous point \(M^{'}\) resulting from \(M\) by the rotation \((\epsilon', \alpha)\).

1. Covariant components. — Formula (3.3.2) shows that:

\[
[C_{ij}] \cong u_{\text{cov}} \otimes u_{\text{cov}}
\]

and then:

\[
[C_{ij}] \cong (R u_{\text{cov}}) (R u_{\text{cov}}) .
\]

a) Molecular case.

\[
[C_{ij}] \cong \begin{bmatrix} \frac{2(\cos \alpha - \cos^2 \beta) u_1 - u_2}{\sin^2 \beta} & \frac{2\cos \beta(1 - \cos \alpha) u_3}{\sin^2 \beta} \\ u_1 & u_3 \end{bmatrix} \text{ (idem)}. \tag{3.3.7a}
\]

Equating term by term, we find:

\[
C_{11}' = \frac{4(\cos \alpha - \cos^2 \beta)^2}{\sin^4 \beta} C_{11} + \frac{4\cos^2 \beta(1 - \cos \alpha)^2}{\sin^4 \beta} C_{33} - \frac{4(\cos \alpha - \cos^2 \beta)}{\sin^2 \beta} C_{12} - \frac{4\cos \beta(1 - \cos \alpha)}{\sin^2 \beta} C_{23} + \frac{8\cos \beta(1 - \cos \alpha)(\cos \alpha - \cos^2 \beta)}{\sin^4 \beta} C_{13}
\]

\[
C_{12}' = \frac{2(\cos \alpha - \cos^2 \beta)}{\sin^2 \beta} C_{11} - C_{12} + \frac{2\cos \beta(1 - \cos \alpha)}{\sin^2 \beta} C_{31}
\]

\[
C_{13}' = \frac{2(\cos \alpha - \cos^2 \beta)}{\sin^2 \beta} C_{13} - C_{23} + \frac{2\cos \beta(1 - \cos \alpha)}{\sin^2 \beta} C_{33}
\]

\[
C_{22}' = C_{11}
\]

\[
C_{23}' = C_{13}
\]

\[
C_{33}' = C_{33}
\]

(3.3.8a)

b) Crystalline case.

\[
[C_{ij}] \cong \begin{bmatrix} \left(\frac{\sin (\alpha + \theta)}{\sin \alpha} q_1 - \frac{\sin \theta}{\sin \alpha} q_2 \right) & \left(\frac{\sin (\alpha + \theta)}{\sin \alpha} q_1 - \frac{\sin \theta}{\sin \alpha} q_2 \right) \\ \left(\frac{\sin \theta}{\sin \alpha} q_1 + \frac{\sin (\alpha - \theta)}{\sin \alpha} q_2 \right) & \left(\frac{\sin \theta}{\sin \alpha} q_1 + \frac{\sin (\alpha - \theta)}{\sin \alpha} q_2 \right) \end{bmatrix}
\]

where \((q_1, q_2, q_3)\) is the molecular or crystalline base.

(3.3.8b)
By equating term by term:

\[ C_{11} = \frac{\sin^2 (\alpha + \theta)}{\sin^2 \alpha} C_{11} - 2 \frac{\sin (\alpha + \theta) \sin \theta}{\sin^2 \alpha} C_{12} + \frac{\sin^2 \theta}{\sin^2 \alpha} C_{22} \]
\[ C_{12} = \frac{\sin (\alpha + \theta) \sin \theta}{\sin^2 \alpha} C_{11} + \frac{\sin (\alpha + \theta) \sin (\alpha - \theta) - \sin^2 \theta}{\sin^2 \alpha} C_{12} - \frac{\sin \theta \sin (\alpha - \theta)}{\sin^2 \alpha} C_{22} \]
\[ C_{22} = \frac{\sin^2 \theta}{\sin^2 \alpha} C_{11} + 2 \frac{\sin \theta \sin (\alpha - \theta)}{\sin^2 \alpha} C_{12} + \frac{\sin^2 (\alpha - \theta)}{\sin^2 \alpha} C_{22} \]
\[ C_{13} = \frac{\sin (\alpha + \theta)}{\sin \alpha} C_{13} - \frac{\sin \theta}{\sin \alpha} C_{23} \]
\[ C_{23} = \frac{\sin \theta}{\sin \alpha} C_{13} + \frac{\sin (\alpha - \theta)}{\sin \alpha} C_{23} \]
\[ C_{33} = C_{33}. \]

2. Contravariant components. — In the same way, formula (3.1.15b) gives the contravariant components.

Geometrical interpretation of the tensor \([C]\) components in oblique axes \(\beta = \gamma = \frac{\pi}{2}\) in the central force case.

a) Rectangular coordinates. — For the central force case, the components \(C_{ij}\) of \([C]\) in rectangular coordinates have a clear significance which allows one to calculate them easily [3]. \(C_{ij}\) is the force exerted in the direction \(e_j\) on the atom located at 0 when the atom \(B\) is displaced a unit distance in the \(e_i\)-direction:

\[ C_{ij} = -\gamma(e_i, u)(u, e_j) \] (3.3.9)

\(u\) is the unit vector along \(OB\), and \(\gamma\) is a force constant (Fig. 1).

b) Covariant components (oblique axis). — Let us suppose that the tensor \([C]\) is now expressed with the help of its covariant components \(C_{ij}\) in the basis \(e'_k\). We intend to interpret these new components. Now, the two-times covariant tensor \([C_{ij}]\) changes as:

\[ C'_{ij} = a_{ir} a_{jr} C_{kl}. \] (3.3.10)

If the \(C_{kl}\) rectangular components of \([C]\) is introduced:

\[ C_{kl} = -\gamma(e_k, u)(u, e_l). \]

Then:

\[ C'_{ij} = a_{ir} a_{jr} C_{kl} = -\gamma(a_{ir} e_k u, u, a_{jr} e_l) = -\gamma(e'_i, u)(u, e'_j). \] (3.3.11)

So \([C']\) receives the following interpretation:

The components \(C'_{ij}\) in oblique axes of the force tensor \([C]\) are the forces exerted in the \(e'_j\)-direction on the atom located at 0 when the atom \(B\) is displaced a unit distance in the \(e'_i\)-direction.

As in rectangular coordinates, the orthogonal projections of the displacements and the forces on the axes must be taken.

c) Contravariant components. — The tensor \([C]\) may also be expressed in terms of its contravariant components \(C'^{ij}\):

\[ C'^{ij} = g^{ik} g^{jl} C_{kl} \]
\[ = g^{ik} g^{jl} (-\gamma)(e'_i, u)(u, e'_j). \] (3.3.12)

But the covariant components of \(e'_k\) along \(u\) can be written as:

\[ x_k = e'_k, u \] (3.3.13a)

and its contravariant components:

\[ x^i = g^{ik} e'_k, u. \] (3.3.13b)

It follows that:

\[ C'^{ij} = -\gamma(g^{ik} e'_k, u)(u, g^{jl} e'_l) = -\gamma x^i x^j. \] (3.3.14)

Consequently, \(C'^{ij}\) is still the force exerted in the direction \(e'_j\) on the atom located at 0 when the atom \(B\) is displaced a unit distance in the direction \(e'_i\). But, in this case, it is necessary to consider the contravariant components of the displacements and the forces.

Contravariant projection. — The application of the formulas in oblique axes is made easier by using a geometrical construction. Let us consider two base vectors \(e'_p\), \(e'_q\) and a direction signified by \(u\) along which the contravariant projection of the vector \(e'_k\) is taken (Fig. 4).

---

**FIG. 4.** — The contravariant projection of a vector \(e'_k\) along \(u\).
In the previous paragraph, we have seen that expressions like \( x^k \Xi^1 \), where:

\[
x^k = g^{kj} e_j \cdot u
\]

must be manipulated.

To the vector \( u \) one associates the vector \( v \) so that \( (u, v) = \alpha \). Then, \( x' \) is obtained by drawing through the extremity of \( e'_k \) the parallel to \( v \) until its intersection \( P \) with \( u \).

It can be said that \( OP \) is the contravariant component of \( e'_k \) on \( u \).

**Proof.** Let us first consider the two-dimensional case. The vector \( u \) is the projection on the plane of the vector \( U \) along which the component of \( e'_k \) is sought:

\[
x^k = g^{kl} (e'_k \cdot u) + g^{kl}_{\xi_k \eta_k} (e'_j \cdot u).
\]

Let us look for the contravariant component \( y'' \) of \( e'_k \) along \( (u, v) \):

\[
y'' = g^{vw} (e'_k \cdot u) + g^{vw}_{\xi_k \eta_k} (e'_j \cdot u)
\]

by construction. q.e.d.

In the three-dimensional case, if \( u' \) is the component of \( u \) in the plane \( (e'_i, e'_j) \):

\[
C_{kl} = \gamma (e'_k \cdot u')(u' \cdot u)(u' \cdot v)
\]

and:

\[
C^{ij} = \gamma [g^{ij}(e'_k \cdot u')(u' \cdot u)] [g^{ij}(e'_k \cdot u')(v' \cdot u')].
\]

Thus the contravariant projection of \( e'_k \) over \( u' \) is first considered, following by the projection of the vector \( u' \) on \( u \).

**Remark.** The physical meaning of the components of \( [C] \) allows their direct derivation without calculations. We will give an example in part 4.

### 3.4 EQUATIONS OF IONIC DISPLACEMENTS. EIGENVALUES AND EIGENVECTORS.

#### 1. Equations of motion expressed with contravariant coordinates.

Lagrange's equations give atomic motions in terms of the contravariant components of the vectors:

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial u'} \right) = \frac{\partial L}{\partial u'} - \frac{\partial L}{\partial u'} = 0
\]

where:

\[
L = T - V = \frac{1}{2} \sum_{s} M_s \left( \frac{\partial}{\partial u'} \right)(G) \left( \frac{u'}{s} \right) - \sum_{s} \left( \frac{\partial}{\partial u'} C_{\text{cov}} \left( \frac{u'}{s}, \frac{u'}{s'} \right) \left( \frac{u'}{s'} \right) \right)
\]

After differentiation, the following system of second order differential equations is obtained:

\[
M_s (G) \left( \frac{\partial}{\partial u'} \right) \left( \frac{u'}{s} \right) = - \sum_{s} C_{\text{cov}} \left( \frac{u'}{s}, \frac{u'}{s'} \right) \left( \frac{u'}{s'} \right)
\]

As the crystal is invariant under translation, the solutions are the Bloch functions [4]:

\[
\left( \frac{u'}{s} \right) = \frac{1}{\sqrt{M_s}} \left( \frac{u}{0} \right) e^{i(k \cdot R + \omega t)}
\]

which, when introduced in eq. (3.4.3), give:

\[
- \omega^2 M_s \frac{1}{2} \left( G \right) \left( \frac{u'}{s} \right) = - \sum_{s} C_{\text{cov}} \left( \frac{u'}{s}, \frac{u'}{s'} \right) \times \left( \frac{u'}{s'} \right) \times e^{i(k \cdot (R' - R))}.
\]

The Fourier transform [4] of \( C_{\text{cov}} \left( \frac{u'}{s}, \frac{u'}{s'} \right) \) yields:

\[
\left( \frac{D_{\text{cov}} \left( \frac{k}{s}, \frac{u'}{s'} \right)}{s'} \right) = \frac{1}{M_s} \sum_{s} \frac{C_{\text{cov}} \left( \frac{u'}{s}, \frac{u'}{s'} \right)}{s'} e^{i(k \cdot (R' - R))}.
\]

Then we get the following equations:

\[
\omega^2 \left( \frac{u}{s} \right) = \sum_{s} \left( \frac{D_{\text{cov}} \left( \frac{k}{s}, \frac{u'}{s'} \right)}{s'} \right) \left( \frac{u}{s'} \right).
\]

which are simultaneous linear equations. It is necessary to separate the variables by multiplying by \( (G^{-1}) \) both sides of the eq. (3.4.7):

\[
\omega^2 \left( \frac{u}{s} \right) = \sum_{s} \left( \frac{D_{\text{cov}} \left( \frac{k}{s}, \frac{u'}{s'} \right)}{s'} \right) \left( \frac{u}{s'} \right).
\]

The eigenvalue equation of the system is now given by the resolution of the determinant:

\[
\left( G^{-1} \right) \left( \frac{D_{\text{cov}} \left( \frac{k}{s}, \frac{u'}{s'} \right)}{s'} \right) - \omega^2 \delta_{ss'} \delta_{ss'} = 0.
\]

It is easy to verify that \( D_{\text{cov}} \left( \frac{k}{s}, \frac{u'}{s'} \right) \) is hermitian, which is not the case for \( (G^{-1}) \).

#### 2. Equations of motion expressed with covariant coordinates.

In the same way, one gets:

\[
\omega^2 \left( \frac{u}{s} \right) = \sum_{s} \left( G D_{\text{cov}} \left( \frac{u'}{s}, \frac{u'}{s'} \right) \right) \left( \frac{u}{s'} \right).
\]

a very simple eigenvalue equation is thus obtained.
The flexibility of the formalism is interesting and one has now to choose the best adjusted formalism to treat each problem.

Remark. — It can be shown that the eigenvalues which are given by the two formalisms are the same.

3. General symmetry properties. — The symmetry properties are the same as in rectangular coordinates [10]. We give some illustrating examples.

a) Translational invariance. — $C_{\text{cov}} \left( \frac{l'}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right)$ possess invariance properties for the translation and rotation of the lattice as a whole. Particularly, one has:

$$\sum_{s' t} C_{\text{cov}} \left( \frac{l'}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right) = 0 \quad \text{(3.4.11)}$$

b) Permutation of the indices.

$$C_{\text{cov}} \left( \frac{l'}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right) \approx u_{s} \left( \frac{l}{s} \right) u_{s} \left( \frac{l'}{s} \right) \approx C_{\text{cov}} \left( \frac{l'}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right) \quad \text{(3.4.12)}$$

c) Properties of the dynamical matrix $D_{\text{cov}} \left( \frac{k}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right)$.

$$D_{\text{cov}} \left( \frac{k}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right) \approx \sum_{l} u_{s} \left( \frac{l}{s} \right) u_{s} \left( \frac{l'}{s} \right) e^{-i k \cdot R(l' - l)} \quad \text{(3.4.13)}$$

Let us examine several cases:

\begin{itemize}
  \item $e^{-i k \cdot R}$ only is modified by the symmetry operation:
    \begin{equation}
      k \rightarrow k + 2 \pi b (b \in \text{Reciprocal lattice}).
    \end{equation}
  \item $i \rightarrow -i$; $u$ being real, only $e^{-i k \cdot R}$ is transformed:
    \begin{equation}
      D_{\text{cov}} \left( \frac{k}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right) = D_{\text{cov}} \left( \frac{-k}{s} \right) \left( \frac{s}{s'} \right) \left( \frac{a}{a'} \right) \quad \text{(3.4.14)}
    \end{equation}
  \end{itemize}

\section*{4. Study of the vibrational modes of MoS$_2$ using oblique axes.}

- Let us use the former formalism (part 3) to study the crystalline vibrational modes of the H$_2$O molecule (C$_{2v}$) — Table I : $\Gamma_{\text{vib}} = 2A_1 \oplus B_1$.

The non-zero matrix elements $C_{a''}$, belong to the irreducible representations:

$$\left( A_1 \oplus B_1 \right) \otimes \left( A_1 \oplus B_1 \right) = 2 \left( A_1 \oplus B_1 \right) .$$

Consequently:

$$x^2 \times x^2 \times x^3 \times x^3 \times x^3 = 0 .$$

\begin{table}[h]
\begin{center}
\begin{tabular}{cccc}
\hline
& C$_{2v}$ & E & C$_2$ & $\sigma_v$ & $\sigma'_v$ \\
\hline
$A_1$ & 1 & 1 & 1 & 1 \\
$A_2$ & 1 & 1 & -1 & -1 \\
$B_1$ & 1 & -1 & 1 & -1 \\
$B_2$ & 1 & -1 & -1 & 1 \\
\hline
\end{tabular}
\end{center}
\end{table}

\section*{Remark. — In the case of the molecules [11], for example, the character tables of the symmetry group do not allow one to know how the homologous ions, nor the coordinates, transform one into the other. It remains possible however to prove without calculations the nullity of some coordinate products. If one considers indeed, in a very general way, the tensor product of coordinates like $(x_1 \times x_2 \times x^3) \otimes (x_1 \times x^2 \times x^3)$, it is necessary to restrict the ionic displacements to those of the normal coordinates.

But the character table I of the group shows also to which irreducible representations the products $x^1 \times x^2$, $x^2 \times x^3$, $x^3 \times x^4$ belong. If the irreducible representations of the direct product of the normal coordinates do not contain them, the considered products of coordinates are then necessarily equal to zero.

\section*{Example : H$_2$O molecule (C$_{2v}$)}

- The non-zero matrix elements $C_{a''}$, belong to the irreducible representations:

$$\left( A_1 \oplus B_1 \right) \otimes \left( A_1 \oplus B_1 \right) = 2 \left( A_1 \oplus B_1 \right) .$$

Consequently:

$$x^1 \times x^2 \times x^3 \times x^3 \times x^3 = 0 .$$

\section*{Character table of the group C$_{2v}$ (after [11])}

\begin{table}[h]
\begin{center}
\begin{tabular}{cccc}
\hline
& $x^1$ & $x^2$ & $x^3$ \\
\hline
$A_1$ & 1 & 1 & 1 \\
$A_2$ & 1 & -1 & -1 \\
$B_1$ & 1 & -1 & -1 \\
$B_2$ & 1 & 1 & 1 \\
\hline
\end{tabular}
\end{center}
\end{table}
of MoS$_2$. We perform the calculations in the natural crystallographic axes.

4.1 GENERALITIES. — The MoS$_2$ crystal studied here is the hexagonal $D_{6h}$ layer compound. The elementary cell consists of two sheets (Fig. 5) bound by weak van der Waals forces which may be neglected in a first approximation. In such a case, the crystal has a two dimensional periodicity with a $D_{3h}$ symmetry. This approach is justified because the ratio of the crystal parameters: $a = 3.16$ Å and $c = 12.30$ Å is a very high one.

Fig. 5. — Elementary cell of MoS$_2$ according to Wyckoff [12].

Two indices: $m$ and $n$ are now sufficient to characterize the position of one cell with respect to an origin cell ($m = 0$, $n = 0$) (Fig. 6).

According to Wyckoff [12], the position of the ions Mo and S in a cell is given by:

$$\begin{align*}
\text{Mo} : & \left( \frac{1}{3}, \frac{2}{3}, \frac{1}{4}; u \right) \\
\text{S} : & \left( \frac{2}{3}, \frac{1}{3}, u \right)
\end{align*}$$

with $u = \pm 0.629$. The $S^+$ ($+u$) ions are distinguished from the $S^-$ ($-u$) ions.

We intend to test the method described in the part 3 of this paper. To simplify, we assume only first neighbour interactions and central forces (Fig. 7) as in the case of the previous paper of Bromley [13] which contains some errors. Three elastic constants are now introduced: $\alpha'$, $\beta$, $\gamma$ corresponding to the interactions Mo-Mo, S-S and Mo-S respectively.

Fig. 7. — Illustration of the contravariant projection method in the case of MoS$_2$.


It is easy to write down the contravariant components of the Mo(00)-Mo(mn) interaction tensor.

a) Interactions between Mo(00)-Mo(10) and Mo(00)-Mo(01)

$$[C_{(10)}^{\text{contr}}] = \begin{bmatrix}
-\alpha' & \cdot \\
\cdot & \cdot
\end{bmatrix} = [C_{(10)}^{\text{contr}}]. \quad (4.2.1)$$

b) Interactions between Mo(00)-Mo(01) and Mo(00)-Mo(11)

$$[C_{(01)}^{\text{contr}}] = \begin{bmatrix}
\cdot & -\alpha' \\
\cdot & \cdot
\end{bmatrix} = [C_{(01)}^{\text{contr}}]. \quad (4.2.2)$$

c) Interactions between Mo(00)-Mo(11) and Mo(00)-Mo(11)

$$[C_{(11)}^{\text{contr}}] = \begin{bmatrix}
-\alpha' & -\alpha' \\
\cdot & \cdot
\end{bmatrix} = [C_{(11)}^{\text{contr}}]. \quad (4.2.3)$$
According to the rule of the force parallelogram, if Mo(11) is displaced a unit distance in the \( e_1 \) direction, this displacement can be decomposed along the direction Mo(00)-Mo(11) in unit vectors (equilateral triangle) and gives rise to a \(-\alpha' u\) force which is decomposed similarly along \( e_1' \) or \( e_2' \).

It easy to find directly these formulae, for example on the bond Mo(00)-Mo(10) by use of the rotation operator \( R(0z, \theta = 4 \pi/3) \).

**Remark.** — The transformation of the contravariant components of \( [c] \) to the covariant ones is given by:

\[
C_{ij} = \delta_{ik} \theta_{jk} C^{kl} \tag{4.2.4}
\]

and formula (3.3.4b) gives directly the rectangular components.

2. Interactions S-S. — The same calculations are valid for the interactions between the S-S ions of a plane, provided \( \alpha' \) is replaced by \( \beta \). In a first approximation, the same force constant \( \beta \) represents the \( S^+ - S^- \) interactions.

3. Interactions Mo-S. — The calculations of the Mo-S interactions are directly obtained using the contravariant projection method (3.3). Let \( u \) be the unit displacement along \( e_2 \) (Fig. 7). Its contravariant projection is called \( x \). In the triangle MoXu we have:

\[
\frac{x}{\sin (\alpha + \varphi)} = \frac{1}{\sin \alpha} \quad x = \frac{\sin (\alpha + \varphi)}{\sin \alpha}. \tag{4.2.5}
\]

But the orthogonal projection is to be considered in the Mo(00)-S(00) direction, since \( e_3' \) is perpendicular to the plane \( (e_1', e_2') \). Consequently, the force exerted along Mo-S has the value:

\[-\gamma \sin \theta \frac{\sin (\alpha + \varphi)}{\sin \alpha} \cdot \tag{4.2.6}\]

It follows immediately that:

\[
C_{Mo-S}(00; 00) = -\gamma \frac{\sin^2 \theta \sin^2 (\alpha + \varphi)}{\sin^2 \alpha} \tag{4.2.6}
\]

\[
C_{Mo-S}(00; 00) = -\gamma \frac{\sin \theta \sin (\alpha + \varphi) \cos \theta}{\sin \alpha} \cdot \tag{4.2.7}
\]

Direct inspection allows construction of the tensor \([C_{Mo-S}^{\text{contr}}(00; 00)]\). The application of the general formula (3.3.8) gives immediately the tensors \([C_{Mo-S}^{\text{ent}}(00; 01)]\) and \([C_{Mo-S}^{\text{contr}}(00; 10)]\), taking into account that:

\[
\alpha = \frac{2 \pi}{3} \quad \alpha + \varphi = \frac{5 \pi}{6} \quad \tan \theta = \frac{2}{\sqrt{3}}
\]

\[
\begin{bmatrix}
-\gamma' & \gamma' & \gamma'' \\
3 & 3 & 2\sqrt{3} \\
\gamma'' & -3 & 2\sqrt{3} \\
\gamma'' & -2\gamma'' & -2\gamma''
\end{bmatrix}
\]

\[
\begin{bmatrix}
-\gamma' & -\frac{2\gamma'}{3} & \gamma'' \\
3 & 3 & 2\sqrt{3} \\
\gamma'' & -\frac{4\gamma'}{3} & \frac{\gamma''}{\sqrt{3}} \\
\gamma'' & -\frac{\gamma''}{\sqrt{3}} & -\gamma''
\end{bmatrix}
\]

\[
\begin{bmatrix}
-\frac{4\gamma'}{3} & -\frac{2\gamma'}{3} & -\gamma'' \\
3 & 3 & \sqrt{3} \\
\gamma'' & -\frac{2\gamma'}{3} & -\gamma'' \\
\gamma'' & -\frac{\gamma''}{\sqrt{3}} & -\gamma''
\end{bmatrix}
\]

with:

\[
\gamma' = \gamma \sin^2 \theta \\
\gamma'' = \gamma \cos^2 \theta \\
\gamma''' = \gamma \sin 2 \theta.
\]

**Remark.** — In the case of Mo-S interactions, only the \( C_{Mo-S}^{13} \) and \( C_{Mo-S}^{23} \) elements change their signs \((\gamma \rightarrow -\gamma)\) with respect to the corresponding elements \( C_{Mo-S}^{13} \) and \( C_{Mo-S}^{23} \),

4. 3 BRILLOUIN ZONES. — In the same manner as in rectangular axes [7], Bloch solutions are sought:

\[
u \begin{bmatrix}
1 \\
0
\end{bmatrix} = \begin{bmatrix}
0 \\
1
\end{bmatrix} e^{\left[ k \cdot R \right] - \text{est}} \tag{4.3.1}
\]

where \( k \) represents a vector of the reciprocal lattice (R.L.) and \( R \) designates a vector of the primitive lattice (P.L.). Let us remark that the exponential terms contain the scalar product \( k \cdot R \), which must stay invariant whatever the nature co- or contravariant of \( R \), according to the fundamental tensor theorem [5]. As a consequence, this product remains invariant under a change of coordinates system. Of course, the \( k \) components will be different in rectangular and oblique coordinates.
**Primitive and reciprocal lattices.** — Each point of the primitive lattice is defined by two contravariant \((m,n)\) components, \(a\) being the unit of length.

Let \(a\) and \(b\) be the base vectors of the P.L. and \(A\) and \(B\) the base vectors of the R.L. defined by:
\[
\begin{align*}
\mathbf{a}_{\text{cov}} \cdot \mathbf{A}_{\text{cov}} &= 2\pi \\
\mathbf{b}_{\text{cov}} \cdot \mathbf{A}_{\text{cov}} &= 0 \\
\mathbf{a}_{\text{cov}} \cdot \mathbf{B}_{\text{cov}} &= 0 \\
\mathbf{b}_{\text{cov}} \cdot \mathbf{B}_{\text{cov}} &= 2\pi
\end{align*}
\]

Then:
\[
A_1 = \frac{2\pi}{\alpha}; \quad A_2 = 0; \quad B_1 = 0; \quad B_2 = \frac{2\pi}{\alpha}
\]
so that:
\[
\mathbf{A} \perp \mathbf{b} \quad \text{and} \quad \mathbf{B} \perp \mathbf{a}.
\]

Figure 8 schematizes the R.L. The coordinates of the remarkable points \(\Gamma, \mathbf{P}, \mathbf{Q}'\) are given by:
\[
\begin{align*}
\Gamma: (0, 0); \quad \mathbf{P}: \left(-\frac{2\pi}{3\alpha}; \frac{4\pi}{3\alpha}\right); \quad \mathbf{Q}': \left(-\frac{\pi}{\alpha}; 0\right).
\end{align*}
\]

In the general case, the covariant components \((k_1, k_2)\) of the \(k\) vector are deduced from the rectangular one by:
\[
\begin{pmatrix} k_1 \\ k_2 \end{pmatrix} = (A) \begin{pmatrix} k_x \\ k_y \end{pmatrix}.
\]

**4.4 Dynamical matrix.** — It is now necessary to construct expressions of the form:
\[
\mathbf{D}_{\text{contr}} \begin{pmatrix} \mathbf{k} \\ \mathbf{ss}'' \end{pmatrix} = \frac{1}{\sqrt{M_j M_k}} \sum C_{\text{contr}} \begin{pmatrix} \mathbf{l}'' \\ \mathbf{xx}'' \end{pmatrix} e^{i\langle \mathbf{k}, (\mathbf{R}_j - \mathbf{R}_k) \rangle}
\]
where the following factors are to be considered:
\[
\begin{align*}
C^{(00;01)}_{\text{Mo-Mo}} &= C^{(00;01)}_{\text{Mo-Mo}} : e^{-2j\xi} \\
C^{(01;10)}_{\text{Mo-Mo}} &= C^{(01;10)}_{\text{Mo-Mo}} : e^{-2j\eta} \\
C^{(01;11)}_{\text{Mo-Mo}} &= C^{(01;11)}_{\text{Mo-Mo}} : e^{-2j(\xi + \eta)} \\
C^{(00;01)}_{\text{Mo-S}^+} &= C^{(00;01)}_{\text{Mo-S}^+} : e^{2j\xi} \\
C^{(00;10)}_{\text{Mo-S}^+} &= C^{(00;10)}_{\text{Mo-S}^+} : e^{2j\eta} \\
C^{(01;11)}_{\text{Mo-S}^+} &= C^{(01;11)}_{\text{Mo-S}^+} : e^{2j(\xi + \eta)}
\end{align*}
\]
with:
\[
\begin{align*}
\eta' &= \frac{1}{2} k_1 a \\
\xi' &= \frac{1}{2} k_2 a.
\end{align*}
\]

The calculation of the dynamical matrix coefficients is now easy.

**4.5 Eigenvalues and dispersion curves.** — At this step, the problem of finding the eigenvalues and the eigenvectors can be solved in two ways.

In principle, formula (3.4.10) can be applied but leads to a search for the eigenvalues and eigenvectors of a non-hermitian matrix.

Another possibility is to use the transformation (3.3.4a or b) which gives a hermitian matrix: for simplicity we have preferred this procedure.

After some calculations, it is found that:
\[
\begin{align*}
m_1 D^{11}_{\perp} (\text{Mo-Mo}) &= 3(\alpha' + \gamma') - \frac{\alpha'}{4} e^{-j(\xi + \eta)} - \frac{\alpha'}{4} e^{-j(\xi - \eta)} - \alpha' e^{-2j\xi} + \text{C.C.} \\
m_1 D^{12}_{\perp} (\text{Mo-Mo}) &= \frac{\sqrt{3}}{4} \alpha' e^{-j(\xi - \eta)} - \frac{\sqrt{3}}{4} \alpha' e^{-j(\xi + \eta)} + \text{C.C.} \\
D^{13}_{\perp} (\text{Mo-Mo}) &= 0 \\
m_1 D^{22}_{\perp} (\text{Mo-Mo}) &= 3(\alpha' + \gamma') - \frac{3}{4} \alpha' e^{-j(\xi + \eta)} - \frac{3}{4} \alpha' e^{-j(\xi - \eta)} + \text{C.C.} \\
D^{23}_{\perp} (\text{Mo-Mo}) &= 0 \\
m_1 D^{33}_{\perp} (\text{Mo-Mo}) &= 6 \gamma'' \\
\sqrt{m_1 m_2} D^{11}_{\perp} (\text{Mo-S}^+) &= - \frac{3}{4} \gamma' - \frac{3}{4} \gamma' e^{-2j\xi} \\
\sqrt{m_1 m_2} D^{12}_{\perp} (\text{Mo-S}^+) &= - \frac{\sqrt{3}}{4} \gamma' + \frac{\sqrt{3}}{4} \gamma' e^{-2j\xi} \\
\sqrt{m_1 m_2} D^{13}_{\perp} (\text{Mo-S}^+) &= - \frac{\sqrt{3}}{4} \gamma'' + \frac{\sqrt{3}}{4} \gamma'' e^{-2j\xi} \\
\sqrt{m_1 m_2} D^{22}_{\perp} (\text{Mo-S}^+) &= - \frac{1}{4} \gamma' - \gamma' e^{-j(\xi + \eta)} - \frac{\gamma'}{4} e^{-2j\xi} \\
\sqrt{m_1 m_2} D^{23}_{\perp} (\text{Mo-S}^+) &= - \frac{\gamma''}{4} + \frac{\gamma''}{2} e^{-j(\xi + \eta)} - \frac{\gamma''}{4} e^{-2j\xi} \\
\sqrt{m_1 m_2} D^{33}_{\perp} (\text{Mo-S}^+) &= - \gamma'' - \gamma'' e^{-2j\xi} - \gamma'' e^{-j(\xi + \eta)} \\
m_2 D^{33}_{\perp} (\text{S}^+ - \text{S}^-) &= - \beta
\end{align*}
\]
The other terms $D_{ij} (S^+ - S^-)$ are equal to zero.

The parameters $\alpha'$, $\beta$, $\gamma$ are adjusted by comparison with the optical and neutron data [14]. The $\beta$ and $\gamma$ parameters are fixed at point $\Gamma$ of the Brillouin zone and the $\alpha'$ parameter at point $Q'$ of the upper acoustical branch $A(y)$. The following values of the parameters have been found:

$$\alpha' = 0.56 \times 10^5 \text{ dynes cm}^{-1}$$
$$\beta = 0.33 \times 10^5 \text{ dynes cm}^{-1}$$
$$\gamma = 0.185 \times 10^6 \text{ dynes cm}^{-1}$$

and used to draw the theoretical phonon dispersion curves in the $\Gamma Q'$ direction (Fig. 9).

The acoustical branches are well reproduced, in particular the typical bidimensional acoustical branch $A(z)$. From these, the elastic constants are calculated:

$$C_{11} = 1.39 \times 10^{12} \text{ dynes cm}^{-2}$$
$$C_{12} = 0.97 \times 10^{12} \text{ dynes cm}^{-2}$$
or:

$$(v_{LA})_{\text{optical}} = 7.49 \times 10^5 \text{ cm s}^{-1}$$

instead:

$$(v_{LA})_{\text{neutron}} = 6.7 \times 10^5 \text{ cm s}^{-1}.$$
These quantities contain other operators which are respectively of the form:

\[ U_{sp}(l, k') = \frac{\partial^2}{\partial u_s(l, k) \partial u_p(l', k')} u_s(l, k) u_p(l', k') \]  

\[ \hat{U}_s(l, k') \hat{U}_p(l', k') = \frac{\partial}{\partial u_s(l, k)} \frac{\partial}{\partial u_p(l', k')} u_s(l, k) u_p(l', k') \]  

(5.2)

(5.3)

So, the same rules as are applied to the molecules can be used in the present case [2].

b) Operators \( \hat{T} \) and \( \hat{S} \). — \( \hat{T} \) represents the short range interaction operator between core and shell for two different ions.

\( \hat{S} = \hat{S} + \hat{K} \) is the short range interaction operator, \( \hat{S} \) between neighbouring shells, \( \hat{K} \) between the core of the ions and their own shell (self-interaction). These operators involve expressions of the following kind:

\[ Q_s(l, k) U_p(l', k') = \frac{\partial}{\partial q_s(l, k)} \frac{\partial}{\partial u_p(l', k')} q_s(l, k) u_p(l', k') \]  

(5.4)

\[ Q_s(l, k) U_p(l', k') = \frac{\partial^2}{\partial q_s(l, k) \partial q_p(l', k')} q_s(l, k) q_p(l', k') \]  

\[ U_{sp}(l, k') = \frac{\partial^2}{\partial u_s(l, k) \partial u_p(l', k')} u_s(l, k) u_p(l', k') \]  

(5.5)

(5.6)

\( \mathbf{u} \) represents an ionic displacement which must be consistent with the vibrations and \( \mathbf{q} \) is a dipole moment shaped by the surroundings of the considered ion, since it represents the relative core-shell displacement, which is determined by the environment of the ion. This deformation has necessarily the symmetry of the neighbouring ions which cause the deformation of the shell by electrostatic interaction.

Conclusion. — Finally, it is necessary to examine how the vectors \( \mathbf{u}(l, k) \) and \( \mathbf{q}(l, k) \) change with respect to the symmetry operators of the crystal.

But in the shell model, \( \mathbf{q} \) is transformed like \( \mathbf{u} \) and the method for the molecules can also be applied in this case [2].

Furthermore, the shell model is seen to be an harmonic approximation.

5.2 BREATHING SHELL MODEL (B.S.M.). — In this model, a new degree of internal symmetry, the variation of the volume of each ion, is introduced [16].

Two other operators \( \hat{Q} \) and \( \hat{H} \) appear, which describe the coupling between the variation of the volume of the shell and the displacement of the cores and the shells. These operators have the following form:

\[ \frac{\partial}{\partial r^2} \cong r^2 \text{ or } r_1 r_2 \]  

(5.7)

\( r_i \) being the radius of the shell with respect to the core. They are isotropic.

5.3 GENERALIZED SHELL MODEL (G.S.M.). — In this model, introduced by Fischer and coworkers [17] all the possible modes of the local displacements of the ions surrounding a particular ion of the lattice are taken into account. In such a case, the displacements of the electronic shells are not arbitrary but correspond to the symmetries of the ionic displacements. Accordingly, the induced moments \( \mathbf{q} \) possess also the same symmetries.

Three cases can occur:

a) \( \mathbf{q} \) has the same symmetry properties as \( \mathbf{u} \) which can be substituted for \( \mathbf{q} \) and the problem to be solved is the same as for the S.M., that is to study the transformations of the tensor product \( \mathbf{u} \otimes \mathbf{u} \).

Example:

S.M. \( \mathbf{q} \in \Gamma_{15} \) (AgCl) [17].

b) \( \mathbf{q} \) does not belong to the same irreducible representations as \( \mathbf{u} \), but is transformed like one of the product of coordinates. It is also possible to apply the general treatment.

Example: shear mode \( \Gamma_{25}^+ \) (AgCl) [17].

c) \( \mathbf{q} \) does not correspond to any of the two former cases.

Example: tetragonal deformation \( \Gamma_{25}^+ \) (AgCl) [17].

It is necessary to examine the transformations of the normal coordinates \( Q(\Gamma_{25}) \) with respect to the \( \hat{L} \) operators. Therefore, the relation (3.3.2) will be more generally written as:

\[ \mathbf{u}(l, k) \otimes \mathbf{q}(l', k') = S \mathbf{u}(l, k) \otimes \mathbf{q}(l', k') \]  

(5.8)

In this expression, any physical quantity, simpler but which belongs to the same irreducible representations as \( \mathbf{u} \) and \( \mathbf{q} \) respectively, can be substituted for \( \mathbf{u} \) and \( \mathbf{q} \).

The matrix elements of (5.1) which are zero or equivalent are then directly obtained.

Conclusion. — It has been shown how it is possible to substitute for the differential matrix elements appearing in the theory of the lattice dynamics, other simpler quantities from which the transformation
rules through the symmetry operator $L$ of the crystal are known. The non-zero or equivalent matrix elements constituting the dynamical matrix are then easily obtained.

Finally, this method allows one to verify the homogeneity of the formulae and thus plays a role which is similar to that of an equation of dimensions.

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References