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WAVE VECTOR DEPENDENCE OF THE RAMAN EFFECT IN CRYSTALS (1)

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Résumé. — On évite le calcul des états intermédiaires, dans l'expression générale en mécanique quantique du tenseur de Raman, en remplaçant les différents dénominateurs de résonance entre les états fondamental et intermédiaire, par un dénominateur moyen. Cela simplifie beaucoup les formules qui permettent l'estimation quantitative du tenseur de Raman, sans employer l'approximation dipolaire. Les composantes $a_{ij}$ du tenseur de diffusion s'obtiennent par la somme $G_{ij} + J_{ij} + H_{ij}$, où $G_{ij}$ peut être appelé le tenseur conventionnel de diffusion. $J_{ij}$ est la contribution de l'opérateur de densité de charge à l'hamiltonien d'interaction, que l'on néglige habituellement, et $H_{ij}$ est un tenseur asymétrique dont les composantes dépendent explicitement des vecteurs d'onde $\mathbf{q}$ et $\mathbf{q}'$ des radiations incidente et diffuse. $J_{ij}$ se trouve être du même ordre de grandeur que $G_{ij}$, mais $H_{ij}$ est environ cent fois plus petit si l'on néglige les interactions de Coulomb à longue distance entre les ions oscillants, et si l'on admet que les fonctions d'onde électroniques des ions dans le cristal sont localisées comme dans les vapeurs. On suggère que la suppression de ces deux dernières approximations pourrait expliquer l'échec des règles de sélection de Raman du premier ordre pour la calcite et les cristaux analogues.

Abstract. — The sum over intermediate states in the general quantum mechanical expression for the Raman tensor is removed by replacing the different resonance denominators between the ground and intermediate states with one average denominator. This procedure leads to a substantial simplification of the formulas which allows one to compute quantitative estimates of the Raman tensor without employing the dipole approximation. The components $a_{ij}$ of the scattering tensor are obtained as a sum $G_{ij} + J_{ij} + H_{ij}$, where $G_{ij}$ may be termed the conventional scattering tensor, $J_{ij}$ is the contribution from the charge density operator in the interaction Hamiltonian which is usually neglected, and $H_{ij}$ is a nonsymmetric tensor the components of which depend explicitly on the wave vectors $\mathbf{q}$ and $\mathbf{q}'$ of the incident and scattered radiation. $J_{ij}$ is found to be of the same order of magnitude as $G_{ij}$, but $H_{ij}$ is about a hundred times smaller if long-range Coulomb interactions between the vibrating ions are neglected, and if it is assumed that the electronic wave functions of the ions in crystals are as localized as in vapors. It is suggested that removal of these two latter approximations may explain the breakdown of the 1st-order Raman selection rules in calcite and similar crystals.

I. Introduction. — Numerous investigations of the first order Raman effect in calcite and other crystals [1-8] suggest that the scattering tensor is a joint property of crystal and radiation field with components explicitly depending on the wave vectors $\mathbf{q}$ and $\mathbf{q}'$ of the incident and scattered radiation. Selection rules based on the crystal symmetry alone break down and should be replaced by rules which take into account the influence of the radiation field. While several proposals of this kind have been made in the past [8, 9] a detailed mechanism for the coupling between radiation field and scattering tensor has never been suggested, and the question as to whether or not such a coupling exists is still unanswered. This situation has motivated the present paper which attempts a detailed quantum mechanical analysis of the scattering tensor with special emphasis on its wave vector dependence, and other commonly neglected features.

A wave vector dependent coupling between radiation and scattering tensor will, indeed, be demonstrated in this paper, and it will be shown that the conditions most favorable for its experimental detection are a strong delocalization of electron orbits and long range Coulomb forces between the vibrating atoms and ions. A semi-quantitative investigation of the scattering tensor of calcite will be presented, but in view of computational difficulties and insufficient knowledge of electronic orbitals a full explanation of the experimental Raman spectrum of calcite will not yet be achieved. The theory will be based on an ideal crystal model. Lattice imperfections which may be quite essential for a complete understanding of the Raman effect in crystals will be ignored.

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II. The scattering tensor of crystals. — We consider scattering of an incident plane polarized wave with frequency $\nu$, wave vector $\mathbf{a}$, polarization vector $\mathbf{f}$, and intensity $I$, by a single crystal. The scattered radiation has frequency $\nu'$, wave vector $\mathbf{a}'$, polarization vector $\mathbf{f}'$, and intensity per unit solid angle $I'$ 

$$I_{kn}(\nu, \nu') = \left(\frac{\nu'}{\nu}\right)^3 e^{-4\sum_i (C_{ij})_{kn} \mathbf{f}^i \mathbf{f}'^j} I, \quad i, j = x, y, z$$

(1)

where the subscripts, $kn$, indicate that the scattering of a photon is accompanied by a transition of the crystal from an initial state $n$ to a final state $k$. The coefficient of $I$ is the scattering cross section for a transition $n \rightarrow k$. The component $(C_{ij})_{kn}$ of the scattering tensor has the form

$$I_{kn}(\nu, \nu') = \sum_k \left\{ \frac{(I)(k)_{kn} (I)(k)_{rm}}{h(\nu_m - \nu) + h(\nu_m + \nu)} \right\}$$

(2)

$$h(\nu_m - \nu) = E_r - E_n$$

(3)

is the energy difference between the intermediate state $r$ and the initial state $n$,

$$[I](r) = \int [p\nu \exp (-i\mathbf{\sigma} \cdot \mathbf{r})]_{kr} d\mathbf{r},$$

(4)

$$[I](r) = \int [p\nu \exp (i\mathbf{\sigma} \cdot \mathbf{r})]_{rn} d\mathbf{r},$$

(5)

$$[R](kn) = m^{-1} \int [p\nu \exp \{i(\mathbf{\sigma} - \mathbf{\sigma}').(\mathbf{r})\}]_{kn} d\mathbf{r}$$

(6)

where $\Phi_e(\mathbf{r}, \mathbf{Q})$ represents an electronic, and $U_{ee}(\mathbf{Q})$ a vibrational eigenfunction of the crystal. $\Phi_e(\mathbf{r}, \mathbf{Q})$ and the notation indicates that $\Phi_e(\mathbf{r}, \mathbf{Q})$ is assumed to depend on the nuclear normal coordinates $a_1, a_2, \ldots, a_3M$. $U_{ee}(\mathbf{Q})$ is a 3MN-dimensional vector with components $Q_{p}$ representing the vibrational normal coordinates which are characterized by the wave vector $Q$ and the branch label $p$ ($p = 1, 2, \ldots, 3M$).

Substituting (9) into the matrix elements (4), (5), and (6) one gets

$$[I']_{kr} = \left\{ \{ I'(\mathbf{Q}) \}_{ee} \right\}_{ee}$$

(10)

where $\{ I'(\mathbf{Q}) \}_{ee}$ is obtained from (4) and (7) by replacing $\Psi_k$ and $\Psi_e$ with $\Phi_e(\mathbf{r}, \mathbf{Q})$ and $\Phi_e(\mathbf{r}, \mathbf{Q})$. Similar expressions result for $[I](kn)$ and $[R](kn)$.

Next, we assume that the initial and final electronic state of the crystal is equal and denoted by $\Phi_e(\mathbf{Q})$ and that the final vibrational state is obtained from the initial one by absorption or emission of one phonon (1st-order Raman effect). Furthermore, we assume that the vibrational frequencies are negligibly small compared to the electronic transition frequencies

$$\nu_{ee} = (E_{ee} - E_e)/\hbar$$

(11)

are negligibly small compared to the electronic transition frequencies

$$\nu_{ee} = (E_{ee} - E_e)/\hbar,$$

(12)

so that $\nu_{ee}$ in the denominators of Eq. (2) may be replaced by $\nu_{ee}$. In this approximation the scattering tensor is obtained as the matrix element of the electronic polarizability [16] between the initial and final vibrational state. This may be seen as follows. We write

$$(C_{ij})_{kn} = [\alpha_{ij}(\mathbf{Q})]_{ee} - [R_{ee}(\mathbf{Q})]_{ee} \delta_{ij}$$

and remove the summation over the intermediate vibrational states $\nu'$ by means of the rules of matrix multiplication. This can be done since the resonance denominators are, by assumption, practically independent of the vibrational state of the crystal. Thus,

$$[\alpha_{ij}(\mathbf{Q})]_{ee} = [R_{ee}(\mathbf{Q})]_{ee} \delta_{ij} - \sum_{\nu'} \left\{ \frac{\{ I'(\mathbf{Q}) \}_{ee} \nu_{ee} \{ I'(\mathbf{Q}) \}_{ee} \nu_{ee}}{h(\nu_{ee} - \nu) + h(\nu_{ee} + \nu)} \right\}$$

(13)
he case of greatest interest for this work is the 1st-order Raman effect in crystals, i.e., scattering accompanied by absorption or emission of one phonon with wave vector \( \mathbf{q} \) and branch label \( p \). Thus, the vibrational quantum number \( v_{qp} \) changes by plus or minus one, while all other quantum numbers \( v_{q'p'} \) remain unchanged. Consequently, if \( \alpha(Q) \) is expanded as a power series in the normal coordinates \( Q_{q'p'} \) only the term proportional to \( Q_{qp} \) contributes strongly to the 1st-order Raman effect, and all other terms are usually neglected. While this procedure may not always be justified we shall adopt it in this paper in order to bring out the phenomena of interest unmarred by complications of a different nature, e.g., mechanical and electrical unharmonicity.

The properties of the polarizability \( \alpha(Q) \) are most clearly demonstrated by representing the electronic eigenfunction \( \Phi_n(r, Q) \) as a Slater determinant of one-electron "modified" Bloch functions \( \psi_{kn}(r, Q) \) with wave vector \( k \) taken from the first Brillouin zone. The subscript \( n \) denotes the energy bands and the superscript \( s \) the electrons. The labels \( r \) and \( Q \) in the bracket indicate that \( \psi_{kn} \) is a space function which depends on the vibrational state \( Q \) as a consequence of electron-phonon interaction. Because of this interaction \( \psi_{kn}(r, Q) \) is called modified Bloch function since it is a plane wave with an amplitude function which does not have exactly the same translatory symmetry as the unperturbed lattice.

We write the Slater determinant in the form

\[
\Phi_n(r, Q) = \frac{1}{\sqrt{N_e}} \sum (-1)^{in} \psi^1 \psi^2 \ldots \psi^k_{kn} \psi^N_{N_e}, \tag{15}
\]

where \( in \) is the number of inversions in the permutation \( P \), and substitute it into the matrix element (7). This matrix element is a sum of terms each of which depends on the velocity operator of one single electron only. Hence, this matrix element vanishes unless \( \Phi_n \) and \( \Phi_e \) differ by just one of the occupied orthogonal orbitals \( \psi_{kn} \). On the basis of such arguments the Eqs. (7) and (8) can be easily transcribed in terms of the modified Bloch functions if the summation over the electron labels is replaced by a summation over the initially occupied orbitals \( \psi_{kn} \). One finds

\[
\langle p \psi \mid e^{-i\mathbf{q} \cdot \mathbf{r}} \rangle_{ee'} = \sum_{kn} \langle p \psi \mid e^{-i\mathbf{q} \cdot \mathbf{r}} \rangle_{kn, k_{n'}} \psi_{k_{n'}} \psi_{kn} e^{-i\mathbf{q} \cdot \mathbf{r}}, \tag{16}
\]

where \( \psi_{k_{n'}} \) is the excited orbital, and

\[
\langle p \psi \mid e^{i\mathbf{q} \cdot \mathbf{r}} \rangle_{ee'} = \sum_{kn} \langle p \psi \mid e^{i\mathbf{q} \cdot \mathbf{r}} \rangle_{kn, kn} \psi_{kn} \psi_{kn} e^{i\mathbf{q} \cdot \mathbf{r}}. \tag{17}
\]

Substituting the Eqs. (16) and (17) into (14) the polarizability tensor assumes the form

\[
\alpha_{ij}(Q) = \sum_{kn} \left( \frac{[R(Q)]_{kn, kn} \delta_{ij}}{E_{kn}} - \sum_{k'_{n'}} \left\{ \frac{[I_j(Q)]_{kn, k_{n'}} [I_i(Q)]_{k_{n'}, kn}}{h(v_{\mathbf{q} \cdot \mathbf{r}_{kn, kn} - \nu})} + \frac{[I_i(Q)]_{kn, k_{n'}} [I_j(Q)]_{k_{n'}, kn}}{h(v_{\mathbf{q} \cdot \mathbf{r}_{kn, kn} + \nu})} \right\} \right). \tag{18}
\]

The matrix elements \( \langle \Gamma \rangle_{k_{n'} kn} \) etc... are now to be formed with the one-electron modified Bloch functions.

Because of the summation over the intermediate states \( (k'_{n'}) \) Eq. (18) is still very cumbersome and the polarizability of the crystal in its ground state \( (kn) \) depends explicitly on the properties of all the higher electronic states. This feature which effectively prevents a quantitative evaluation of the polarizability can be removed by the following considerations. We are dealing with transparent ionic crystals which are almost perfect insulators. Thus, the initially occupied energy bands which provide the initial states \( (kn) \) are completely filled, and are separated by a large energy gap from the empty conduction bands which provide the intermediate states \( (k'_{n'}) \). For this reason the resonance denominators in Eq. (18) are essentially determined by the energy gap and are slowly varying functions of the labels \( (k'_{n'}) \) provided that the radiation frequency \( \nu \) is much smaller than the transition frequencies \( v_{\mathbf{q} \cdot \mathbf{r}_{kn, kn}} \). The latter condition is certainly satisfied if the energy gap is larger than \( h \nu \), a situation which should be realized in crystals transparent for visible light. It is then possible to replace the slowly varying resonance denominators by suitably chosen averages \( E_{kn}^- \) and \( E_{kn}^+ \) which do not depend on the labels \( (k'_{n'}) \), and which may be approximated by the relation

\[
E_{kn}^- \lesssim E_{kn}^+ \pm h \nu. \tag{19}
\]

where \( E_{kn}^\pm \) is the energy gap between the initially occupied state \( (k, n) \) and the lowest conduction band. In typical cases \( h \nu \approx \frac{1}{2} E_{kn}^\pm \) and \( E_{kn}^+ \approx 3 E_{kn}^- \).

We have calculated the polarizability of the ground state of the hydrogen atom by the device of pulling out an average resonance denominator and found excellent agreement with the results of more rigorous calculations if \( E_{\alpha} \) was chosen 11.9 eV, i.e., as the average between the first excitation and the ionization energy.

Having removed the resonance denominators from the summation over \( (k'_{n'}) \) we can again invoke the rules of matrix multiplication to eliminate this sum completely. We find

\[
\alpha_{ij}(Q) = \sum_{kn} \left( \frac{[R(Q)]_{kn, kn} \delta_{ij}}{E_{kn}} \right) - \left\{ \frac{[I_j(Q)]_{kn, kn} [I_i(Q)]_{kn, kn}}{E_{kn}} \right\}. \tag{20}
\]
and see that the electronic polarizability of a transparent crystal depends only on the initially occupied one-electron orbitals, i.e., on its electronic ground state if the thermal energy, \( kT \), is much smaller than the energy gap.

It should be noted that energy bands may be classified as core bands, valence bands, and conduction bands, and that they may be further characterized by the atomic species and the angular momentum quantum number \( l \) (s, p, d-states) of the atomic orbitals to which they are uniquely related in a tight binding approximation. In view of this situation it is sometimes convenient to replace the simple bond label \( n \) by the double label, \( bl \) (\( l = s, p, d \ldots \)) where \( b \), the position vector of an atom inside the unit cell, may be used for indicating the atomic species.

To complete the general analysis of the polarizability tensor we have to evaluate the diagonal matrix elements \( \langle \Psi \mid I_{i} I_{j} \mid \Psi \rangle \) of the products \( I_{i} I_{j} \), etc. Using Eq. (16) and the relation

\[
\Psi = - \langle \mathbf{k} \mid m \rangle \mathbf{v}
\]

we find

\[
[I_{i} I_{j}]_{\mathbf{k}n, \mathbf{k}n} = - \frac{\varepsilon_{2} k^{2}}{m} \int \Psi_{\mathbf{k}n}^{*} \mathbf{v}_{i} e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{v}_{j} e^{i\mathbf{k} \cdot \mathbf{r}} \Psi_{\mathbf{k}n} \, d\mathbf{r}
\]

\[
[\Psi_{\mathbf{k}n}^{*} e^{i(\sigma - \sigma') \cdot \mathbf{r}} (i\sigma_{i} - \sigma_{j}) (i\sigma_{j} + \sigma_{i}) + (i\sigma_{i} \mathbf{v}_{i} + i\sigma_{j} \mathbf{v}_{j})] \Psi_{\mathbf{k}n} \, d\mathbf{r}.
\]

Because of the transverse nature of electromagnetic radiation,

\[
\sum_{i} \sigma_{i} I_{i} = \sum_{j} \sigma_{j} I_{j} = 0,
\]

some of the terms in (22) do not contribute to the scattering cross section (1). Omitting these terms

\[
[I_{i} I_{j}]_{\mathbf{k}n, \mathbf{k}n} = - \frac{\varepsilon_{2} k^{2}}{m} \int \Psi_{\mathbf{k}n}^{*} e^{i(\sigma - \sigma') \cdot \mathbf{r}} (\mathbf{v}_{i} \mathbf{v}_{j} + i\sigma_{i} \mathbf{v}_{j}) \Psi_{\mathbf{k}n} \, d\mathbf{r},
\]

\[
[I_{j} I_{i}]_{\mathbf{k}n, \mathbf{k}n} = - \frac{\varepsilon_{2} k^{2}}{m} \int \Psi_{\mathbf{k}n}^{*} e^{i(\sigma - \sigma') \cdot \mathbf{r}} (\mathbf{v}_{j} \mathbf{v}_{i} - i\sigma_{i} \mathbf{v}_{j}) \Psi_{\mathbf{k}n} \, d\mathbf{r},
\]

\[
[I_{j} I_{j}]_{\mathbf{k}n, \mathbf{k}n} = - \frac{\varepsilon_{2} k^{2}}{m} \int \Psi_{\mathbf{k}n}^{*} e^{i(\sigma - \sigma') \cdot \mathbf{r}} (\mathbf{v}_{j} \mathbf{v}_{j} - i\sigma_{j} \mathbf{v}_{j}) \Psi_{\mathbf{k}n} \, d\mathbf{r},
\]

the conventional and the \( \sigma \)-terms contain the phase factor \( \exp[i(\sigma - \sigma') \cdot \mathbf{r}] \). The same is true for the term \( [I_{j}]_{\mathbf{k}n, \mathbf{k}n} \) of Eq. (26). This phase factor is responsible for the familiar translatory selection rules (45), but it does not generate any other wave vector dependence of the Raman intensity if only nearest neighbor interactions between the vibrating atoms are considered. However, if the vibrating atoms have a net electric charge they interact with long range forces and this may introduce an additional wave vector dependence of the Raman intensities. The actual magnitude of such effects can be estimated if a specific crystal model, with realistic electron orbitals and interaction forces is introduced. This will be done in the next sections.

### III. Effect of lattice vibrations on the electronic polarizability.

In the preceding sections the effect of lattice vibrations on the polarizability is implicitly accounted for by the use of modified Bloch functions which depend on the vibrational normal coordinates. In this section we shall introduce an explicit analytical representation for the modified Bloch functions which is sufficiently simple to allow for numerical calculations.

We consider an atom with equilibrium position, \( \mathbf{l} + \mathbf{b} \), where \( \mathbf{l} \) is the position vector of a point characteristic for the location of a unit cell, e.g. the centre of mass, and \( \mathbf{b} \) determines the position of the atom in the cell. We denote the vibrational displacement of this atom \( \eta_{\mathbf{b}} \) and treat the displacements of all the atoms as a perturbation of the undistorted Bloch functions,

\[
\Psi_{\mathbf{k}n}(\mathbf{r}) = N^{-1/2} \sum_{\mathbf{k} \mathbf{b}} a_{\mathbf{k}n}(\mathbf{r} - \mathbf{l} - \mathbf{b}) e^{i\mathbf{k} \cdot \mathbf{b}},
\]

which correspond to the equilibrium configuration of the lattice. The \( a_{\mathbf{k}n} \) are localized atomic orbitals centered about the equilibrium site, \( \mathbf{l} + \mathbf{b} \). In the tight binding approximation they are identical with the free-atom orbitals and do not depend on the wave vector \( \mathbf{k} \). However, if the atomic orbitals overlap, \( a_{\mathbf{k}n} \) depends on \( \mathbf{k} \) and should be interpreted as a Wannier function [17], i.e., the Fourier transform of a delocalized, one-electron Bloch function. In this case the \( a_{\mathbf{k}n} \) may be quite different from the Slater functions [18] which are often used to approximate the wave functions of atoms and ions in crystals.

Each atom is the source of an electrical field \( \mathbf{E}_{\mathbf{b}}(\mathbf{r}) \) which has the following properties. If the atom is neutral and has a spherical complete shell of valence electrons, \( \mathbf{E}_{\mathbf{b}}(\mathbf{r}) \) is a strongly shielded Coulomb field the range of which is comparable to the atomic radius. However, the range may be quite a bit longer if the outer shell contains \( d \) and \( f \) electrons, if it is not spherical, and, of course, if the atom carries a net charge. The latter case is
realized by ions and by atoms forming polar bonds, e.g., the $\text{o}$-atoms in calcite, and leads to a Coulomb field which is only weakly shielded by dielectric effects. The electric field of the atoms produces a potential $v(r)$ which is a sum of contributions from all atoms of the crystal. Naturally, if the electric field is essentially short range the nearest neighbors of the field point $r$ will mostly contribute to $v(r)$. But the accumulated effect of distant neighbors may be appreciable in crystals containing ions or strongly polar bonds.

Let us now consider a crystal in which the atoms are displaced a distance $\eta_{l'w'}$ from their equilibrium positions. An observer on the atom $(l, b)$ will register a change in potential which is, in a first approximation, a linear function of the relative displacements, $\eta_{l'w'} - \eta_{lb}$, of the form

$$
\Delta_{lb} v(r) = \sum_{r'w'} \nabla_{r'} v(r' - r - b') (\eta_{r'w'} - \eta_{lb}).
$$

When the atom $(lb)$ is essentially free and not influenced by the other atoms in the crystal (tight binding approximation) the potential (28) can be treated as an external perturbation of the atom $(lb)$, producing first-order corrections to the electronic orbitals of the form [19]

$$
a^{(1)}_{kn}(r - 1 - b) = \sum_{n'w'n'} \frac{[\Delta_{lb} v(r)]_{kn,w'n'}}{E^2_{kn} - E^2_{kn'}} a^{(0)}_{kn'}(r - 1 - b).
$$

The sum in Eq. (29) can be fairly well approximated as a property of the state $a^{(0)}_{kn}$ if the resonance denominators are replaced by a constant average which is approximately equal to the quantity $E^2_{kn}$ of Eq. (19). Assuming that the atomic orbitals $a^{(0)}_{kn}$ form a complete set one finds readily that (see Appendix)

$$
\sum_{n'w'n'} [\Delta_{lb} v(r)]_{kn,w'n'} a^{(0)}_{kn'}(r - 1 - b)
= \frac{a^{(0)}_{kn}}{E^2_{kn}} \Delta_{lb} v(r) - \frac{[\Delta_{lb} v(r)]_{kn,ks}}{E^2_{kn}}.
$$

Thus, the perturbed orbital $a_{kn}(r - 1 - b)$ is, in first approximation,

$$
a_{kn}(r - 1 - b) = a^{(0)}_{kn}(r - 1 - b)
\left\{ 1 + \frac{\Delta_{lb} v(r) - [\Delta_{lb} v(r)]_{kn,ks}}{E^2_{kn}} \right\}.
$$

We can now treat $E^2_{kn}$ as a variational parameter to be determined by minimizing the average ground state energy of the atom $(lb)$. In this spirit we can rewrite Eq. (31) in the equivalent form

$$
a_{kn}(r - 1 - b) = C_{kn} a^{(0)}_{kn}(r - 1 - b) \left[ 1 + \lambda_{kn} \Delta_{lb} v(r) \right],
$$

where $C_{kn}$ is a normalization constant of the order unity and $\lambda_{kn}$ a variational parameter of order of magnitude $(1/E^2_{kn})$. If the tight binding approximation is not valid, the $a_{kn}(r - 1 - b)$ should be interpreted as Wannier functions which are perturbed by the displacements $\eta_{lb}$. The form (32) may be preserved in this case but the $\lambda_{kn}$ are determined by minimizing the ground state energy of the whole crystal, not just one atom, using the modified Bloch functions

$$
\Psi_{kn}(rQ) = \sum_{lb} a_{kn}(r - 1 - b - \eta_{lb}) e^{i(kl + \eta_{lb})}
$$
as trial functions. While this distinction is essential in principle it does not affect our previous estimate of $\lambda_{kn}$ as the reciprocal of $E^2_{kn}$. The form of Eq. (33) indicates that the modified Bloch functions are linear superpositions of atomic orbitals which are centered about the displaced nuclear sites, $l + b + \eta_{lb}$, and have phase angles, $k(l + \eta_{lb})$, corresponding to these sites. This special choice of the phase angles is certainly not the only one possible. However, since Eq. (33) is to be interpreted as a trial function for a variational problem a detailed justification of this choice is not required. Other assumptions concerning the phases would lead to slightly different values of the parameters $\lambda_{kn}$ without affecting the essential properties of the polarizability $\alpha(Q)$.

For the purpose of deriving the translatory selection rules we define a tensor $\Gamma d''b''$ by the relation

$$
(\eta_{l'w'} - \eta_{lb}) = \Gamma d''b'' \eta_{lb},
$$

which depends only on the relative distance $d'' = l' - 1$. For applications to the lst-order Raman effect this is convenient to expand (33) into a Taylor Series with respect to the small displacements $\eta_{lb}$ and to neglect terms of second or higher order in $\eta_{lb}$.

Using (32) and (28) one finds

$$
\Psi_{kn}(rQ) = N^{-1/2} \sum_{lb} \left[ 1 + W_{kn,lb}(rQ) \right] a^{(0)}_{kn}(r - 1 - b) e^{i(kl + \eta_{lb})}
$$

where

$$
W_{kn,lb}(rQ) = (ik + \nabla_r) \cdot \eta_{lb}
+ \lambda_{kn} \sum_{l'w'b'} (\eta_{l'w'} - \eta_{lb}) \nabla_r v(r - l' - b').
$$

For the purpose of deriving the translatory selection rules we define a tensor $\Gamma d''b''$ by the relation

$$
(\eta_{l'w'} - \eta_{lb}) = \Gamma d''b'' \eta_{lb},
$$

where $\eta_{lb}$ is expanded in terms of the normal coordinates $Q_{qp}$ the electronic polarizability becomes a function of the normal coordinates. If then the polarizability is expanded in terms of the $Q_{qp}$ various powers of the normal coordinates contribute to the lst-order Raman effect even if the lattice vibrations are harmonic. However, it is generally assumed that terms of higher than lst-order in the $Q_{qp}$ contribute little to the Raman effect and may be neglected. See Ref. [8].
associated with one single normal mode $Q_\text{qp}$ (see discussion on page 701 and footnote (2)). Thus

$$\eta_{lb} = N^{-1/2} Q_{\text{qp}} \delta_{qb} e^{-i q \cdot l},$$

(38)

and

$$W_{kn,lb}(rQ) = \omega_{kn}(rQ) e^{-i q \cdot l},$$

(39)

where

$$\omega_{kn}(rQ) = N^{-1/2} \eta_{k} + \nabla r + \lambda_{kn}$$

and the factors $\hat{v}(r-d')$ and $\Gamma(d'v_{kn})$ are introduced.

The last term in the square bracket represents an intrinsic physical change of the crystal caused by the relative displacements of the vibrating nuclei. The first two terms represent the purely geometrical affect of atomic displacements relative to the radiation field.

We can now write explicit expressions for the matrix elements (24)-(26) which determine the electronic polarizability. Keeping only terms linear in the normal coordinate $Q_{\text{qp}}$, as indicated by the superscript (1), we find

$$[I \, I']_{kn,kl} = -\frac{e^2 \hbar^2}{N^{3/2} m^3} \left\{ \int dr \psi(\sigma - \sigma').r \sum_{l'l'} \sum_{l'l'} \psi_{l'q} \psi_{l'q} \right.$$  

$$\times \left[ C_{kn}^2 \alpha_{kn}' \alpha_{kn}(r - l - b) \nabla_{\nu} \nabla \{ \psi_{kn} \alpha_{kn}(r - l - b) \} e^{i k \cdot (l-l')} \right]$$  

$$+ \int dr \psi(\sigma - \sigma').r \sum_{l'l'} \sum_{l'l'} \psi_{l'q} \psi_{l'q} \left[ C_{kn}^2 \alpha_{kn}' \alpha_{kn}(r - l - b) \nabla_{\nu} \nabla \{ \psi_{kn} \alpha_{kn}(r - l - b) \} e^{i k \cdot (l-l')} \right]$$

$$+ \text{Terms obtained by substitution } \nabla_{\nu} \rightarrow \sigma_{\nu}.$$  

(41)

and a similar expression for $[I \, I']_{kn,kl}$.

We can now derive the translatory selection rules. First we note that the terms in the square brackets of (41) and (42) depend only on the difference $(l-l')$ but not on $l$ or $l'$ alone. Hence, only the isolated phase factors $i q \cdot l$ or $i q \cdot l'$ are effective in generating selection rules. As an example, we consider the first term in Eq. (41). We introduce the variable

$$r' = r \pm l'$$

(43)

and note that space integrals in a periodic crystal are invariant against the transformation (43). This circumstance permits the transformation

$$\psi(\sigma - \sigma').r \sum_{l'l'} \sum_{l'l'} \psi_{l'q} \psi_{l'q} \rightarrow \psi(\sigma - \sigma').r \sum_{l'l'} \sum_{l'l'} \psi_{l'q} \psi_{l'q}$$

(44)

which allows one to utilize the well-known relation

$$\sum_{l'l'} = \begin{cases} N, & A = K, \\ 0, & A \neq K \end{cases}$$

where $K$ is a reciprocal lattice vector, including $K = 0$. Because of the complete physical equivalence of the phonon wave vectors $q$ and $q + K$, we can ignore the reciprocal lattice vectors $K \neq 0$. Thus, we have found the familiar selection rule

$$\sigma = -\sigma', \pm q = 0.$$  

(45)

The same result can be obtained from all the other terms in the Eqs. (41) and (42).
In the last two equations it has been assumed, without loss of generality, that \( l = l' = 0 \).

If the tight binding approximation is not valid the situation is more complicated. All terms in the Eqs. (41) and (42) are then \( k \)-dependent, and the selection rule (47) breaks down. However, it still remains a good approximation because of the localized nature of the Wannier functions. Hence, the Eqs. (48) and (49) can still be used if the integrands are taken to represent a suitable average over the electron wave vectors \( k \). It is then evident that the square of the polarizability, and with it the Raman intensity, is proportional to the number \( N \) of unit cells in the scattering crystal.

In order to achieve a quantitative estimate of the operator \( \bar{w}_{ab} \) must be explicitly introduced into the Eqs. (48) and (49). We use Eq. (40) and the definition of \( \bar{w}_{ab} \) on page 702, and let

\[
\begin{align*}
Q_{QP} C_{ab}^2 e^2 & h^2 |E_{k-}\rangle^2 m^2 = + \sum_{\nu} A_{\nu b} e_{\nu b}, \\
Q_{QP} C_{ab}^2 e^2 |m\rangle & = e_{Q_{QP}}.
\end{align*}
\]

Then

\[
\begin{align*}
\sum_{k} \langle I_i J_k \rangle_{k,n,k,n} |E_{k-}\rangle & = - N^{1/2} c_{Q_{QP}} \sum_{\nu} \sum_{b} G_{\nu b b} + H_{\nu b b}, \\
\sum_{k} \langle J_i I_k \rangle_{k,n,k,n} |E_{k+}\rangle & = - N^{1/2} c_{Q_{QP}} \sum_{\nu} \sum_{b} [G_{\nu b b} - H_{\nu b b}], \\
\sum_{k} \langle R \rangle_{k,n,k,n} & = N^{1/2} c_{Q_{QP}} \sum_{\nu} \sum_{b} [I_{\nu b b}].
\end{align*}
\]

The \( G_{\nu b b} \) etc... are listed below, and in order to simplify the notation, obvious labels which occur repeatedly are omitted. Thus, \( a_{\nu}^b (r - b) \) for \( a_{\nu}^b \) stands for \( a_{\nu}^b (r - b) \), \( v \) for \( v (r - b) \), \( \lambda \) for \( \lambda_{k} \), \( \Gamma_{\nu b} \) for \( \Gamma_{\nu b} \), \( \epsilon_{b} \) for \( \epsilon_{b} \), and \( \sum_{a' + b' \neq a} \) with this notation.

\[
\begin{align*}
\langle G_{i b b} \rangle_{i j} & = \int \left( \langle \nu | a_{\nu}^b (r - b) | \nu' \rangle \langle \nu' | e_{\nu b} \rangle \right) \nu \nu' \langle \nu \nu' | e_{\nu b} \rangle \ dr, \\
\langle G_{i b b} \rangle_{i b} & = \int \left( \nu (r - b) \langle \nu | a_{\nu}^b (r - b) | \nu' \rangle \langle \nu' | e_{\nu b} \rangle \right) \nu \nu' \langle \nu \nu' | e_{\nu b} \rangle \ dr.
\end{align*}
\]

Finally

\[
\begin{align*}
\langle J_{1, i b b} \rangle_{i j} & = \int \left( \langle \nu | a_{\nu}^b (r - b) | \nu' \rangle \langle \nu' | e_{\nu b} \rangle \right) \nu \nu' \langle \nu \nu' | e_{\nu b} \rangle \ dr, \\
\langle J_{3, i b b} \rangle_{i j} & = \int \left( \langle \nu | a_{\nu}^b (r - b) | \nu' \rangle \langle \nu' | e_{\nu b} \rangle \right) \nu \nu' \langle \nu \nu' | e_{\nu b} \rangle \ dr.
\end{align*}
\]

The \( H_{\nu b b} \) are obtained from the \( G_{i b b} \) by replacing \( \nu \) with \( \nu' \) and \( \nu' \) with \( \nu' \). If that is done one sees readily that \( H_{\nu b b} = H_{\nu b b}^{T} \), and \( H_{\nu b b} = H_{\nu b b}^{T} \) since \( \nu \) and \( \nu' \) are not differential operators. In order to avoid counting one single term twice we put

\[
H_{\nu b b} = H_{\nu b b}^{T} = 0.
\]

The terms with \( \nu < 3 \) represent contributions to the 1st-order polarizability from atomic displacements relative to the radiation field. They are usually neglected. The remaining terms represent intrinsic, 1st-order changes in the polarizability caused by the displacement of the atoms relative to each other. The matrix elements \( J_{1, i b b} \) and \( J_{3, i b b} \) result from the second order term (charge density operator) in the Hamiltonian [12]

\[
H = - \frac{e}{c} \sum_{s} v_{s} A_{s} + \frac{e^{2}}{2mc} \sum_{s} A_{s}^{2},
\]

where \( A_{s} \) is the vector potential of the radiation field at the position of the electron with label \( s \). This term is usually omitted. It is the purpose of this paper to estimate the relative magnitudes of the various types of matrix elements, in particular of the matrix elements \( H_{\nu b b} \) which are proportional to \( \sigma \) and \( \sigma' \), and of those which are commonly neglected. Such an estimate will be attempted in the next chapters.

IV. General properties of one-center integrals.

As pointed out in the preceding section, the
tensors $G_v, b', H_v, b'$ and $J_v, b'$ with $v < 3$ have a different physical origin than all the others. Mathematically, they are distinguished from the rest by the feature that they are integrals of a product of only two space functions $a_l^2(r - b)$ and $a_l^2(r - b')$. If $b = b'$, they represent one-center integrals and if $b \neq b'$, two-center integrals. Because of the generally weak overlap of the Wannier functions in ionic crystals the two-center integrals should be much smaller than the one-center integrals unless the latter vanish for reasons of symmetry or because of a more accidental cancellation of positive and negative terms. We shall show that such an accidental cancellation does, in fact, occur if the radial part of the Wannier functions is approximated by Slater functions of the form $N_n^{*} \exp (-z^n r/n^*)$, where $z^*$ and $n^*$ are effective charge and principal quantum numbers, and $N_n^{*}$ a normalization constant.

The integrals of the terms $J_v, b', G_v, b'$, and $H_v, b'$ with $v > 2$, are products of the three space functions $a_l^2(r - b), a_l^2(r - b')$, and $u_l(r - d^l - b^l)$. Since $(d^l + b^l)$ is, by definition, different from $b$, we are dealing now with two- and three-center integrals, the latter being negligible because of the small overlap of the ionic Wannier functions. Thus, throughout, we shall be concerned only with the numerical estimate of two-center integrals.

In spite of this situation we wish to demonstrate a few general properties of the one-center integrals which are useful to know in those cases where they do not vanish because of accidental cancellations. First we have to specify the analytical form of the Wannier functions. If they are centered about points with high local symmetry and if one is dealing with ions having a closed noble gas shell, the Wannier functions may be well approximated by hydrogen-like wave functions with orbital quantum number $l = 0$ ($s$-states) and $l = 1$ ($p$-states) of the form

$$a_l^2(r) = N_l^* P_l^*(r^{l*} - 1) e^{-z^l r/n^*}, \quad s\text{-states}$$

$$a_l^2(r) = N_l^* P_l^*(r^{l*} - 1) x_l e^{-z^l r/n^*}, \quad x_l = x, y, z, \quad p\text{-states}, (66)$$

where $P_l^*$ is a polynomial of the $i$-th degree, $N_l^*$ is a normalization constant, and the notation $z^l_*$ etc... indicates that the effective charge and quantum number is different for $s$-and $p$-states. In Slater’s approximation this difference is neglected and the polynomial is replaced by its highest term.

If the atomic centers are points of low local symmetry, e.g., the O-atoms in calcite, $l$ is not a good quantum number, and the Wannier functions may be approximated as linear superpositions of $s$- and $p$-functions of the form

$$a_l^2(r) = \sum c_{lm} a_l^2(r) x_{lm}, \quad m = 0, 1, 2, 3, (68)$$

where, in the Slater approximation,

$$o_0 = N_0^* e^{-\beta z r/n^*}, (69)$$

$$o_m = N_m^* e^{-\beta z r/n^*}, (70)$$

$$x_0 = 1, \quad x_m = x, y, z \quad for \quad m = 1, 2, 3, (71)$$

and the $c_{lm}$ are expansion coefficients satisfying

$$\sum_{m} c_{lm} ^* c_{lm} = \delta_{mm}. (72)$$

We shall now show that one-center integrals vanish rigorously, for reasons of symmetry, unless we have $s$-$p$ hybridization, i.e., unless $c_{00}$ and at least one other coefficient $c_{mm}$, $m \neq 0$, is different from zero. We demonstrate this result for the matrix element $\langle G_{2,b'} | b \rangle_i$ which apart from constants, has an integrand of the form

$$I = \sum_{m} c_{lm}^* c_{lm} I_{mm'} = \sum_{mm'} c_{lm}^* c_{lm'} o_m x_m \nabla_i \tilde{\psi}_i (\nabla_m \tilde{\psi}_m'), (73)$$

where $x_i$ is in the direction of the unit vector $\tilde{\psi}_b$. We invoke the relation

$$\nabla_i \tilde{\psi}_i = \frac{\partial}{\partial x_i} = \frac{x_i}{r} \partial r$$

and find

$$I_{mm'} = o_m h_{m'} x_i x_l x_m x_m' x_m'$$

$$+ o_m g_m \{ x_m \tilde{\psi}_m (x_i \delta_{mm'} + x_l \delta_{ml} + x_m \delta_{im'}) + x_m \tilde{\psi}_m (x_i \delta_{mm'} + x_l \delta_{ml} + x_m \delta_{im'}) \}$$

$$+ o_m p_{m'}' x_m \delta_{im'} + \delta_{m'l'} + \delta_{m'1} + \delta_{m'2} \delta_{im'} \delta_{m'2}, (75)$$

where

$$p_m = \langle 1 | r | \delta_{lm} \rangle, (76)$$

$$g_m = \langle 1 | r | \delta_{lm} \rangle, (77)$$

$$h_m = \langle 1 | r | \delta_{lm} \rangle. (78)$$

It is now readily seen that without $s$-$p$ hybridization ($x_m = x_m$), $I$ is a sum of terms with odd parity, independent of the analytical form of $o_d(r)$ and, hence, it must vanish on space integration.

Further analysis of the matrix element $\langle G_{2,b'} | b \rangle_i$ will be based on the Slater functions (69) and (70). From the definitions (76)-(78) we get, with $n^* = 2$ and $z^l/n^* = \beta$

$$p_0 = N_0 e^{-\beta z r}, (79)$$

$$p_1 = -N_1 e^{-\beta z r}, (80)$$

$$g_0 = N_0 e^{-\beta z r} - \beta z r - \beta^* r^2 - 3 \beta r, (81)$$

$$g_1 = N_1 e^{\beta z r} (\beta z r + \beta^* r^2 + 3 \beta r), (82)$$

$$h_0 = N_0 e^{-\beta z r} (\beta z r + 3 \beta^* r - 3 \beta r), (83)$$

$$h_1 = N_1 e^{-\beta z r} (\beta z r + 3 \beta^* r - 3 \beta r), (84)$$

We can now calculate the quantities $(I_{om} + I_{mo})$, $m \neq 0$, for all possible combinations of $i$ and $j$. For each pair $(ij)$, we first select those terms in the general formulas (75) which have even parity, and
integrate over all space. To our great surprise, one finds, for all combinations \(ij\), complete cancellation of positive and negative terms. However, this cancellation is accidental, and is removed if the more general form (66) and (67) for the Wannier functions is used. The behavior of the matrix elements \(J_\nu\) and \(H_\nu\) is essentially the same as that of \(G_\nu\). They vanish if the Slater functions (69) and (70) are used and they remain finite if the more general functions (66) and (67) are employed. There is, however, one special feature of the matrix elements \(H_\nu\) which makes them relatively larger than the terms \(G_\nu\) and \(J_\nu\). Since the \(H_\nu\) contain an even number of gradient operators it turns out that the terms \(I_{mn}\), which are allowed by symmetry have \(m\) and \(m'\) different from zero. This shows that \(s-p\) hybridization is not required for getting nonvanishing one-center integrals of the type \(H_\nu\). This result is important since the \(H_\nu\) represent the \(\sigma\)-terms which are the main subject of this paper. Another special property of the \(H_\nu\) may be presented by the relation,

\[
[H_{1,\nu}v]_{ij} = -[H_{2,\nu}v]_{ij},
\]

for the case of Slater functions. Thus, the \(H_\nu\) do not vanish individually, but only in pairs.

Summarizing, we can say that one-center integrals tend to be small compared to two-center integrals since they arise only from corrections to the well-tested Slater functions and, with the exception of the \(H_\nu\), only if \(s-p\) hybridization is present. On the other hand, one-center integrals tend to be larger than two-center integrals because of the presumably small overlap of Wannier functions in ionic crystals. In view of the great sensitivity of the one-center integrals to the analytical form of the Wannier functions our neglect of these integrals reflects more our ignorance than our conviction that they are really negligible.

V. Two-center integrals in calcite. — Since we found that two-center integrals do not, either for reasons of symmetry or by accidental cancellation, vanish, a general discussion as presented in the preceding chapter is not very fruitful. We shall therefore, immediately attack the case of calcite which should provide a good test for our theory, since the calculations can be made sufficiently accurate. At present, such an accuracy is not yet feasible and we shall content ourselves with a quantitative estimate of matrix elements which is based on a number of simplifying assumptions about the properties of calcite. The two most important approximations are the following:

1) We neglect the net electrical charge of the ions and treat each ion and atom as the source of a strongly shielded Coulomb potential of the form

\[
v(\mathbf{r} - \mathbf{b}) = (e^2/|\mathbf{r} - \mathbf{b}|) e^{-\alpha |\mathbf{r} - \mathbf{b}|},
\]

with effective range \(\alpha^{-1} \sim 1/a_0\) of the same order as the atomic radius \(2a_0^{-1} = n_b^2/2a_0^2\). The omission of an unshielded Coulomb potential which should be added to the potential (86) does not imply that its contributions to the first-order polarizability are negligible. But the analysis of these contributions is very complicated and will be attempted in another paper.

2) The charge cloud overlap between the oxygen atoms in a carbonate ion is much larger than the overlap between oxygen and a neighboring carbon atom or calcium ion. For this reason we shall neglect calcium and carbon altogether and shall treat a carbonate ion as a system consistent of three neutral, strongly overlapping oxygen atoms. However, the presence of the calcium ion and carbon atom will be implicitly taken into account by using the hybrid orbitals (68) to (71).

The assumptions (1) and (2) establish the nearest neighbor approximation to the first order polarizability. It allows one to approximate the phase factors \(i(\sigma - \sigma')\cdot \mathbf{r}\) in the Eqs. (55) to (64) by the value unity. For calcite, the nearest neighbor approximation implies that the only overlap integrals assumed to be different from zero are those involving two oxygen atoms of the same carbonate group. Consequently, the summations over \(b, b', b''\), and \(d'\) in the matrix elements \(G_\nu, H_\nu, and J_\nu\) involve only the three oxygen atoms of a carbonate group which will be denoted by the label \(b = 1, 2, 3\).

Each two-center integral can be characterized by the label \(b\) and \(b'\) of the two centers and by the kind of space functions which are attached to the centers. The classification by the label \(b\) leads to three different types of integrals corresponding to the combinations \((1,2), (2,3),\) and \((3,1)\) of the labels \(b\) and \(b'\). We shall henceforth denote these three combinations by the superscript \(B = 1, 2, 3\). For each combination we can define a local cartesian coordinate system \(\{x_B^2\}\) such that \(x_B^2\) is along the line joining the centers \(b\) and \(b'\) of the two oxygen atoms, \(x_B^2\) is normal to the plane of the carbonate ion and, hence, parallel to the principal crystal axis, and \(x_B^1\) is in the plane of the carbonate ion normal to \(x_B^2\).

Next we remember that we have two different kinds of matrix elements, those depending on the potential \(v\) \((v > 2)\) and those which do not \((v < 3)\). The former depend on three space functions, \(a^2_b, a^2_b',\) and \(v\), the latter only on the two functions \(a^2_b\) and \(a^2_b'\). We shall, therefore, base our general discussion on the more complicated \(v\)-dependent terms, since the properties of the other terms can then be readily understood by letting \(v\) be a constant. We note that each of the \(v\)-dependent two-center integrals is associated with the vibrational displacements \(\delta_{\mathbf{q}},\) \(\delta_{\mathbf{q}'}\), the second displacement \(\delta_{\mathbf{q}''}\), being contained in the tensor \(\Gamma_\nu\) of the
formulas (57)-(64). For the totally symmetric vibration of calcite with wave number 108 cm\(^{-1}\) the three displacements \(\xi_{11}, \xi_{22},\) and \(\xi_{33}\) are along the three C-O bonds, and have the same direction in their respective local coordinate system. The three types of integrals (1,2), (2,3), and (3,1) are then formally identical when expressed in their respective local coordinate systems and, for this reason, they will be evaluated in them. Other normal modes of calcite will not be analysed. Let us now consider a specific \(\nu\)-dependent matrix element, say \([G_{a,\nu b}])\). In order to avoid complicated indices we replace the labels \(b\) and \(b'\) by \(a\) and \(b\) respectively, and introduce local coordinates by means of the relations

\[
\begin{align*}
    x_{1a} &= x_{1b} = x_1, \\
    x_{2a} &= x_{2b} = x_2, \\
    x_{3a} &= x_3 + Rf_2, \\
    x_{3b} &= x_3 - Rf_2, \\
    \sum_{i=1}^{3} x_{ia}^2 &= r_a^2, \\
    \sum_{i=1}^{3} x_{ib}^2 &= r_b^2.
\end{align*}
\]

The \(x_i\) are identical with the coordinates \(x_i^p\) of page 705; they are local coordinates for the two-center system with origin at the midpoint of the line joining the two centers, which are separated by the distance \(R\). The \(x_{ia}\) and \(x_{ib}\) are local coordinates for the individual centers \(a\) and \(b\) with origin at these centers. Throughout, the superscript \(B\) has been neglected to simplify the notation.

Any quantity occurring in the matrix elements needs now a label indicating whether it belongs to center \(a\) or \(b\). Thus,

\[
a_{\mu b}(r_b) = \sum_{m_b} c_{m_b} a_{m_b}(r_b) x_{m_b},
\]

and

\[
\nu(r_a) = (e^2/r_a) e^{-\alpha x_r a}.
\]

Before writing the complete expressions for the matrix elements \([G_{a,\nu b}])\) we remember that the origin of the potential \(\nu\) must be different from the center \(b\). Thus, the origin of \(\nu\) is the center \(a\) and the summation symbol in the Eqs. (57)-(61) is not required. We can now distinguish between two kinds of matrix elements \([G_{a,\nu b}])\), namely \([G_{a,a})\), which have both Wannier functions attached to the same center \(b\), and \([G_{a,ba})\), which have one Wannier function attached to center \(a\), and the other to center \(b\). Formally, we get

\[
\begin{align*}
[G_{a,bb})]_{ij} &= \lambda \sum_{m_b m_b} c_{m_b} c_{m_b}^* \\
&= \int \langle \nabla_a \nu(r_a) . D \rangle a_{m_b} x_{m_b} \langle \nabla_b \nu(r_b) a_{m_b}^* x_{m_b}^* \rangle dr, \\

[G_{a,ba})]_{ij} &= \lambda \sum_{m_a m_a} c_{m_a} c_{m_a}^* \\
&= \int \langle \nabla_a \nu(r_a) . D \rangle a_{m_a} x_{m_a} \langle \nabla_b \nu(r_b) a_{m_a} x_{m_a}^* \rangle dr,
\end{align*}
\]

where, \(D = \nabla_q b = \nabla_q a - \nabla_q b\),

\[
\nabla\nu(r_a).D = \nabla_{x_b} \nu(r_a) D, \quad D = 1.
\]

Next, we invoke the relations

\[
\nabla_{x_a} = \frac{x_a}{r_a} \frac{\partial}{\partial r_a}, \text{ etc...}
\]

and find that the integrands of the matrix elements (91) and (92) are expressions of the form (75) with the extra feature that all \(x_i\) and \(x_m\) have now the additional label \(a\) or \(b\), and that more radial functions than those listed in Eqs. (76) to (78) are now involved. As in Eq. (75) the integrands are sums of a large number of terms. Many of these terms vanish on space integration because they are anti-symmetric with respect to rotation through an angle \(\pi\) about the two-center axis. But there are no selection rules which require complete vanishing of the matrix elements for reasons of symmetry, and accidental cancellation of positive and negative terms in the radial functions is never complete. In particular, the two-center integrals are fairly insensitive to the amount of hybridization of the Wannier functions. The only rigorous selection rule we could discover affects the matrix elements \([H_{ba})\) and says that these matrix elements are zero for pure \(s\)-states. However, for \(p\)-states or \(p-s\) hybrids no such selection rule could be discovered.

The terms which are symmetric with respect to rotation through \(\pi\) about the two-center axis have the form

\[
\int J_{ab}(r) dr = \int r_2^2 x_{2a} x_{2b} P \{ x_{m_a} x_{m_b} \} e^{-A r_a + B r_b} dr,
\]

where \(p\) and \(q\) are positive or negative integers, \(r, s = 1, 2, 3\). \(P \{ x_{m_a} x_{m_b} \}\) is a product of even powers of the \(x_{m_a}\) and \(x_{m_b}\) \((m_a, m_b \neq 2)\), and the coefficients \(A\) and \(B\) are linear combinations of the reciprocal " radii " \(\alpha\) and \(\beta\) such as \((\alpha + \beta)\) or \((2\beta)\). If the overlap between the space functions centered about \(a\) and \(b\) is small, the integrand \(J_{ab}\) drops rapidly to zero with increasing distance from the two-center axis. The main contribution to the integral comes from the near neighborhood of the axis and in this region we have, with good approximation,

\[
x_{3a} \sim r_a, \quad x_{3b} \sim r_b, \quad x_{m_a} \sim x_{m_b} \sim 0, \quad m = 1, 3.
\]

The integrals needed for computing the matrix
elements $G_{v,ab}$, $H_{v,ab}$, and $J_{v,ab}$ are then of the form

$$\int I_{ab} \, \text{d}r = \int \frac{r_\alpha^2 \, r_\beta^2}{r_{ab}} \, e^{-(A r_\alpha + B r_\beta)} \, \text{d}r,$$

(98)

and they are listed in several books [20].

Having obtained the matrix elements $[G_{v,ab}]_i$ in their local coordinate system it still remains to perform the sum over the three different two-center systems $\{(1,2), (2,3), \text{and} (3,1)\}$. This requires to transform from the local system to a crystal system $\{\sigma_{\nu}\}$ which is common to all three two-center integrals and which we let coincide with the local system $B = 1$. The local systems are then characterized by the angles $\theta^B$ with

$$\theta^1 = 0, \quad \theta^2 = 120^\circ, \quad \theta^3 = 240^\circ,$$

(99)

and transformations from the crystal system (primed labels) to the local systems (unprimed labels) are generated by the transformation matrices

$$T^B = \begin{pmatrix} \cos \theta^B & \sin \theta^B & 0 \\ -\sin \theta^B & \cos \theta^B & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

(100)

In particular, the transformation relations for vectors are

$$\alpha_i^B = \sum_T T_{i\nu}^B \alpha_{\nu}$$

(101)

and for tensors

$$H_{\nu\nu}^B = \sum_{ij} T_{i\nu}^B T_{j\nu}^B H_{ij}^B.$$

(102)

If we apply the relations (102) to the tensor component $G_{i\nu}$ we note that the $G_{i\nu}$ are identical in all three local systems, i.e., they are independent of $\theta^B$. This leads to the simple result

$$G_{\nu\nu}^B = G_{\nu\nu}^B = 0, \quad i' = \neq i'.$$

(103)

$$G_{\nu\nu} = \sum_B G_{\nu\nu}^B = (3/2) \, (G_{11} + G_{22}), \quad i' = 1, 2,$$

(104)

$$G_{\nu\nu} = \sum_B G_{\nu\nu}^B = 3G_{33}.$$

(105)

The Eqs. (103)-(105) demonstrate that the crystal system is the principal axes system for the tensors $G_{\nu}$ and the same could be demonstrated for the tensors $J_{\nu}$. But the behavior of the tensors $H_{\nu}$ is quite different since the local components $H_{ij}^B$ depend on the angles $\theta^B$. This follows from the explanation on page 703 according to which

$$H_{\nu\nu}^B = \alpha_i^B V_{ij}, \quad H_{ij}^B = V_{ij} \alpha_i^B$$

(106)

where $V_{ij}$ stands for the integrals (55) to (64) if $\Delta_1$ is replaced by unity. We can now introduce the inverse transformation

$$\alpha_i^B = \sum_{k'} T_{i\nu}^{B^*} \alpha_{k'},$$

(107)

where $T_{i\nu}^{B^*}$ stands for $(T_{i\nu}^{B})^T$ and is obtained from (100) by changing the sign of $\sin \theta^B$. Substituting (107) into (106), and (106) into (102) gives

$$H_{\nu\nu}^B = \sum_{ik'} T_{i\nu}^B T_{k\nu}^B T_{k\nu}^B \sigma_k^B V_{ij}.$$

(108)

But

$$\sum_{ij} T_{i\nu}^B T_{k\nu}^B = \delta_{ij},$$

(109)

hence,

$$H_{\nu\nu}^B = \sum_i \sigma_i^B V_{ij}.$$

(110)

We can now perform the summation over $B$ and find

$$H_{\nu\nu} = \sum_B H_{\nu\nu}^B = \left(\sum_i \sigma_i^B V_{ij}\right) \delta_{ij}.$$

(111)

Eq. (111) shows that the tensor $H^-$ is not diagonal in the crystal system, and has nonvanishing components $H_{1\nu}$ and $H_{2\nu}$, the magnitude of which depends on the direction of the wave vector $\mathbf{a}$. Furthermore, $H^-$ is not symmetric since $H_{1\nu} = H_{2\nu} = 0$. For the tensor $H^+$ we find the similar result

$$H_{\nu\nu} = \sum_B H_{\nu\nu}^B = \left(\sum_i \sigma_i^B V_{ij}\right) \delta_{ij}.$$

Before we can draw any conclusions from the properties of the tensors $H$ we must estimate their magnitude relative to the well-behaved tensors $G$ and $J$. This will be done in the last chapter.

VI. Numerical estimate of matrix elements and conclusions. — We have calculated the tensor components $[G_{\nu}]_i$, $[H^\pm_{\nu}]_i$, and $[J_{\nu}]_i$ as two-center integrals by the methods outlined in the preceding sections. We found that the tensor components of the class $G_\nu$ ($\nu = 1, 2, \ldots, 7$) vary greatly among each other and that their relative and absolute magnitude is quite sensitive to the choice of the parameters $\alpha$ and $\beta$ which characterize respectively the range of the atomic potential and of the atomic orbitals. Since the tensor components of the classes $H^\pm_\nu$ and $J_\nu$ exhibit the same kind of diversity the following statements refer to those tensors which, for a given choice of $\alpha$ and $\beta$, are the largest members of their class. We can then summarize our results as follows:

1) The tensors $J_\nu$ which are produced by the charge density operator are of the same order of magnitude as the tensors $G_\nu$ which are generated by the current density operator. Thus, the usual neglect of the charge density operator in the theory of the Raman effect in crystals is not justified.

2) The tensors $G_\nu$, $H^\pm_\nu$, and $J_\nu$ with $\nu < 3$, which represent the purely geometrical effect of atomic displacements relative to the radiation field are, in the average, a little smaller than the tensors
with \( v > 2 \), which describe the intrinsic effect of relative atomic displacements. But essentially, the "geometrical" terms are of the same order as the "intrinsic" terms and should not be neglected.

3) The tensors \( H_{\nu} \) which depend explicitly on the direction of the radiation wave vectors \( \sigma \) and \( \sigma' \) are about one hundred times smaller than the tensors \( G_{\nu} \), if Slater's free ion parameters for oxygen, \( a^1 \approx 10^{-8} \text{ cm} \) are used. The contribution of these small terms to the total Raman scattering would be barely observable and could not explain the observed properties of the Raman spectrum of calcite. Only if \( a^{-1} \) and \( \beta^{-1} \) in crystals were at least ten times larger than in free ions could the tensors \( H_{\nu} \) produce significant observable phenomena, such as off-diagonal, wave vector dependent components of the Raman tensor which violate conventional selection rules.

We do not wish to speculate about this possibility. Rather, we point out that the effect of long range Coulomb forces is more promising to generate a wave vector dependent Raman tensor. This expectation is based on the phase factors \( \exp [i(\sigma - \sigma') \cdot \mathbf{r}] \) in the formulas (55) to (64) and on the fact that the summation \( \sum_{\mathbf{r}} \) in these formulas includes now distant neighbors of arbitrary large separation. An investigation of these phenomena is in progress.

4) The tensors \( G_{\nu}, H_{\nu}, \) and \( J_{\nu} \) are not explicitly proportional to the fourth power of the scattered frequency. This property which appears to be a common feature of all theories of the Raman effect in crystals not using the dipole approximation is being investigated. We have reasons to believe that the theory in its present form is a good approximation only in the visible domain, i.e., if the radiation frequency \( \nu \) is not much smaller than the gap frequency \( \hbar \cdot \nu \) of Eq. (19). An extrapolation to very small radiation frequencies appears to be not feasible in terms of the present formalism.

APPENDIX

Consider the sum

\[
b_i(\mathbf{r}) = \sum_{\nu \neq \mu} [g(\mathbf{r})]_{\nu \mu} \cdot a_{\nu}(\mathbf{r}),
\]

where the \( a_{\nu} \) are members of a complete set of eigenfunctions of a one-particle Hamiltonian, and \( [g(\mathbf{r})]_{\nu \mu} \) is the matrix element of a space function \( g(\mathbf{r}) \). The sum over the states \( \nu \) may be transformed into a property of the state \( i \) only, by use of the completeness theorem which allows for the expansion

\[
a_{\nu}(\mathbf{r}) = \sum_{\nu} C_{\nu} \cdot a_{\nu}(\mathbf{r}),
\]

\[
\int a_{\nu}(\mathbf{r}) \cdot a_{\nu}(\mathbf{r}) \, d\mathbf{r} = \sum_{\nu} C_{\nu} \int a_{\nu}(\mathbf{r}) \cdot a_{\nu}(\mathbf{r}) \, d\mathbf{r} = C_{\nu}.
\]

Thus,

\[
b_i(\mathbf{r}) = \sum_{\nu} \{ [g(\mathbf{r})]_{\nu \mu} \cdot a_{\nu}(\mathbf{r}) - [g(\mathbf{r})]_{\nu \mu} \cdot a_{\nu}(\mathbf{r}) \}
\]

\[
= \{ [g(\mathbf{r})]_{\nu \mu} \cdot a_{\nu}(\mathbf{r}) \}.
\]

Discussion

M. Giordmaine. — Observations of calcite show \( \alpha_{xy} \neq 0 \), but \( \alpha_{xz} = \alpha_{zy} = 0 \). Can this result be quantitatively understood from the theory?

M. Burstein. — It is of interest to note that the question of the relative importance of the \( A^2 \) terms and the \( (p \cdot A)^2 \) term was discussed at length "in the corridors", at the lattice dynamics conference in Copenhagen, and at the Aarhus Summer School on phonons which followed the conference. There were no conclusions. It was clear that a new attack on the problem was needed, and I am glad to see that Dr. Theimer and Saxman have undertaken. It would be helpful to have a more physical feeling for the \( A^2 \) term. I wonder if you might clarify the nature of this contribution. How does the exciting field accelerate the electrons without causing any intermediate transitions?

REFERENCES