Dynamics of Molecular Crystals

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I. Introduction

Molecular crystals are solids in which the atoms group together in well-defined stable entities arranged in some periodic way. In general, these entities can be molecules or molecular ions, but in this paper we mainly restrict ourselves to crystals built from neutral molecules. The binding forces keeping the atoms together in the molecules are much

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stronger than the van der Waals forces that cause the condensation of the molecules in the crystal. As a consequence, the atoms in the solid take part in two types of motions that, to a good approximation, can be assumed to be uncoupled. First, they perform rapid oscillations around instantaneous positions in such a way as to keep the positions, orientations, and geometries of the molecules nearly unchanged. These motions are called intramolecular vibrations. In the solid, when their frequencies are slightly shifted by the crystal field and they are very weakly coupled, they are called vibrons. Second, the equilibrium positions of the atoms undergo displacements that are such that they amount to translations and rotations of the molecules as a whole. These motions, the intermolecular vibrations, usually called lattice vibrations, are much slower than the intramolecular vibrations, and they are the subject of this paper.

Because we are dealing with molecules, two types of lattice vibrations can be distinguished: translational and rotational. In order to describe these motions we have to know the potential energy of the crystal, expressed as a function of the center of mass positions and the orientations of all molecules. In Section II, we give a fairly detailed description of the different ways in which the potential can be expressed, each way having its own merits, depending on the subsequent calculations in which it has to be used.

Depending on the character of the molecular motions, one can distinguish several physical situations. In most cases, the molecules are trapped in relatively deep potential wells. Then, they perform small translational and orientational oscillations around well-defined equilibrium positions and orientations. Such motions are reasonably well described by the harmonic approximation. The collective vibrational excitations of the crystal, which are considered as a set of harmonic oscillators, are called phonons. Those phonons that represent pure angular oscillations, or librations, are called librons. For some properties it turns out to be necessary to look at the effects of anharmonicities. Anharmonic corrections to the harmonic model can be made by perturbation theory or by the self-consistent phonon method. These methods, which are summarized in Section III under the name quasi-harmonic theories, can be considered to be the standard tools in lattice dynamics calculations, in addition to the harmonic model. They are only applicable in the case of fairly small amplitude motions. Only the simple harmonic approximation is widely used; the calculation of anharmonic corrections is often hard in practice. For detailed descriptions of these methods, we refer the reader to the books and reviews by Maradudin et al. (1968, 1971, 1974), Cochran and Cowley (1967), Barron and Klein (1974), Birman (1974), Wallace (1972), and Califano et al. (1981).
A second situation occurs when the molecules perform angular oscilla-
tions, usually with large amplitudes, around one of a set of equilibrium
orientations and randomly jump from one orientation to the other. Some-
times the librations are so violent that the molecules perform more or less
hindered rotations. An extreme case is solid hydrogen, at normal pres-
sure, in which the free-molecule rotations are only weakly perturbed and
one speaks of rotons instead of librions. In all these cases the molecular
crystal is called orientationally disordered or plastic, in contrast with the
ordered or localized crystals discussed in the preceding paragraph. The
only standard method to deal with this type of molecular motion is the
mean field or (time-independent) Hartree approximation. By using the
mean-field single-particle states as a basis, the collective motions of all
molecules in the crystal can be described via the random phase approxi-
mation or time-dependent Hartree method. These methods are outlined in
Section IV. Mostly the centers of mass of the molecules are thought of as
being fixed. This approximation will rarely be justified in practice, how-
ever. Most molecular crystals are rather closely packed, which forces the
molecules to separate before they can substantially change their orienta-
tions. As a result, there will be considerable coupling between the transla-
tional vibrations of the molecules and their rotational motions and mixing
of the translational phonons and librions. The effects of such coupling on
the properties of molecular crystals have been discussed by Michel and
co-workers (Michel and Naudts, 1978; de Raedt et al., 1981; Michel,
1984), and by Raich et al. (1983) and illustrated by semiempirical model
calculations. A way to deal with this coupling via the time-dependent
Hartree method has been proposed by ourselves (Briels et al., 1984). This
extension of the theory is included in Section IV.

All the lattice dynamics methods that we have just mentioned neglect
the exchange of identical molecules. The mean-field method, for instance,
is based on the Hartree approximation rather than on the Hartree–Fock
model. This concerns, of course, the exchange of identical nuclei, since
we are dealing with the nuclear motions and the effects of electron ex-
change are already contained in the intermolecular potential used. In
practically all cases, even for the lightest nuclei, the nuclear wave func-
tions have negligible overlap and the exchange effects may be safely
omitted.

Let us now discuss to what extent the lattice vibrations are important
for the macroscopic properties of molecular crystals. First of all, we have
to consider the zero-point vibrations, i.e., the energy difference between
the quantum-mechanical ground state of the system and the minimum of
its potential energy. Since the van der Waals interactions among the
molecules are rather weak, their zero-point motions affect the cohesion
energy of the crystal to a nonnegligible extent. Second, the characteristic excitation energies of the lattice vibrations are of the same order of magnitude as $k_B T$ ($k_B$ being the Boltzmann constant) in most experimental circumstances. The excited states are populated and thus contribute to the properties of the system. Their effective contributions are strongly dependent on the size of the excitation energies and may vary considerably from one system to the other. As an illustration, let us briefly discuss the phase transition between the ordered and disordered modifications that often exist for the same material. Usually the ordered phase is thermodynamically stable at low temperatures, the plastic phase at high temperatures. The stability of the ordered phase is mainly due to the packing of the molecules in such a manner that the ground-state energy of the system is as low as possible. The stability of the disordered phase at high temperature is caused by its excitation energies, which are typically those of hindered rotors, being much lower than the excitation energies of the ordered phase, which are more like those of harmonic oscillators. Consequently, the excited states in the plastic phase will be more populated, its entropy will be larger, and its free energy ($A = E - TS$) will be lower at high temperature. It will be clear from this example that in order to give a reasonable account of any phase transition, one must accurately calculate the ground state and the excitation energies of the phases involved. The comparison between the calculated and observed phase transition temperatures and pressures yields a sensitive test, both for the potential and for the method used to describe the lattice dynamics.

In most cases, the crystal potential is not known a priori. The usual procedure is to introduce some model potential containing several parameters, which are subsequently found by fitting the calculated crystal properties to the observed data available. This procedure has the drawback that the empirical potential thus obtained includes the effects of the approximations made in the lattice dynamics model, which is mostly the harmonic model. It is very useful to have independent and detailed information about the potential from quantum-chemical ab initio calculations. Such information is available for nitrogen (Berns and van der Avoird, 1980) and oxygen (Wormer and van der Avoird, 1984), and we have chosen the results calculated for solid nitrogen and solid oxygen to illustrate in Sections V and VI, respectively, the lattice dynamics methods described in Sections III and IV. Nitrogen is the simplest typical molecular crystal;* as such it has received much attention from theorists and

* Hydrogen is even simpler, but solid hydrogen is very atypical. Because of the large splitting between the rotational states of the free $\text{H}_2$ molecule and the weak anisotropy of the $\text{H}_2-\text{H}_2$ interaction potential, the free molecule rotations are nearly unperturbed in the solid. This system has been extensively discussed by van Kranendonk (1983).
experimentalists and many data have been collected. It has several phases, ordered as well as disordered. Oxygen is especially interesting because it combines the properties of a molecular crystal with those of a magnetic material. It exhibits both structural and magnetic order–disorder phase transitions.

II. Intermolecular Interactions and the Crystal Hamiltonian

In the Born–Oppenheimer approximation the potential energy of a molecular crystal depends on the internal and external degrees of freedom of all molecules. As mentioned before, it is a very good approximation in most cases to separate the intramolecular vibrations from the center of mass vibrations and rotations of the molecules, i.e., the lattice vibrations. Then one can average the potential energy over the vibrational wave functions of the molecules and obtain the effective potential for the lattice vibrations. If one wishes to obtain this effective intermolecular potential by calculation, it is a good approximation to use the vibrationally averaged molecular geometries from theory or experiment. The (average) geometry of the molecules in the crystal is usually not very different from the free-molecule geometry.

A further approximation, which is applied in almost all practical treatments, is to write the intermolecular potential for the crystal as a sum over molecular pair potentials. For van der Waals solids—in which the electrostatic interactions, the exchange repulsion, and the London dispersion attraction are the main contributors to the potential—this is fairly well justified. However, when the molecules have large dipole moments (in ice, for example) or even more so in ionic crystals, the induction (multipole-induced multipole) interactions become substantial, and the three-body interaction energy will be comparable in size to the pair energy. This is because one has to add pairwise the polarizing electric fields from all neighbors in order to calculate the polarization energy of a given molecule that is quadratic in the field strength. Moreover, one has to take into account self-consistently the mutual interactions among the induced dipole moments. In the present paper, we focus on molecules with relatively small dipole moments, for which we estimate the exchange, induction, and dispersion three-and-more-body contributions to be not larger than about 10% of the pair potential (van der Avoird et al., 1980), and we further neglect these deviations from pairwise additivity.

In order to be useful in crystal dynamics calculations, the intermolecular potential must be represented in a manageable, preferably analytic, form. The form chosen to express the potential will depend on the type of application. If, for example, the intermolecular potential is to be deduced
from the agreement between calculated and observed crystal properties, it is important to have a representation that is as simple as possible, depending only on a few parameters. The same requirement has to be fulfilled when during the calculation the numerical value of the intermolecular potential is needed many times, for instance, in classical molecular dynamics or Monte Carlo simulations. For such purposes a representation in terms of atom–atom interaction potentials is convenient. On the other hand, if one intends to make statistical mechanics calculations with an "ab initio" potential without losing too much accuracy, an expansion of the potential in terms of orthogonal symmetry-adapted functions is suitable. In the sequel, we briefly describe in Section II,A the atom–atom potential model, in Section II,B the representation of the potential in terms of symmetry-adapted functions, and in Section II,C the relation between the two formalisms. Finally, in Section II,D we discuss the full crystal Hamiltonian.

A. Atom–Atom Potentials

The concept of an atom–atom potential (Kitaigorodsky, 1973) is based on the idea that the interaction potential between two molecules $P$ and $P'$ can be approximated by pairwise additive interactions between the constituent atoms, $\alpha \in P$ and $\beta \in P'$, which, in practice, are nearly always taken to be isotropic, i.e., dependent only on the interatomic distances $r_{\alpha \beta}$:

$$V_{PP'} = \sum_{\alpha \in P} \sum_{\beta \in P'} v_{X_{\alpha}X_{\beta}}(r_{\alpha \beta})$$  \hspace{1cm} (1)

The labels $X_{\alpha}$ and $X_{\beta}$ denote the types of the atoms $\alpha$ and $\beta$. Popular forms for the atom–atom potentials are the Lennard–Jones 12–6 form

$$v_{X_{\alpha}X_{\beta}}(r_{\alpha \beta}) = A_{X_{\alpha}X_{\beta}}r_{\alpha \beta}^{-12} - B_{X_{\alpha}X_{\beta}}r_{\alpha \beta}^{-6}$$  \hspace{1cm} (2)

and the Buckingham exp $-6$ or exp $-6-1$ form

$$v_{X_{\alpha}X_{\beta}}(r_{\alpha \beta}) = A_{X_{\alpha}X_{\beta}} \exp(-B_{X_{\alpha}X_{\beta}}r_{\alpha \beta}^{-6}) - C_{X_{\alpha}X_{\beta}}r_{\alpha \beta}^{-6}(+q_{X_{\alpha}}q_{X_{\beta}}r_{\alpha \beta}^{-1})$$  \hspace{1cm} (3)

The first term always represents the exchange repulsion and the second term the London dispersion attraction. The Coulomb term is sometimes added in order to represent the electrostatic interactions among molecules, with fractional atomic point charges $q_{X_{\alpha}}$ and $q_{X_{\beta}}$ used. Alternatively, one has included these electrostatic contributions by adding the leading molecular multipole–multipole interaction term to an atom–atom potential of 12–6 or exp $-6$ type.

The interaction parameters $A_{X_{\alpha}X_{\beta}}$, $B_{X_{\alpha}X_{\beta}}$, $C_{X_{\alpha}X_{\beta}}$, and $q_{X_{\alpha}}$ are mostly obtained by fitting calculated crystal properties to experimental data. The quality of the resulting empirical potentials is rather uncertain, however,
since the fit will try to compensate for the inaccuracies in the dynamical model used and in the atom–atom model itself. Moreover, the different parameters are often strongly correlated. This implies that such empirical potentials are usually not very effective in predicting properties other than those to which they have been fitted.

In some cases (see van der Avoird et al., 1980, and references therein) atom–atom potentials, which are subsequently used to calculate crystal properties, have been obtained from an independent source, viz., from \textit{ab initio} quantum-chemical calculations. The individual terms in an atom–atom potential of the form in Eq. (3), for example, are then fitted to the corresponding interaction energy contributions calculated for a more or less extensive set of geometries of a molecular pair. It appears that the Buckingham form (in Eq. 3) especially can yield a reasonably accurate representation of an \textit{ab initio} calculated potential, provided that the individual terms are given different force centers (sites) whose positions are shifted away from the atomic nuclei and optimized in fitting the \textit{ab initio} data.

It is convenient for further use to summarize the various atom–atom potentials as given in Eqs. (2) and (3) in the single formula

$$u_{\alpha\beta}(\mathbf{r}_{\alpha\beta}) = \sum_{n,\exp} A_{n,\exp}^{X_{\alpha\beta}} f^{(n/\exp)}(\mathbf{r}_{\alpha\beta})$$

with parameters $A_{n,\exp}^{X_{\alpha\beta}}$, $A_{\exp}^{X_{\alpha\beta}}$, and distance functions $f^{(n)}(\mathbf{r}_{\alpha\beta}) = r_{\alpha\beta}^{-n}$ (e.g., $n = 12, 6, 1$) and $f^{(\exp)}(\mathbf{r}_{\alpha\beta}) = \exp(-B^{X_{\alpha\beta}} r_{\alpha\beta})$.

B. Intermolecular Potential in Terms of Symmetry-Adapted Functions

In order to describe the orientation of a given molecule we attach a rectangular coordinate frame $M$ to it and specify the Euler angles $\omega = \{\alpha, \beta, \gamma\}$ of this frame relative to a fixed global frame $G$. The position vector of the center of mass of the molecule is denoted by $\mathbf{r}$. The potential between two molecules at $\mathbf{r}_P$ and $\mathbf{r}_P'$, respectively, can then be expanded (Steele, 1963; Yasuda and Yamamoto, 1971; Egelstaff, Gray and Gubbins, 1975; van der Avoird et al., 1980; Briels, 1980) in a complete set of functions of the variables $\omega_P$, $\omega_{P'}$, and $\hat{r}_{PP'}$, where $\hat{r}_{PP'}$ is the unit vector in the direction of $\mathbf{r}_{PP'} = \mathbf{r}_P - \mathbf{r}_P$. The coefficients of the expansion depend on $r_{PP'}$, the length of $\mathbf{r}_{PP'}$. As a basis for the expansion we use the products

$$D_{n_1 m_1}^{(l_1)}(\omega_P)D_{n_2 m_2}^{(l_2)}(\omega_{P'})C_{m_3}^{(l_3)}(\hat{r}_{PP'})$$

where the $D_n^{(l)}(\omega)$ are Wigner functions and $C_m^{(l)}(\hat{r})$ is a Racah spherical harmonic. For these functions as well as for the Euler angles, we use the definitions of Edmonds (1957). This expansion can be greatly simplified if we exploit the full symmetry of the molecular pair.
In order to incorporate the symmetry requirements into our expansion, we need the transformation properties of the Wigner functions, both with respect to rotations $R^G(\omega)$ of the global frame and with respect to rotations $R^M(\omega)$ of the molecular frames. If we rotate the global frame through the Euler angles $\omega$, then a scalar quantity that was described in the original frame by a function $F$ will be described in the new frame by $R^G(\omega)F$; the two functions are related by $R^G(\omega)F(\omega) = F(\omega')$, where $\omega$ and $\omega'$ are the Euler angles of the molecular frame relative to the new and old global frames, respectively. Similarly, if we rotate a molecular frame through the Euler angles $\omega$, $F$ will transform into $R^M(\omega)F$. With the conventions that we have adopted, the transformed Wigner functions are given by

$$R^G(\omega)D_{nm}(\omega) = \sum_{m'} D_{nm'}(\omega)D_{m'm}(\omega)$$  \hspace{1cm} (5)$$

$$R^M(\omega)D_{nm}(\omega) = \sum_{n'} D_{n'm}(\omega)D_{n'n}(\omega)$$  \hspace{1cm} (6)$$

The well-known transformation properties of the Racah spherical harmonics can be obtained from the relation

$$C_m^{(l)}(\hat{r}) = C_m^{(l)}(\theta, \phi) = D_{0m}(\phi, \theta, 0)$$  \hspace{1cm} (7)$$

and Eq. (5):

$$R^G(\omega)C_m^{(l)}(\hat{r}) = \sum_{m'} C_m^{(l)}(\hat{r})D_{m'm}(\omega)$$  \hspace{1cm} (8)$$

The expression for the intermolecular potential must satisfy two symmetry requirements. First, it must be invariant if we rotate the molecular frame of either of the two molecules through specific Euler angles $\omega_g$ that correspond with a symmetry element of the molecule in question. This means that our basis must be invariant under rotations of the outer direct product group $G_P \otimes G_{P'}$, where $G_P$ is the symmetry group of molecule $P$ and $G_{P'}$ that of molecule $P'$. Acting with the projection operator of the totally symmetric irreducible representation of the group $G_P$ (of order $\#G_P$),

$$P = \frac{1}{\#G_P} \sum_{g \in G_P} R^M(\omega_g)$$  \hspace{1cm} (9)$$

on the Wigner functions, and using Eq. (6), we construct linear combinations

$$G_m^{(l)}(\omega_P) = \sum_n A_n^{(l)}D_{nm}(\omega_P)$$  \hspace{1cm} (10)$$
which are invariant under the group \( G_P \). We choose as the expansion basis the set of all products:

\[
G_{m_1}^{(l_1)}(\omega_P)G_{m_2}^{(l_2)}(\omega_P)C_{m_3}^{(l_3)}(\hat{f}_{pp'}).
\]  

(11)

It may happen that for certain values of \( l \) more than one totally symmetric combination (10) may exist. In that case, the \( l \) index should be understood as a composite label. As an example, we list in Table I, for values of \( l \) up to 10, the tetrahedral rotation functions that transform according to the totally symmetric representation of the tetrahedral group \( T \). These functions are normalized such that

\[
(8\pi^2)^{-1} \int d\omega T_{m_1}^{(l_1)}(\omega)*T_{m_2}^{(l_2)}(\omega) = \delta_{l_1 l_2} \delta_{m_1 m_2}(2l_1 + 1)^{-1}
\]

The coefficients \( A_n^{(l)} \) in these functions depend on the way in which the molecular coordinate frame is fixed on the molecule, for which we use the standard convention in this example (see Table I).

\[
\begin{array}{ll}
T_n^{(l)} & \text{Function} \\
0 & T_0^{(0)} = D_{00}^{(0)} \\
3 & T_3^{(3)} = -i(2)^{1/2}\{D_{2m}^{(3)} - D_{-2m}^{(3)}\} \\
4 & T_4^{(4)} = \left(\frac{5}{3}\right)^{1/2}\{D_{0m}^{(4)} + \left(\frac{5}{14}\right)^{1/2}(D_{4m}^{(4)} + D_{-4m}^{(4)})\} \\
6 & T_6^{(6)} = \left(\frac{1}{2}\right)^{1/2}\{D_{0m}^{(6)} - \left(\frac{3}{2}\right)^{1/2}(D_{4m}^{(6)} + D_{-4m}^{(6)})\} \\
T_6^{(6)} & = \left(\frac{1}{2}\right)^{1/2}\{D_{2m}^{(6)} + D_{-2m}^{(6)}\} - \left(\frac{5}{14}\right)^{1/2}(D_{6m}^{(6)} + D_{-6m}^{(6)})} \\
7 & T_7^{(7)} = -i(3)^{1/2}\{(D_{2m}^{(7)} - D_{-2m}^{(7)}) + \left(\frac{13}{2}\right)^{1/2}(D_{6m}^{(7)} - D_{-6m}^{(7)})\} \\
8 & T_8^{(8)} = \left(\frac{5}{3}\right)^{1/2}\{D_{0m}^{(8)} + \left(\frac{9}{16}\right)^{1/2}(D_{4m}^{(8)} + D_{-4m}^{(8)}) + \left(\frac{165}{108}\right)^{1/2}(D_{8m}^{(8)} + D_{-8m}^{(8)})\} \\
9 & T_9^{(9)} = -i(3)^{1/2}\{(D_{2m}^{(9)} - D_{-2m}^{(9)}) - \left(\frac{13}{2}\right)^{1/2}(D_{6m}^{(9)} - D_{-6m}^{(9)})\} \\
T_9^{(9)} & = -i(3)^{1/2}\{(D_{4m}^{(9)} - D_{-4m}^{(9)}) - \left(\frac{13}{2}\right)^{1/2}(D_{8m}^{(9)} - D_{-8m}^{(9)})\} \\
10 & T_{10}^{(10)} = \left(\frac{9}{16}\right)^{1/2}\{D_{0m}^{(10)} - \left(\frac{9}{16}\right)^{1/2}(D_{4m}^{(10)} + D_{-4m}^{(10)}) - \left(\frac{197}{30}\right)^{1/2}(D_{8m}^{(10)} + D_{-8m}^{(10)})\} \\
T_{10}^{(10)} & = \left(\frac{247}{494}\right)^{1/2}\{(D_{2m}^{(10)} + D_{-2m}^{(10)}) + \left(\frac{1}{26}\right)^{1/2}(D_{6m}^{(10)} + D_{-6m}^{(10)}) \\
& - \left(\frac{247}{494}\right)^{1/2}(D_{10m}^{(10)} + D_{-10m}^{(10)})\} \\
\end{array}
\]

* The z axis of the molecule fixed system is a two-fold axis; the [1, 1, 1] axis is a threefold axis.
The second symmetry requirement that the expression for the intermolecular potential has to meet is that it must be invariant under any rotation of the global coordinate frame. The transformation properties of the symmetry-adapted functions $G^{(l)}_m(\omega)$ under such a rotation are easily obtained from Eqs. (10) and (5):

$$R^{G}_G(\hat{\omega})G^{(l)}_m(\omega) = \sum_{m'} G^{(l)}_{m'}(\omega)D^{(l)}_{m'm}(\hat{\omega}) \tag{12}$$

We now construct the invariant basis in which we shall expand the intermolecular potential by acting on the products (11) with the projection operator

$$(8\pi^2)^{-1}\int d\hat{\omega} \, R^{G}_G(\hat{\omega}) \tag{13}$$

using the transformation formulas (8) and (12) and the relation

$$(8\pi^2)^{-1}\int d\hat{\omega} \, D^{(l_1)}_{m_1m_1}(\hat{\omega})D^{(l_2)}_{m_2m_2}(\hat{\omega})D^{(l_3)}_{m_3m_3}(\hat{\omega}) = \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1' & m_2' & m_3' \end{pmatrix} \begin{pmatrix} l_2 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \tag{14}$$

The symbols on the right-hand side are $3-j$ coefficients.

The expansion of the intermolecular potential then reads

$$V(\omega_P, \omega_P', r_{PP'}) = \sum_l v_l(r_{PP'}) \sum_m \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \times G^{(l_1)}_{m_1}(\omega_P)G^{(l_2)}_{m_2}(\omega_P')C^{(l_3)}_{m_3}(r_{PP'}) \tag{15}$$

The summation labels are defined as $l = \{l_1, l_2, l_3\}$ and $m = \{m_1, m_2, m_3\}$. We note again that for certain values of $l_1$ and $l_2$ more than one symmetry-adapted function $G^{(l)}_m$ exists and that in this case $\Sigma_l$ includes all these functions.

From Eq. (15) we observe that the intermolecular potential is completely specified by the coefficients $v_l(r_{PP'})$. These expansion coefficients can be obtained in various ways. If the intermolecular potential is given in terms of atom–atom potentials, it is possible to obtain explicit expressions for these coefficients (see Section II,C). If the long-range part of the potential is known from perturbation theory calculations in the multipole expansion, the expansion coefficients, after some angular momentum recoupling, can also be obtained from explicit formulas (see van der Avoird et al., 1980). If the (short- and intermediate-range) potential is known
numerically from \textit{ab initio} calculations for a grid of distances \(r_{pp'}\) and molecular orientations \(\omega_p\) and \(\omega_{p'}\), the expansion coefficients can be found by numerical integration for each value of \(r_{pp'}\):

\[
\nu_i(r_{pp'}) = (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(8\pi^2)^{-2} \\
\times \int d\omega_p \int d\omega_{p'} \sum_m \begin{pmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{pmatrix} \\
\times G_m^{(l_1)}(\omega_p) * G_m^{(l_2)}(\omega_{p'}) * V(\omega_p, \omega_{p'}, r_{pp'})
\]

Here we have used the fact that one can always choose to perform the \textit{ab initio} calculations on the pair \(PP'\) in a coordinate frame with the \(z\) axis along \(r_{pp}\). Then we have \(r_{pp'} = (\theta, \phi) = (0, 0)\) and \(C_m^{(l)}(r_{pp'}) = \delta_{m0}\). The integral can be further simplified by noting that the internal geometry of any molecular pair can be specified by at most five Euler angles, so that one of the six angles \(\omega_p\), \(\omega_{p'}\) can also be set to zero and left out of the integration. In special cases, even more simplifications can be made. For example, if the molecules \(P\) and \(P'\) are linear, two more Euler angles can be omitted. Once the coefficients \(\nu_i(r_{pp'})\) are calculated for several values of \(r_{pp'}\), it is convenient to fit their \(r_{pp'}\) dependence by means of simple analytic forms \((r^{-n}\text{ in the long range, }\exp(-Br)\text{ in the short range})\). For further details of this procedure we refer to the review by van der Avoird et al. (1980) and the references therein.

Finally, we observe that, in principle, one may truncate the expansion (15) after a few terms and thus model the anisotropy of the potential (the term \(I = \{0, 0, 0\}\) is the isotropic part). Simple parameterized \(r_{pp}\) functions for the expansion coefficients \(\nu_i(r_{pp'})\) can then be introduced and the parameters can be fitted empirically. The latter procedure is similar to the empirical way of obtaining atom–atom model potentials and the same questions can be raised regarding the validity of the resulting potentials.

C. Expansion of Atom–Atom Potentials in Symmetry-Adapted Functions

In atom–atom potentials the anisotropy of the intermolecular potential, i.e., its dependence on the molecular orientations \(\omega_p\) and \(\omega_{p'}\), is implicitly determined by the model. One can make this dependence explicit by expanding a given atom–atom potential in the form (15). It has been demonstrated by Sack (1964), Yasuda and Yamamoto (1971), and Downs et al. (1979) that analytic expressions can be derived for the expansion coefficients \(\nu_i(r_{pp'})\) in (15) for atom–atom potentials (see Section II,A) with \(f^{(n)}(r_{ab}) = r_{ab}^{-n}\) dependence and by Briels (1980) that they can be derived for atom–atom interactions with exponential dependence.
\[ f^{(\text{exp})}(r_{ab}) = \exp(-r_{ab}). \]
In order to derive such expressions these authors use the two-center expansion of the functions:

\[ f^{(n/\text{exp})}(r_{ab}) = f^{(n/\text{exp})}(|r_{PP'} - d_{\alpha} + d_{\beta}|) \]

where \(d_{\alpha}\) is the position vector of atom \(\alpha\) relative to the center of mass of the molecule \(P\) to which it belongs and \(d_{\beta}\) is the same vector for atom \(\beta\) in molecule \(P'\). The result is the formula (Briels, 1980):

\[
\begin{align*}
 f^{(n/\text{exp})}(r_{ab}) &= \sum_{l} \left( \begin{array}{ccc}
 l_1 & l_2 & l_3 \\
 0 & 0 & 0
 \end{array} \right) g^{(n/\text{exp})}_{1}(d_{\alpha}, d_{\beta}, r_{PP'}) \\
 &\times \sum_{m} \left( \begin{array}{ccc}
 l_1 & l_2 & l_3 \\
 m_1 & m_2 & m_3
 \end{array} \right) C_{m1}^{(l1)}(d_{\alpha}) C_{m2}^{(l2)}(d_{\beta}) C_{m3}^{(l3)}(r_{PP'})
\end{align*}
\]

with

\[
 g^{(1)}_{1}(d_{\alpha}, d_{\beta}, r_{PP'}) = \delta_{l_{1}+l_{2}+l_{3}}(-1)^{l_{3}}[I] \frac{(2l_{3})!}{(2l_{1} + 1)! (2l_{2} + 1)! l_{3}!} \\
\times \frac{1}{r_{PP'}} \left( \frac{d_{\alpha}}{r_{PP'}} \right)^{l_{1}} \left( \frac{d_{\beta}}{r_{PP'}} \right)^{l_{2}}
\]

\[
 g^{(n)}_{1}(d_{\alpha}, d_{\beta}, r_{PP'}) = (-1)^{l_{2}} \frac{[I]}{(n - 2)!} \left( \frac{1}{r_{PP'}} \right)^{n} \left( \frac{d_{\alpha}}{r_{PP'}} \right)^{l_{1}} \left( \frac{d_{\beta}}{r_{PP'}} \right)^{l_{2}} \\
\times \sum_{m_{1}=0}^{\infty} \sum_{m_{2}=0}^{\infty} \left( \frac{d_{\alpha}}{r_{PP'}} \right)^{2m_{1}} \left( \frac{d_{\beta}}{r_{PP'}} \right)^{2m_{2}} \\
\times \frac{(n - 2 + l_{1} + l_{2} - l_{3} + 2m_{1} + 2m_{2})!}{(2l_{1} + 2m_{1} + 1)!(2m_{1}!!)(2l_{2} + 2m_{2} + 1)!!(2m_{2}!!)} \\
\times \frac{(n - 2 + l_{1} + l_{2} + l_{3} + 2m_{1} + 2m_{2}!!)}{(n - 2 + l_{1} + l_{2} - l_{3} + 2m_{1} + 2m_{2}!!)}
\]

for \(n \geq 2\), and

\[
 g^{(\text{exp})}_{1}(d_{\alpha}, d_{\beta}, r_{PP'}) = (-1)^{l_{2}+1}[I] \{(1 + l_{1} + l_{2} + l_{3}) J_{l_{1}}(d_{\alpha}) J_{l_{2}}(d_{\beta}) K_{l_{3}}(r_{PP'}) \\
+ d_{\alpha} J_{l_{1}+1}(d_{\alpha}) J_{l_{2}}(d_{\beta}) K_{l_{3}}(r_{PP'}) \\
+ d_{\beta} J_{l_{1}}(d_{\alpha}) J_{l_{2}+1}(d_{\beta}) K_{l_{3}}(r_{PP'}) \\
- r_{PP'} J_{l_{1}}(d_{\alpha}) J_{l_{2}}(d_{\beta}) K_{l_{3}+1}(r_{PP'})\}
\]

We use the abbreviated notation \([I] = (2l_{1} + 1)(2l_{2} + 1)(2l_{3} + 1)\). The functions \(J_{l}(z)\) and \(K_{l}(z)\) are related to the modified spherical Bessel
functions (Antosiewicz, 1970) of the first and third kind, respectively, by
\( J_1(z) = (\pi/2z)^{1/2} J_{1+(1/2)}(z) \) and \( (\pi/2) K_1(z) = (\pi/2z)^{1/2} K_{1+(1/2)}(z) \). It is interesting to notice that Eq. (19) is in closed form, whereas Eq. (18) contains an infinite sum.

Using the general expressions (1) with (4) for an atom–atom model and substituting the two-center expansion (16), we write the intermolecular atom–atom potential as

\[
V_{pp'} = V(\omega_p, \omega_{p'}, r_{pp'}) = \sum_{l_1} \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{array} \right) \sum_{a \in P} \sum_{b \in P'} \times \sum_{n, \text{exp}} A_{n, \text{exp}} X_a X_b s_{1}^{(n/\text{exp})} (d_a, d_b, r_{pp'}) \times \sum_{m} \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array} \right) \sum_{a \in a} C_{m_1}^{(l_1)} (\hat{d}_a) \times \left\{ \sum_{b \in b} C_{m_2}^{(l_2)} (\hat{d}_b) \right\} C_{m_3}^{(l_3)} (r_{pp'}) \tag{20}
\]

Here we have partitioned the sums over all atoms \( \alpha \) and \( \beta \) in the molecules \( P \) and \( P' \) in the following manner. First, we sum over equivalent atoms within the same class \( \alpha \in a \) and \( \beta \in b \), which have the same chemical nature \( X_\alpha = X_\alpha \) and \( X_\beta = X_\beta \) and the same distance \( d_\alpha = d_\alpha \) and \( d_\beta = d_\beta \) to the respective molecular center of mass. Next, we sum over classes \( a \in P \) and \( b \in P' \). The orientations \( \hat{d}_\alpha \) and \( \hat{d}_\beta \) of the position vectors of the atoms \( \mathbf{d}_\alpha \) and \( \mathbf{d}_\beta \), relative to the molecular centers of mass, are still given with respect to the global coordinate frame. If we denote the polar angles of \( \mathbf{d}_\alpha \) and \( \mathbf{d}_\beta \) in the molecule fixed frames by \( \tilde{d}_\alpha \) and \( \tilde{d}_\beta \) and remember that the molecular frames are related to the global frame by rotations through the Euler angles \( \omega_p \) and \( \omega_{p'} \), respectively, we find that

\[
\sum_{a \in a} C_{m_1}^{(l_1)} (\tilde{d}_a) = \sum_{n_1} \left\{ \sum_{a \in a} C_{n_1}^{(l_1)} (\tilde{d}_a) \right\} D_{m_1}^{(l_1)} (\omega_p) = k_a^{(l_1)} G_{m_1}^{(l_1)} (\omega_p) \tag{21}
\]

and a similar expression for atoms \( \beta \in b \in P' \). The latter equality, which is related to Eq. (10), follows from the fact that the left-hand side must be invariant under all rotations of the molecular point group \( G_P \); these rotations just interchange the equivalent atoms \( \alpha \in a \). Introducing Eq. (21) and the corresponding result for atoms \( \beta \in b \) into Eq. (20), the general atom–atom potential is expressed in the form of Eq. (15), with
D. The Crystal Hamiltonian

Now that we have expressed the intermolecular potential, it is easy to write down the crystal Hamiltonian. We associate with each point \( P = \{n, i\} \) of the lattice a molecule with position vector \( r_P = R_P + u_P \). The vector \( R_P \) denotes the position of the lattice point \( P \), i.e., \( R_P = R_n + R_i \) with \( R_n \) being the position vector of the origin of the unit cell to which \( P \) belongs and \( R_i \) the position vector of \( P \) relative to this origin. The displacement vector \( u_P \) describes the position of the center of mass of the molecule at \( P \) relative to the lattice point \( P \). The Hamiltonian then reads

\[
H = \sum_P \left\{ T(u_P) + L(\omega_P) \right\} + \frac{1}{2} \sum_{P+i} \sum_{P+i'} V_{PP'}(u_P, \omega_P; u_{P'}, \omega_{P'})
\]

where

\[
V_{PP'}(u_P, \omega_P; u_{P'}, \omega_{P'}) = V(\omega_P, \omega_{P'}, r_{PP'})
\]

In the latter equation \( r_{PP'} = r_{P'} - r_P = R_{P'} - R_P + u_{P'} - u_P = R_{PP'} + u_{P'} - u_P \), from which the dependence of \( V_{PP'} \) on \( u_P \) and \( u_{P'} \) follows. In Eq. (23) the kinetic energy operators for the translational and rotational motions are defined, respectively, as

\[
T(u_P) = -\frac{\hbar^2}{2M} \Delta(u_P)
\]

\[
L(\omega_P) = \frac{J_a^2(\omega_P)}{2I_a} + \frac{J_b^2(\omega_P)}{2I_b} + \frac{J_c^2(\omega_P)}{2I_c}
\]

Here \( \Delta(u_P) \) is the Laplacian and \( J_a, J_b, \) and \( J_c \) are the components of the angular momentum operator with respect to the principal \( a, b, \) and \( c \) axes of the molecule; \( I_a, I_b, \) and \( I_c \) are the principal values of the molecular moment of inertia. For simplicity we have assumed that the crystal is composed of just one type of molecules. Otherwise, the molecular mass \( M \) and the moments of inertia have to carry the sublattice label \( i \), appearing in \( P = \{n, i\} \).

The dependence of the potential \( V_{PP'} \) on the translational degrees of freedom \( u_P \) is rather intricate, and in order to use this potential in lattice dynamics calculations, we have to rewrite it in more tractable form. Beforehand, we make some remarks concerning the case when only rotational motions are considered. This is useful when the rotation–transla-
tion coupling is weak, for instance, as in hydrogen or methane crystals, or, in general, at certain points of high symmetry in the Brillouin zone, where the rotation and translation modes are decoupled because of this symmetry. In these cases, the potential for the rotational problem is an effective potential in the sense that it can be obtained from the complete intermolecular potential by averaging over the translational motions. This effective potential can be written in the form of Eq. (15) with coefficients \( \langle \upsilon_l(r_{PP'}) \rangle = \upsilon_l(R_{PP'}) \). The crystal Hamiltonian then reads

\[
H = U^C + \sum_p \{ L(\omega_p) + V_p(\omega_p) \} + \frac{1}{2} \sum_{p \neq p'} \Phi_{pp'}(\omega_p, \omega_{p'})
\]

The two-body potential \( \Phi_{pp'} \) consists of those terms that depend on the orientations of both molecules; i.e., \( \Phi_{pp'} \) is equal to \( V_{pp'} \) minus the terms, with one or both of \( l_1 \) and \( l_2 \) equal to zero. The terms with either \( l_1 \) or \( l_2 \) equal to zero are contained in \( V_p \), which depends only on the orientation of molecule \( P \), and the isotropic term \( l_1 = l_2 = 0 \) is just the constant \( U^C \):

\[
U^C = \frac{1}{2} \sum_{p \neq p'} U_p
\]

\[
V_p(\omega_p) = \sum_{l,m} V_m^{(l)}(P) G_m^{(l)}(\omega_p)
\]

\[
\Phi_{pp'}(\omega_p, \omega_{p'}) = \sum_{l_1, m_1, l_2, m_2} \sum_{l_1, l_2} G_m^{(l_1)}(\omega_p) X_m^{(l_1, l_2)}(P, P') G_m^{(l_2)}(\omega_{p'})
\]

with

\[
V_m^{(l)}(P) = (2l + 1)^{-1/2} (-1)^l \frac{1}{2} \sum_{p \neq p'} \left\{ \upsilon_{l,0,0}(R_{PP'}) C_m^{(l)}(\hat{R}_{PP'})^* \right. \\
+ \upsilon_{0,l,0}(R_{PP'}) C_m^{(l)}(-\hat{R}_{PP'})^* \right. \\
= (2l + 1)^{-1/2} (-1)^l \sum_{p \neq p'} \upsilon_{l,0,0}(R_{PP'}) C_m^{(l)}(\hat{R}_{PP'})^*
\]

\[
X_m^{(l_1, l_2)}(P, P') = \sum_{l_3, m_3} \upsilon_l(R_{PP'}) \binom{l_1}{m_1} \binom{l_2}{m_2} \binom{l_3}{m_3} C_m^{(l_3)}(\hat{R}_{PP'})
\]

In Eq. (31) we have used the relation \( \upsilon_{0,l,0}(R_{PP'}) = (-1)^l \upsilon_{l,0,0}(R_{PP'}) \) (Briels, 1980). The primes on the summation signs indicate that the terms with \( l = 0 \) have to be omitted.

The term \( V_p(\omega_p) \) in Eq. (27) is called the crystal field term. From Eqs. (29) and (31) it is clear that this term is invariant under all rotations of the global frame that correspond to symmetry operations on the lattice. As a
result \( V_P(\omega_P) \) contains only linear combinations of the functions \( G_{m}^{(l)}(\omega_P) \), which transform according to the totally symmetric representation of the site group \( S_P \). Note that \( S_P \) contains all rotations around \( P \) that leave the point lattice invariant; this group is larger than the point group of the crystal, which is not yet defined as long as the equation of motion is not solved. The functions adapted to the site symmetry can be obtained by acting with the projection operator:

\[
P_S = \frac{1}{\#S_P} \sum_{g \in S_P} R^G(\omega_g)
\]

on the functions \( G_{m}^{(l)}(\omega_P) \). In Table II we have given the results for the octahedral group \( S_P = O \), which is the site group of all sites in the fcc lattice.

In order to obtain the explicit translational dependence of the complete intermolecular potential (15), we expand the translationally dependent part of Eq. (15) as a Taylor series in the displacement vectors \( u_P \) and \( u_P' \):

\[
u_{l}(r_{pp'})C_{m3}^{(l3)}(\hat{r}_{pp'}) = \sum_{\alpha_1, \alpha_2} \frac{-u_P \cdot \nabla)^{\alpha_1}}{\alpha_1!} \frac{(u_{pp'} \cdot \nabla)^{\alpha_2}}{\alpha_2!} \eta_l(r_{pp'}) C_{m3}^{(l3)}(\hat{r}_{pp'})
\]

In principle, the sums over \( \alpha_1 \) and \( \alpha_2 \) must be extended to infinity. In practice, we apply the truncation condition \( \alpha_1 + \alpha_2 \leq \alpha_{\text{max}} \). The terms with \( \alpha_1 = \alpha_2 = 0 \) give rise to the purely rotational part of the Hamiltonian, which we have just treated. The other terms can be most easily evaluated by applying the gradient formula in spherical tensor form (Edmonds, 1957):

\[
u_{l}(r_{pp'})C_{m3}^{(l3)}(\hat{r}_{pp'}) = u_P \sum_{k} A_{l3k}(R_{pp'}) F(R_{pp'})
\]

\[
\times [C^{(l1)}(\hat{u}_P) \otimes C^{(l'p)}(\hat{r}_{pp'})]_{m3}^{(l3)}
\]

where \( A_{lk} \) is an operator defined by

\[
A_{lk}(R) = -\delta_{k,l-1} \left[ \frac{l(2l-1)}{2l+1} \right]^{1/2} \left( \frac{d}{dR} + \frac{l+1}{R} \right)
\]

\[
+ \delta_{k,l+1} \left[ \frac{(l+1)(2l+3)}{2l+1} \right]^{1/2} \left( \frac{d}{dR} - \frac{l}{R} \right)
\]

The irreducible tensor product between the brackets represents the usual angular momentum coupling.
between two tensors \( \{ C_m^{(l)}(\hat{r}_1) ; m_1 = -l_1, \ldots, l_1 \} \) and \( \{ C_m^{(l_2)}(\hat{r}_2) ; m_2 = -l_2, \ldots, l_2 \} \) to an irreducible tensor that transforms as \( C_m^{(l_3)} \) under rotations of the global frame. Applying Eq. (35) repeatedly to Eq. (34), we find after some tedious algebra (Briels et al., 1984)

\[
\nu_l(r_{pp'}) C_{m_3}^{(l_3)}(\hat{r}_{pp'}) = \sum_{\alpha_1, \alpha_2} \frac{(-u_p)^{\alpha_1} (u_p)^{\alpha_2}}{\alpha_1! \alpha_2!} \times \sum_k \sum_j j W_k^j (R_{pp'} | \alpha_1, \alpha_2) \times [[C^{(l_1)}(\hat{u}_P) \otimes C^{(l_2)}(\hat{u}_{P'})]^j(\hat{R}_{pp'})]_{m_3}^{(l_3)}
\]

### Table II

**Tetrahedral Rotation Functions Adapted to the Site Group O [See Eq. (33)]**

<table>
<thead>
<tr>
<th>( l )</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( O_T^{(0)} = T_0^{(0)} )</td>
</tr>
<tr>
<td>3</td>
<td>( O_T^{(3)} = -\frac{1}{2} i (2)^{1/2} { T_2^{(3)} - T_2^{(3)} } )</td>
</tr>
<tr>
<td>4</td>
<td>( O_T^{(4)} = \frac{1}{2} (\frac{1}{2})^{1/2} { T_0^{(4)} + (\frac{3}{14})^{1/2} (T_4^{(4)} + T_4^{(4)}) } )</td>
</tr>
<tr>
<td>6</td>
<td>( O_T^{(6)} = \frac{1}{2} (2)^{1/2} { T_0^{(6)} - (\frac{1}{2})^{1/2} (T_4^{(6)} + T_4^{(6)}) } )</td>
</tr>
<tr>
<td>7</td>
<td>( O_T^{(7)} = -\frac{1}{2} i (\frac{3}{2})^{1/2} { (T_7^{(7)} - T_7^{(7)}) + (\frac{1}{3})^{1/2} (T_6^{(7)} - T_6^{(7)}) } )</td>
</tr>
<tr>
<td>8</td>
<td>( O_T^{(8)} = \frac{1}{8} (33)^{1/2} { T_0^{(8)} + (\frac{3}{10})^{1/2} (T_4^{(8)} + T_4^{(8)}) + (\frac{65}{198})^{1/2} (T_8^{(8)} + T_8^{(8)}) } )</td>
</tr>
<tr>
<td>9</td>
<td>( O_T^{(9)} = -\frac{1}{2} i (\frac{5}{2})^{1/2} { (T_2^{(9)} - T_2^{(9)}) - (\frac{3}{8})^{1/2} (T_6^{(9)} - T_6^{(9)}) } )</td>
</tr>
<tr>
<td>10</td>
<td>( O_T^{(10)} = -\frac{1}{2} i (\frac{3}{2})^{1/2} { (T_4^{(10)} - T_4^{(10)}) - (\frac{15}{34})^{1/2} (T_8^{(10)} - T_8^{(10)}) } )</td>
</tr>
<tr>
<td>10</td>
<td>( O_T^{(10)} = \frac{1}{16} (\frac{7}{4})^{1/2} { (T_2^{(10)} + T_2^{(10)}) + (\frac{3}{8})^{1/2} (T_6^{(10)} + T_6^{(10)}) - (\frac{65}{198})^{1/2} (T_8^{(10)} + T_8^{(10)}) } )</td>
</tr>
</tbody>
</table>

\* Tetrahedral rotational functions as in Table I.

Site group: z-axis is 4-fold axis, [1, 1, 1] direction is 3-fold axis.
with the following recursion relation for the coefficients:

\[ JW'_{k_1,k_2,k_3}(R_{PP'}) | \alpha_1 + 1, \alpha_2 \rangle = (-1)^{k_2+k_3+l_3}(2j + 1)(2k_1 + 1) \times \sum \sum \left( \begin{array}{ccc} 1 & k_1 & k_3 \\ 0 & 0 & j' \end{array} \right) \left( \begin{array}{ccc} k_1 & k_2 & j \\ j' & 1 & k'_1 \end{array} \right) \left( \begin{array}{ccc} j & k_3 & l_3 \\ j' & 1 & l'_3 \end{array} \right) \]

\[ \times A_{k'_3,k_3}(R_{PP'}) j W^{(l)}_{k'_1,k_2,k'_3}(R_{PP'}) | \alpha_1, \alpha_2 \rangle \] (39)

and an analogous relation to raise the index \( \alpha_2 \). The symbols between braces are 6–j coefficients, which arise from recoupling the spherical harmonics (Edmonds, 1957; Brink and Satchler, 1975). The introduction of Eq. (38) into (15) then yields the final expression for the intermolecular potential:

\[ V_{pp'}(u_P, \omega_P; u_{P'}, \omega_{P'}) = \sum_{\alpha_1,\alpha_2} \left( \frac{-u_{P}\alpha_1}{\alpha_1!} \right)^{a_1} \left( \frac{-u_{P'}\alpha_2}{\alpha_2!} \right)^{a_2} \sum \sum j W^{(l)}_{k}(R_{PP'} | \alpha_1, \alpha_2) \times \sum_{m} \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array} \right) G^{(l_1)}(\omega_P) G^{(l_2)}(\omega_{P'}) \times \left[ [C^{(k_1)}(\hat{u}_P) \otimes C^{(k_2)}(\hat{u}_{P'})](j) \otimes C^{(k_3)}(\hat{R}_{PP'}) \right]_{m_3}^{(l_3)} \] (40)

Another, equivalent, form in which the potential can be written is

\[ V_{pp'}(u_P, \omega_P; u_{P'}, \omega_{P'}) = \sum_{\alpha_1,\alpha_2} \left( \frac{-u_{P}\alpha_1}{\alpha_1!} \right)^{a_1} \left( \frac{-u_{P'}\alpha_2}{\alpha_2!} \right)^{a_2} \sum \sum \sum j B^{(l)}_{j_1,k_1,j_2,k_2}(R_{PP'} | \alpha_1, \alpha_2) \times \left[ [G^{(l_1)}(\omega_P) \otimes C^{(k_1)}(\hat{u}_P)]^{(l_1)}_{m_1} \right] \times \left[ [G^{(l_2)}(\omega_{P'}) \otimes C^{(k_2)}(\hat{u}_{P'})](j_{l_2}) \otimes C^{(k_3)}(\hat{R}_{PP'}) \right]_{m_3}^{(l_3)} \] (41)

The expansion coefficients are related to those of Eq. (40) by

\[ B^{(l)}_{j_1,k_1,j_2,k_2}(R_{PP'} | \alpha_1, \alpha_2) = (-1)^{k_1+k_2}(2l_1 + 1)(2l_2 + 1) \times \sum_{a,b} (-1)^a \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ a_k_1 & k_2 & a \end{array} \right) B^{(l)}_{j_1,j_2,b}(R_{PP'} | \alpha_1, \alpha_2) \] (42)

and they satisfy the recursion relations

\[ B^{(l_1,l_2,l_3)}_{j_1,k_1,j_2,k_2}(R_{PP'}) | \alpha_1 + 1, \alpha_2 \rangle = (-1)^{l_1+l_2}(2k_1 + 1)(2l_1 + 1) \times \sum \sum \left( \begin{array}{ccc} 1 & k_1 & k_3 \\ 0 & 0 & j' \end{array} \right) \left( \begin{array}{ccc} k_1 & j_1 & l_2 \\ j' & 1 & k'_1 \end{array} \right) \left( \begin{array}{ccc} l_1 & l_3 & l_3 \\ l'_1 & l'_3 & l'_1 \end{array} \right) A_{l_1,l_3}(R_{PP'}) \]

\[ \times B^{(l_1,l_2,l_3)}_{j_1,k_1,j_2,k_2}(R_{PP'} | \alpha_1, \alpha_2) \] (43)
These results [(41) and (42)] are obtained from Eq. (40) by angular momentum recoupling (Brink and Satchler, 1975); the symbol between braces in Eq. (42) is a $9-j$ coefficient. The recursion relation (43) is derived analogously to Eq. (39) (see Briels et al., 1984).

By introducing the expanded potential [Eq. (40) or Eq. (41)] into the crystal Hamiltonian [Eq. (23)], we can write the latter as

$$H = U^C + \sum_p \{T(u_p) + V_p^R(u_p)\} + \sum_p \{L(\omega_p) + V_p^B(\omega_p)\}$$

$$+ \sum_p V_p^{TR}(u_p, \omega_p) + \frac{1}{2} \sum_{p+p'} \{\Phi^{TR}_{pp'}(u_p; u_{p'})$$

$$+ \Phi^{R}_{pp'}(\omega_p; \omega_{p'}) + \Phi^{TR}_{pp'}(u_p, \omega_p; u_{p'}, \omega_{p'})\}$$

(44)

in terms of one-body operators and two-body operators affecting the molecular translations $T$, rotations $R$, and their coupling $TR$. This partitioning can give some physical insight; in specific cases, one can study the importance of the different contributions. Just as we did for pure rotational motions, we can use the site symmetry to simplify the expressions. For the crystal field terms $V_p^R$ and $V_p^B$ this can be done exactly as before. For the mixed field terms $V_p^{TR}$ it is somewhat more difficult; one finds that

$$V_p^{TR}(u_p, \omega_p) = \sum_\alpha (u_p)^\alpha \sum_{l_1, l_2} \sum_\mu V^{(\mu)}_{l_1, l_2}(P | \alpha)$$

$$\times \sum_i i^I I_{l_1, \mu}(\hat{u}_p)^* G_i^{(l_2, \mu)}(\omega_p)$$

(45)

where $C_i^{l_1, \mu}$, $i = 1, \ldots, n_\mu$, are linear combinations of $C_m^{(l)}$ that transform according to the unitary representation $\Gamma^{(\mu)}$ of the site group $S_p$; $n_\mu$ is the dimension of this representation. Similarly, $G_i^{l, \mu}$, $i = 1, \ldots, n_\mu$, are linear combinations of $G_m^{l, \mu}$ transforming in the same way. These functions are coupled to an invariant of $S_p$. An explicit inspection of the separate contributions in Eq. (45) is only useful for small values of $\alpha_{\text{max}}$, since $l_1$ is at most equal to $\alpha_{\text{max}}$ [see Eqs. (34)–(36)]. Otherwise, the separation becomes too complicated to provide any insight. For the two-body terms this applies a fortiori. However, even without the partitioning given by Eq. (44), the crystal Hamiltonian (23) with the potential expanded by Eq. (40) or (41) forms a good basis for discussing any lattice dynamics treatment.

### III. Harmonic and Quasi-Harmonic Theories of Lattice Dynamics

In this section we briefly discuss the harmonic and quasi-harmonic models that are commonly used to describe the molecular motions, i.e.,
the lattice vibrations, in molecular crystals. We use the term quasi-harmonic for any theory in which the harmonic approximation plays a central role, although strictly speaking the quasi-harmonic model (Barron and Klein, 1974) is a special theory in this category. We include in this section a description of perturbation theory around the harmonic model and of the self-consistent phonon method. In general, as will be clear from the following, quasi-harmonic theories are suitable for describing anharmonic motions with fairly small amplitudes, for example, the translational motions in most crystals. If, however, the vibrational amplitudes are larger, for instance, for the librational motions, especially of small molecules or in the neighborhood of phase transitions, the quasi-harmonic models are of very limited value. They break down completely if the molecules perform hindered rotations as in plastic crystals. In these cases one must resort to completely different treatments, which we discuss in Section IV.

A. Harmonic Approximation

The harmonic approximation consists of expanding the potential up to second order in the atomic or molecular displacements around some local minimum and then diagonalizing the quadratic Hamiltonian. In the case of molecular crystals the rotational part of the kinetic energy, expressed in Euler angles, must be approximated, too. The angular momentum operators that occur in Eq. (26) are given by

\[
\begin{align*}
J_a(\omega) &= \frac{\hbar}{i} \left( -\cos \gamma \frac{\partial}{\partial \alpha} + \sin \gamma \frac{\partial}{\partial \beta} + \cot \beta \frac{\partial}{\partial \gamma} \right) \\
J_b(\omega) &= \frac{\hbar}{i} \left( \sin \gamma \frac{\partial}{\partial \alpha} + \cos \gamma \frac{\partial}{\partial \beta} - \cot \beta \frac{\partial}{\partial \gamma} \right), \\
J_c(\omega) &= \frac{\hbar}{i} \frac{\partial}{\partial \gamma}
\end{align*}
\]

where \( \omega = \{\alpha, \beta, \gamma\} \) are the Euler angles of the molecule fixed coordinate frame relative to the global frame. The harmonic approximation implies that one replaces the angles \( \omega \) in Eq. (46) by their equilibrium values \( \omega_0 = \{\alpha_0, \beta_0, \gamma_0\} \) and then substitutes the result into the quadratic kinetic energy expression (26). Thus, one neglects the terms linear in the operators \( \partial/\partial \beta \) and \( \partial/\partial \gamma \), which occur in the exact expression (26); these terms arise by commuting \( \partial/\partial \beta \) and \( \partial/\partial \gamma \) with the sine and cosine functions of \( \beta \) and \( \gamma \) in the exact Eq. (46). At the same time, the volume element \( \sin \beta \, d\alpha \, d\beta \, d\gamma \) becomes \( \sin \beta_0 \, d\alpha \, d\beta \, d\gamma \) and the angular displacement coordinates \( \Delta \omega = \omega - \omega_0 \) become rectilinear and formally run from \( -\infty \) to \( \infty \). For
linear molecules this approximation has been applied by Goodings and Henkelman (1971), Schnepf and Jacobi (1972), and Walmsley (1975).

The crystal Hamiltonian now reads

$$H = \frac{1}{2} \sum_{\lambda} \sum_{\lambda'} G_{\lambda \lambda'}^{Q\lambda} P_p P_{p'} + \frac{1}{2} \sum_{\lambda} \sum_{\lambda'} F_{\lambda \lambda'}^{Q\lambda} Q_p Q_{p'}$$

(47)

where

$$Q_p^\lambda = u_p^\lambda \quad \text{for} \quad \lambda = 1, 2, 3$$

$$Q_p^\lambda = \Delta \omega_p^{\lambda-3} \quad \text{for} \quad \lambda = 4, 5, 6$$

and

$$P_p^\lambda = \frac{\hbar}{i} \frac{\partial}{\partial Q_p^\lambda}$$

are the momenta conjugate to these coordinates. These operators satisfy the usual commutation rules:

$$[Q_p^\lambda, P_{p'}^{\lambda'}] = i\hbar \delta_{p, p'} \delta_{\lambda, \lambda'}$$

The first term in Eq. (47) represents the kinetic energy operator. The $6 \times 6$ matrices $G_{\lambda}$ follow from the foregoing discussion; they contain the inverse molecular mass $M^{-1}$ and the inverse inertia tensor depending on the equilibrium angles $\omega_0 = \{\alpha_0, \beta_0, \gamma_0\}$ with respect to the global frame. The second term represents the potential; linear terms are absent because this potential is expanded around a local minimum. The $6 \times 6$ matrices $F_{\lambda \lambda'}$ are defined as the second derivatives

$$F_{\lambda \lambda'}^{Q\lambda} = \left[ \frac{\partial^2 V_{pp'}}{\partial Q_p^\lambda \partial Q_{p'}^{\lambda'}} \right]_0$$

(48)

taken at the equilibrium positions and orientations. The Hamiltonian (47) can easily be diagonalized exactly. First we introduce the operators

$$Q_p^\lambda(q) = \frac{1}{N} \sum_n \exp(iq \cdot R_n) Q_p^\lambda$$

$$P_p^\lambda(q) = \frac{1}{N} \sum_n \exp(-iq \cdot R_n) P_p^\lambda$$

(49)

with $P = \{n, i\}$, where $N$ is the number of unit cells in the crystal and $q$ is a vector in the Brillouin zone. The Hamiltonian transforms into

$$H = \sum_q H(q)$$

(50)
with

\[ H(q) = \frac{1}{2} \sum_i \sum_{\lambda, \lambda'} G^{-1}_{\lambda, \lambda'} P_{\lambda}^i(q) P_{\lambda'}^i(q)^* + \frac{1}{2} \sum_{i,i'} \sum_{\lambda, \lambda'} F_{\lambda, \lambda'}^{i,i'}(q) Q_i^\lambda(q) Q_{i'}^{\lambda'}(q)^* \]

and

\[ F_{\lambda, \lambda'}^{i,i'}(q) = \sum_n F_{\lambda, \lambda'}^{i,i'}(q) \exp (i \mathbf{q} \cdot \mathbf{R}_n) = F_{\lambda, \lambda'}^{i,i'}(-q) = F_{\lambda, \lambda'}^{i,i'}(q)^* \]

Here we have used the property that \( G_p \) and \( F_{pp'} \) are translationally invariant. The commutation rules for the wave-vector-dependent operators are

\[ [Q_i^\lambda(q), P_{i'}^{\lambda'}(q')] = i \hbar \delta_{i,i'} \delta_{\lambda,\lambda'} \delta_{q,q'} \]

Every \( H(q) \), depends on \( 6Z \) operators \( Q_i^\lambda(q) \) and \( 6Z \) operators \( P_{i'}^{\lambda'}(q) \) if \( Z \) is the number of sublattices, i.e., the number of molecules in the unit cell. Finally, we introduce linear combinations

\[ \overline{Q}_r(q) = \sum_{i=1}^{Z} \sum_{\lambda=1}^{6} (c(q)^{-1})_{i,\lambda} Q_i^\lambda(q) \]

\[ \overline{P}_r(q) = \sum_{i=1}^{Z} \sum_{\lambda=1}^{6} c_{r,\lambda}^i(q) P_{i}^\lambda(q) \]

such that \( H(q) \) can be written as

\[ H(q) = \frac{1}{2} \sum_r \{ \overline{P}_r^\dagger(q) \overline{P}_r(q) + \omega_r(q)^2 \overline{Q}_r^\dagger(q) \overline{Q}_r(q) \} \]

The coefficients \( c_r(q) = \{c_{r,\lambda}^i(q), i = 1, ..., Z, \lambda = 1, ..., 6\} \) can be obtained from the generalized eigenvalue problem

\[ \mathbf{F}(q)c_r(q) = \mathbf{G}^{-1}(q)\omega_r(q)^2 \]

with the normalization condition

\[ c_r^\dagger \mathbf{G}^{-1} c_r = \delta_{rr'} \]

The choice of the transformation (53) ensures that

\[ [\overline{Q}_r(q), \overline{P}_r(q')] = i \hbar \delta_{r,r'} \delta_{q,q'} \]
Introducing phonon creation and annihilation operators

\[
a_j^\dagger(q) = [2\hbar\omega_r(q)]^{-1/2}\{\omega_r(q)\overline{Q}_r^\dagger(q) - i\overline{P}_r(q)\}
\]

\[
a_j(q) = [2\hbar\omega_r(q)]^{-1/2}\{\omega_r(q)\overline{Q}_r(q) + i\overline{P}_r(q)\}
\]

with the commutation relations

\[
[a_r(q), a_r^\dagger(q')] = \delta_{r,r'} \delta_{q,q'}
\]

which follow from Eqs. (57) and (58), we can write the Hamiltonian in its well-known form:

\[
H = \sum_q \sum_r \hbar\omega_r(q) \left\{ a_r^\dagger(q) a_r(q) + \frac{1}{2} \right\}
\]

representing a sum of independent harmonic oscillators whose excitations are called phonons. The properties of the crystal can be obtained (see Appendix) from the thermodynamic partition function and its derivatives. The partition function for a system of harmonic oscillators reads

\[
Z = \text{Tr}(e^{-\beta H}) = \prod_q \prod_r \left\{ 2 \sinh \left( \frac{1}{2} \beta \hbar\omega_r(q) \right) \right\}^{-1}
\]

with \(\beta = (k_B T)^{-1}\), \(k_B\) being the Boltzmann constant and \(T\) the temperature.

**B. Anharmonic Corrections by Perturbation Theory**

In contrast with atoms and small molecules, the energy levels of extended systems almost invariably appear as broad bands. Degeneracy and near-degeneracy are the rule rather than the exception, and as a consequence, only weak interactions are needed to obtain intermixings of many states. This intermixing will also be caused by external perturbations applied in measurements, such as the electromagnetic fields in spectroscopic experiments. Another consequence of such close-lying states is that many of these states will be thermally populated. The (measured) properties of the system are not determined by the expectation values of operators over pure states, but by thermodynamic (Boltzmann) averages. These two aspects make it less useful to apply straightforward quantum-mechanical perturbation theory to single eigenstates of the Hamiltonian, as one mostly does for atoms and molecules. Instead, it is desirable to use a perturbation theory that describes the response of the whole system. The most powerful theory of this kind is based on the thermal, or imaginary time, Green's function.

In the perturbation theory of lattice dynamics one starts from the
harmonic approximation. The cubic and higher terms in the Taylor expansion of the potential around some local minimum, which are neglected in this approximation, are taken as perturbations of the harmonic model. Accordingly, the Hamiltonian can be written as (Califano, 1981)

\[ H = H_0 + H_1 \]
\[ = \sum_q \sum_r \hbar \omega_r(q) \left\{ a_r^+(q)a_r(q) + \frac{1}{2} \right\} \]
\[ + \sum_{m=3}^{\infty} \sum_{q_1,...,q_m} \sum_{r_1,...,r_m} \Phi_{r_1,...,r_m}(q_1, ..., q_m) A_{r_1}(q_1) \cdots A_{r_m}(q_m) \] (62)

The operators appearing in the interaction Hamiltonian \( H_1 = \sum_{m=3}^{\infty} H_m \) are defined as

\[ A_r(q) = a_r(q) + a_r^+(-q) \] (63)

and the coupling constants \( \Phi_{r_1,...,r_m}(q_1, ..., q_m) \) are the derivatives of the potential with respect to the coordinates \( \tilde{Q}_r(q) \), multiplied by some constant factors. These coupling constants differ from zero only when \( q_1 + \cdots + q_m \) equals a reciprocal lattice vector. In molecular crystals, the difference between the exact rotational kinetic energy and its harmonic oscillator approximation (see Section III,A) should also be considered as a perturbation. As far as we know, this has never actually been done, however.

The thermal Green’s function, or phonon propagator, that is used in lattice dynamics theory is defined as

\[ G_{r,r'}(q; \tau) = \Theta(\tau)(e^{\tau H}A_r(q)e^{-\tau H}A_{r'}(-q)) \]
\[ + \Theta(-\tau)(A_{r'}(-q)e^{\tau H}A_r(q)e^{-\tau H}) \] (64)

where \( \Theta(\tau) \) is the Heaviside step function and \( \langle X \rangle \) denotes the thermodynamic average of an operator \( X \) over the eigenstates of \( H \), i.e.,

\[ \langle X \rangle = Z^{-1} \text{Tr}(X e^{-\beta H}) \] (65)

with

\[ Z = \text{Tr}(e^{-\beta H}) \]

being the partition function and \( \beta = (k_B T)^{-1} \). Using the invariance of the trace for cyclic permutations of the operators, one easily demonstrates that the phonon propagator (64) is a periodic function of the imaginary time \( \tau \) with period \( \beta \); we may therefore confine the values of \( \tau \) to the interval \( 0 \leq \tau \leq \beta \). The time-dependent perturbation expansion of the
phonon propagator for the Hamiltonian $H = H_0 + H_1$ is given by the formula (Fetter and Walecka, 1971)

$$G_{r,r'}(q; \tau) = \langle S(\beta) \rangle_0^{-1} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \ldots \int_0^\beta d\tau_n$$

$$\times \langle T[\hat{H}^{(1)} \ldots \hat{H}^{(n)}(q)\hat{A}^{(0)}_r(-q)] \rangle_0$$  \hspace{1cm} (66)

with

$$S(\beta) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \ldots \int_0^\beta d\tau_n T[\hat{H}^{(1)} \ldots \hat{H}^{(n)}]$$  \hspace{1cm} (67)

where $\hat{X}^\tau$ denotes the operator $X$ in the (imaginary time) interaction representation

$$\hat{X}^\tau = \exp(\tau H_0)X \exp(-\tau H_0)$$  \hspace{1cm} (68)

and $\langle X \rangle_0$ is the thermodynamic average of $X$ over the eigenstates of the unperturbed Hamiltonian $H_0$. The so-called time-ordering operator $T$ places the operators to its right in the order of decreasing times, from left to right. Introduction of the anharmonic interaction operator $H_1 = \sum_{m=3}^\infty H_m$ defined in Eq. (62) into the expansions (66) and (67) yields many terms of the type written in Eq. (69) below. These can be evaluated by means of the (generalized) Wick theorem (Fetter and Walecka, 1971; Abrikosov et al., 1965):

$$\langle T[\hat{A}^{(i)}_r(q_1) \ldots \hat{A}^{(2n)}_{r_{2n}}(q_{2n})] \rangle_0$$

$$= \sum_p \langle T[\hat{A}^{(i)}_r(q_1)\hat{A}^{(i)}_{r'_j}(q_j)] \rangle_0 \ldots \langle T[\hat{A}^{(i)}_{r_k}(q_k)\hat{A}^{(i)}_{r'_l}(q_l)] \rangle_0$$  \hspace{1cm} (69)

The summation runs over all $(2n - 1)!!$ pairings of the operators $A^{(i)}_{r}(q_i)$. The corresponding expectation value for a product of an odd number of operators is zero. The building blocks are the harmonic propagators

$$\langle T[\hat{A}^{(i)}_r(q)\hat{A}^{(i)}_{r'}(q')] \rangle_0 = \delta_{-q,q'} G^{(0)}_{r,r'}(q; \tau - \tau')$$  \hspace{1cm} (70)

given by Eq. (64) for $H = H_0$; they differ from zero only when $q' = -q$ and $r' = r$ and can be easily calculated.

The terms in the expansion (66), after substituting Eq. (62) and applying Wick’s theorem (69), are usually represented by diagrams, according to the following recipe. For any interaction $H_m$ given by Eq. (62) draw a vertex with $m$ lines. When two operators $A^{(i)}_{r}(q_i)$ and $A^{(i)}_{r'}(q_j)$ are paired in Eq. (69), the corresponding two lines are connected. The two operators $\hat{A}^{(i)}_r(q)$ and $\hat{A}^{(i)}_{r'}(q')$ defining the propagator (64) appear as vertices with just
a single line. As an example we show

$$q_1 r_1$$

$$\tau \frac{q, r}{\tau_1} \frac{-q, r'}{\tau_2} 0 = 18 \sum \sum \Phi_{r_1, r_2}(-q, q_1, q_2)$$

$$q_2 r_2$$

$$\times \Phi_{r_1, r_2}(-q_1, -q_2, q) \frac{(-1)^2}{2!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2$$

$$\times \langle T[\tilde{A}^\tau_{q_1}(q)\tilde{A}^\tau_{q_1}(-q)]\rangle_0 \langle T[\tilde{A}^\tau_{r_1}(q_1)\tilde{A}^\tau_{r_1}(-q_1)]\rangle_0$$

$$\times \langle T[\tilde{A}^\tau_{r_2}(q_2)\tilde{A}^\tau_{r_2}(-q_2)]\rangle_0 \langle T[\tilde{A}^\tau_{r_2}(q)\tilde{A}^\tau_{r_2}(-q)]\rangle_0$$

(71)

The factor 18 appears because there are 18 pairings consistent with this diagram, which all yield the same result; one obtains another 18 diagrams with this result by interchanging the vertices $\tau_1$ and $\tau_2$. There are two kinds of diagrams, those with all lines connected to $(q, r)$ and/or $(-q, r')$, which are called connected, and those diagrams consisting of a connected part and one or more parts connected neither to $(q, r)$ nor to $(-q, r')$, which are called disconnected. The summation in Eq. (66) contains the contributions from all diagrams, connected or disconnected, that have just two external lines, the $(q, r)$ and the $(-q, r')$ lines. It is a simple combinatorial problem to demonstrate that this sum is equal to $\langle S(\beta) \rangle_0$ times the sum over all contributions from connected diagrams only. Thus the expansion (66) for the propagator can be simplified to

$$G_{r, r'}(q; \tau) = \sum_{n=0}^\infty \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \ldots \int_0^\beta d\tau_n$$

$$\times \langle T[\tilde{H}^\tau_i \ldots \tilde{H}^\tau_n \tilde{A}^\tau_q(q)\tilde{A}^\tau_q(-q)]\rangle_0, \text{connected}$$

(72)

where the subscript “connected” indicates that only connected diagrams must be taken into account. A final simplification is possible because a permutation of the interaction vertices of equal order does not affect the numerical value of a diagram. Considering only topologically distinct diagrams removes the factor $1/n!$; this is essential for the derivation of the Dyson equation [Eq. (78) below].

In order to relate the thermal or imaginary time propagator to the measured properties of the system, we shall need its Fourier components:

$$\overline{G}_{r, r'}(q; i\omega) = \beta^{-1} \int_0^\beta d\tau \, G_{r, r'}(q; \tau) \exp(i\omega \tau)$$

(73)
where $\omega_l = 2\pi l/\beta^{-1}$ with integer $l$, since the thermal propagator has the period $\beta$. For the harmonic propagator one derives

$$
\overline{G}_{r,r}^{(0)}(q; i\omega_l) = \delta_{r,r} (\beta\hbar)^{-1} \frac{2\omega_l(q)}{\omega_l(q)^2 + \omega_l^2} = \delta_{r,r} \overline{G}_{r,r}^{(0)}(q; i\omega_l)
$$

(74)

The Fourier representation of the anharmonic propagator is obtained from Eqs. (73) and (72), by using Wick’s theorem (69), together with the Fourier representation of the harmonic phonon propagators. The “time” integrations can then explicitly be performed, yielding the condition $\sum_i \omega_i = 0$ and a factor $\beta$ at every interaction vertex.

The Fourier components of the imaginary time propagator are defined on the imaginary frequency axis. We are interested in the Fourier transform of its real time analog, whose singularities, on the real frequency axis, yield the excitation energies of the system. Therefore, we need expressions for the Fourier components of the thermal phonon propagator that can be analytically continued in the complex plane in such a manner that they correctly yield the shifts of the singularities on the real axis caused by the perturbation. The perturbation expansion (72), truncated at any finite order $n$, does not satisfy this requirement. In order to calculate the frequency shifts caused by specific interactions, one must sum the corresponding diagrams to infinity. The result can be simplified if we define a “proper” diagram as a diagram that cannot be broken into two parts, each of which as two external lines, by cutting a single phonon line. Then the infinite sum can be symbolically written as

$$
\overline{G}_{r,r}(q; i\omega_l) = \sum + \sum + \sum + \cdots
$$

(75)

where the first contribution, the simple line, is the harmonic result $\delta_{r,r} \overline{G}_{r,r}^{(0)}(q; i\omega_l)$. The second term represents the sum of contributions from all proper diagrams, the third term arises from all diagrams consisting of two proper parts connected by an intermediate line, and so on. The second term is usually written as

$$
\overline{G}_{r,r}^{(0)}(q; i\omega_l) S_{r,r}^{(0)}(q; i\omega_l) \overline{G}_{r,r}^{(0)}(q; i\omega_l)
$$

(76)

thus defining the “self-energy” matrix $S(q; i\omega_l)$. Then, one can show that because of the conditions $\sum_i q_i = 0$ and $\sum_i \omega_i = 0$ at any vertex, which causes all intermediate lines to have momentum $q$ and frequency $\omega_l$, the third term yields

$$
\overline{G}_{r,r}^{(0)}(q; i\omega_l) S_{r,r}^{(0)}(q; i\omega_l) \overline{G}_{r,r}^{(0)}(q; i\omega_l)
$$

(77)
This relation can be generalized to diagrams with any number of bubbles, and one can sum Eq. (75) to infinity. The result is the Dyson equation:

$$G(q; i\omega_n) = \{1 - G^{(0)}(q; i\omega_n)S(q; i\omega_n)\}^{-1}G^{(0)}(q; i\omega_n)$$  \hspace{1cm} (78)

All matrices are of dimension 6Z and the harmonic propagator matrix $G^{(0)}(q; i\omega_n)$ is diagonal. The problem of calculating the phonon propagators thus reduces to the calculation of the self-energy matrices $S(q; i\omega_n)$ that contain all anharmonic information. It is not difficult to demonstrate that the self-energy matrix is a Hermitian function of $\omega_n^2$ from which it follows that its analytic continuation in the complex frequency plane, in the neighborhood of the real axis, has the form

$$\lim_{\varepsilon \to 0} S(q; \omega \pm i\varepsilon) = -\beta \hbar \{\Delta(q; \omega) \mp i\Gamma(q; \omega)\}$$  \hspace{1cm} (79)

where $\Delta$ and $\Gamma$ are real symmetric and antisymmetric matrices, respectively.

Now we can show the explicit relation with experiment. What is usually measured in spectroscopic or scattering experiments is the spectral density function $I(\omega)$, which is the Fourier transform of some correlation function. For example, the absorption intensity in infrared spectroscopy is given by the Fourier transform of the time-dependent dipole–dipole correlation function $\langle [\mu(t), \mu(0)] \rangle$. If one expands the observables, i.e., the dipole operator in the case of infrared spectroscopy, as a Taylor series in the molecular displacement coordinates, the absorption or scattering intensity corresponding to the phonon branch $r$ at wave vector $q$ can be written as (Kobashi, 1978)

$$I_{q,r}(\omega) \sim \lim_{\varepsilon \to 0^+} i\{G_{r,r}(q; \omega + i\varepsilon) - G_{r,r}(q; \omega - i\varepsilon)\}$$  \hspace{1cm} (80)

Usually it is justifiable to neglect the nondiagonal elements of the self-energy matrix; if not so, these can be taken into account as a small perturbation. Then, we arrive at the result

$$I_{q,r}(\omega) \sim (\beta \hbar)^{-1} \frac{8\omega_r(q)^2\Gamma_{r,r}(q; \omega)}{\{-\omega^2 + \omega_r(q)^2 + 2\omega_r(q) \Delta_{r,r}(q; \omega)\}^2 + 4\omega_r(q)^2\Gamma_{r,r}(q; \omega)^2}$$  \hspace{1cm} (81)

If $\Delta_{r,r}(\omega)$ and $\Gamma_{r,r}(\omega)$ do not vary much with $\omega$, they may be interpreted as the frequency shift, i.e., the resonance shifts from $\omega_r(q)$ to $\omega_r(q) + \Delta_{r,r}(q; \omega)$, and the bandwidth, respectively. Note that the actual calculation of these quantities will not be easy, however, since the diagrams involved contain summations over the entire Brillouin zone [see Eq. (71), for instance]. Some simplification may arise from the lattice
symmetry. A perturbation theory has been developed (Briels, 1983; Hamer and Irving, 1984) in which successive perturbation corrections are associated with an increasing sequence of clusters on the (real) lattice, thus avoiding the multiple sums over the Brillouin zone. Up until now, this method has only been applied to relatively simple Hamiltonians.

**C. The Self-Consistent Phonon Method**

Just as the perturbation theory described in the previous section, the self-consistent phonon (SCP) method applies only in the case of small oscillations around some equilibrium configuration. The SCP method was originally formulated (Werthamer, 1976) for atomic, rare gas, crystals. It can be directly applied to the translational vibrations in molecular crystals and, with some modification, to the librations. The essential idea is to look for an effective harmonic Hamiltonian $H_0$, which approximates the exact crystal Hamiltonian as closely as possible, in the sense that it minimizes the free energy $A_{\text{var}}$. This minimization rests on the thermodynamic variation principle:

$$A_{\text{var}} = A_0 + \langle H - H_0 \rangle_0 \geq A$$  \hspace{1cm} (82)

The angle brackets denote a thermal average over the eigenstates of $H_0$ [cf. Eq. (65)]. The free energies $A$ and $A_0$ correspond to the Hamiltonians $H$ and $H_0$, respectively:

$$A = -k_B T \ln Z, \quad Z = \text{Tr}[\exp(-\beta H)]$$

$$A_0 = -k_B T \ln Z_0, \quad Z_0 = \text{Tr}[\exp(-\beta H)]$$  \hspace{1cm} (83)

The exact crystal Hamiltonian $H$ is given by Eq. (23) and $H_0$ is of the form given by Eq. (47); the force constants $F_{\lambda p, \lambda' q}$ are not given by Eq. (48), however, but they are chosen such as to minimize $A_{\text{var}}$. Neglecting the difference between the exact kinetic energy operators [(25) and (26)] and their harmonic approximations (see Section III,A), one obtains

$$H - H_0 = \frac{1}{2} \sum_{p, p'} V_{\lambda p}(u_p, \omega_p; u_{p'}, \omega_{p'}) - \frac{1}{2} \sum_{p, p'} \sum_{\lambda, \lambda'} F_{\lambda p, \lambda' q} Q_{\lambda p} Q_{\lambda' q}$$  \hspace{1cm} (84)

with effective force constants $F_{\lambda p, \lambda' q}$ that still have to be optimized. The displacement coordinates $Q_{\lambda p}$ are assumed to be rectilinear, as described in Section III,A. The effective harmonic free energy $A_0$ is given by Eq. (83) with $Z_0$ as in Eq. (61). The expectation value of the harmonic potential, i.e., the second term in Eq. (84), can be written as

$$-\frac{1}{2} \sum_{p, p'} \sum_{\lambda, \lambda'} F_{\lambda p, \lambda' q} D_{\lambda p, \lambda' q}$$  \hspace{1cm} (85)
in terms of the effective force constants and the displacement–displacement correlation functions:

$$D_{p',q'}^{\lambda,\lambda'} = \langle Q_{p'}^\lambda Q_{q'}^\lambda \rangle_0$$ \hspace{1cm} (86)

The expectation value of the exact potential, the first term in Eq. (84), is somewhat more difficult to calculate. Using the properties of the harmonic oscillator eventually leads to (Choquard, 1967; Werthamer, 1976)

$$\langle V_{pp}(u_p, \omega_p; u_{p'}, \omega_{p'}) \rangle_0$$

$$= \left\{ \exp \left\{ \sum_{\lambda} \left( Q_{p}^\lambda \nabla_{p}^{\lambda} + Q_{p'}^{\lambda'} \nabla_{p'}^{\lambda'} \right) \right\} \right\}_0 V_{pp}(0, \omega_p; 0, \omega_{p'})$$

$$= \exp \left\{ \frac{1}{2} \sum_{\lambda,\lambda'} \left( D_{p,p}^{\lambda,\lambda'} \nabla_{p}^{\lambda} \nabla_{p'}^{\lambda'} + 2D_{p',p}^{\lambda,\lambda'} \nabla_{p}^{\lambda} \nabla_{p'}^{\lambda'} + D_{p,p}^{\lambda,\lambda'} \nabla_{p'}^{\lambda} \nabla_{p'}^{\lambda'} \right) \right\} V_{pp}(0, \omega_p; 0, \omega_{p'})$$ \hspace{1cm} (87)

with $\nabla_{p}^{\lambda} = \partial/\partial Q_{p}^\lambda$ acting only on $V_{pp'}$. Substituting the expression for $A_0$ and the results (85) and (87) for $(H - H_0)_0$ into $A_{\text{var}}$ [Eq. (82)] and applying the minimization conditions

$$\frac{\partial A_{\text{var}}}{\partial F_{p,p'}^{\lambda,\lambda'}} = 0$$

one finds the expression for the optimized force constants:

$$F_{p,p'}^{\lambda,\lambda'} = \left\langle \frac{\partial^2 V_{pp'}}{\partial Q_{p}^\lambda \partial Q_{p'}^{\lambda'}} \right\rangle_0 \hspace{1cm} F_{p,p'}^{\lambda,\lambda'} = \sum_{p'} \left\langle \frac{\partial^2 V_{pp'}}{\partial Q_{p'}^\lambda \partial Q_{p'}^{\lambda'}} \right\rangle_0$$ \hspace{1cm} (88)

So, instead of using the second derivatives of the potential in the equilibrium configuration as force constants, the SCP method employs the thermal averages of these derivatives. Equation (88) and the corresponding dynamical equations, given by the generalized eigenvalue problem (55), have to be solved self-consistently. One can do this via the usual iterative procedure, starting with trial values for the effective force constants (88), which can be taken from the harmonic model. The averaging in Eqs. (82) and (88) can be most easily performed (Werthamer, 1976) by first Fourier transforming the function to be averaged, next applying Eq. (87), and then transforming back to the original coordinates, which yields

$$\langle V_{pp}(u_p, \omega_p; u_{p'}, \omega_{p'}) \rangle_0$$

$$= \int d^6Q_p \int d^6Q_{p'} \rho_{pp'}(Q_1^p, ..., Q_6^p) V_{pp'}(Q_1^p, ..., Q_6^p)$$ \hspace{1cm} (89)

and a similar expression for the second derivatives (88). The width of the Gaussian probability distribution $\rho_{pp'}$ is determined by the Hessian of the
quadratic exponent. This Hessian is the inverse of the 12-dimensional matrix
\[
\begin{pmatrix}
D_{pp} & D_{pp'} \\
D_{p'p} & D_{p'p'}
\end{pmatrix}
\]
with elements given by Eq. (86). These elements, the displacement–displacement correlation functions, can easily be calculated by using Eqs. (49), (53), and (58). The result for the minimized free energy $A_{\text{var}}$ is
\[
A = \sum_{q,r} k_B T \ln \left\{ 2 \sinh \left( \frac{1}{2} \beta \hbar \omega_r(q) \right) \right\} \\
+ \frac{1}{2} \sum_{p \neq p'} \left( V_{pp'}(u_p, \omega_p; u_{p'}, \omega_{p'}) \right)_0 \\
- \frac{1}{4} \sum_{q,r} \hbar \omega_r(q) \coth \left( \frac{1}{2} \beta \hbar \omega_r(q) \right)
\]
The calculation of this quantity, and of the displacement–displacement correlation functions, involves a single summation over all wave vectors $q$ in the Brillouin zone.

From the free energy all thermodynamic properties of the system can be calculated. For example, the entropy is $S = -\partial A/\partial T$ and the energy is $E = A + TS$. For more details we refer to the review by Werthamer (1976). One important point should be mentioned. Expanding the potential $V_{pp'}(Q_p, \ldots, Q_{p'})$ as a Taylor series in the displacement coordinates $Q_p$, we observe, using the analog of Eq. (87) for the force constants (88), that the odd power terms do not contribute to the effective force constants; the SCP method neglects these terms. Their relative importance can, of course, be estimated by perturbation techniques as described in Section III,B.

Here we have formulated the SCP method for molecular crystals. We could easily include the librations because the orientational dependence of the potential $V_{pp'}$ has been explicitly given, in Sections II,B and II,C, in terms of the Euler angles $\omega_P$ and thus in terms of the angular displacements $\Delta \omega_P = \omega_P - \omega_{0p}$. In two earlier applications of the SCP method to molecular crystals, one has used atom–atom potentials, however, whose orientational dependence was implicit and the description of librations was still a problem. Raich et al. (1974) in their calculations on $\alpha$-nitrogen (see Section V) have avoided this problem by including the librations implicitly. They did this by considering a molecular crystal as a collection of atoms interacting via strong chemical bonds with their partners within the same molecule and via weak van der Waals potentials with all other
atoms belonging to neighboring molecules. Then they applied the original SCP method to the atomic motions. This approach is, of course, confined to the use of intermolecular potentials of the atom–atom type (see Section II,A). Wasiutynski (1976) has considered the molecular librations explicitly. He has expressed the atom–atom potential as a function of the translational and librational molecular displacements by writing a linear relation between these displacements and the atomic displacements. This relation holds only for small angular displacements.

IV. Dynamical Models for Large-Amplitude Motions

The methods outlined in the preceding section obviously cannot be applied when the molecules in a crystal perform large-amplitude librations or even (hindered) rotations. In this case, one has the tendency to emphasize the motions of the individual molecules rather than the collective motions. Indeed, the most generally applicable method to describe large-amplitude motions is the mean field theory (Kirkwood, 1940; James and Keenan, 1959), which treats the molecules as moving in a field that represents the mean interaction with the neighboring molecules. In a quantum-mechanical description, it is then possible to use the low-lying single-particle states to construct a basis for the whole solid in which the complete crystal Hamiltonian can be diagonalized. Adaptation of this basis to the translational symmetry of the crystal makes this diagonalization practically possible. At the same time, it leads to a labeling of the crystal states by the wave vectors in the Brillouin zone, thus reintroducing the collective aspect of the lattice vibrations. In order to make the frequencies of the acoustical lattice modes go to zero when the wave vector approaches the center of the Brillouin zone, the crystal Hamiltonian has to be diagonalized at the time-dependent Hartree (TDH) or random phase approximation (RPA) level (Fredkin and Werthamer, 1965).

A scheme as described here is indispensable for a quantum dynamical treatment of strongly delocalized systems, such as solid hydrogen (van Kranendonk, 1983) or the plastic phases of other molecular crystals. We have shown, however (Jansen et al., 1984), that it is also very suitable to treat the anharmonic librations in ordered phases. Moreover, the RPA method yields the exact result in the limit of a harmonic crystal Hamiltonian, which makes it appropriate to describe the weakly anharmonic translational vibrations, too. We have extended the theory (Briels et al., 1984) in order to include these translational motions, as well as the coupled rotational–translational lattice vibrations. In this section, we outline the general theory and present the relevant formulas for the coupled
problem. First, we briefly sketch some classical methods, however, that have been used in the literature to study large-amplitude motions in molecular systems.

A. Classical Molecular Dynamics and Monte Carlo Methods

In classical mechanics there exist, apart from the mean field theory, two popular methods to describe the dynamics of molecular systems, viz., the molecular dynamics (MD) method and the Monte Carlo (MC) method (Hansen and McDonald, 1976). In both methods the system is represented by a finite number, usually about 100 to 300, of molecules. In order to reduce boundary effects, this finite system is periodically repeated in all directions.

In the MD method (Rahman, 1966; Verlet, 1967) one specifies the initial conditions, i.e., the positions and orientations of all molecules and their (angular) velocities, and one integrates the classical equations of motion numerically by means of some finite difference scheme. The choice of the time step is mainly determined by the error allowed and the time scale in which one is interested. Usually, one takes time steps of order $10^{-14}$ sec and follows the trajectory for some $10^3$ to $10^5$ steps. Along the whole or part of the trajectory all kinds of quantities can be averaged. The method is especially suitable for calculating time-dependent correlation functions that yield information on the dynamics of the system. An example is the so-called intermediate scattering function:

$$F(q, t) = \frac{1}{4N} \sum_{p,p'} N M_p(q, t) M_{p'}(q, 0)$$

where $N$ is the number of molecules in the system, and the operator

$$M_p(q, t) = \exp[iq \cdot r_p(t)] \sum_{\alpha \in p} \exp[iq \cdot d_\alpha(t)]$$

is related to the scattering of neutrons with scattering vector $q$ by a molecule at the instantaneous position $r_p(t)$. The atoms $\alpha$ belonging to this molecule have (instantaneous) position vectors $d_\alpha(t)$ relative to its center of mass; these vectors depend on the orientation of the molecule. The Fourier transform of this particular correlation function

$$S(q, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \ F(q, t)e^{i\omega t}$$

is called the dynamic structure factor, and it describes the response of the system to a transfer of momentum $q$ and energy $\hbar \omega$. By the nature of the
MD method, the system studied has constant energy. Its temperature can be defined via the mean kinetic energy. Other thermodynamic properties can be calculated from the numerical derivatives of the energy or by using their relations to certain fluctuations of the system. The specific heat, for instance, can be obtained from the derivative of the energy with respect to the temperature or from the temperature fluctuations. It will be clear that for these derived quantities the uncertainties are larger than for the trajectory itself.

The Monte Carlo method is most easily explained by means of a discrete model. One assumes that the system can only be in a configuration corresponding to one of a finite but large number of grid points on a very fine mesh. The idea is to sample this configuration space and to calculate various mean values. Even with the largest computers, however, it is not possible to sample a substantial part of configuration space, and the possibility exists that one samples many highly improbable configurations. The way to avoid this problem is to generate a Markov chain of successive configurations with step probabilities \( p_{ij} \) to get from state \( i \) to state \( j \). The probabilities \( p_{ij} \) are chosen such that the stationary state of the chain has occupation probabilities in accordance with the canonical Boltzmann distribution law. It is also possible to simulate other thermodynamic ensembles, in which case the Boltzmann distribution has to be replaced by the appropriate probability distribution. Of course, the requirement just stated is not sufficient to completely specify the transition matrix \( p_{ij} \). Among the possible choices for \( p_{ij} \) the most popular one, proposed by Metropolis et al. (1953), leads to the following scheme. Given a configuration, randomly generate a new one that differs not too much from the previous one and accept it as a sample point if its energy is lower than that of the previous state. If its energy is higher, accept it with probability \( \exp(-\beta \Delta V_{ij}) \), where \( \Delta V_{ij} = V(j) - V(i) \). This method is very suitable for calculating static correlation functions. The calculation of thermodynamic properties is similar to that in the MD method; one can use the derivatives of the mean energy or the average fluctuations. Another way is to connect the system reversibly to a model system whose properties are known.

Both the MD and MC methods have some limitations that are mainly due to the finite size of the system and to the periodic boundary conditions. Generally, when the number of molecules is 100 or more, the fluctuations are sufficiently weak for the average properties to approach the bulk properties. Because of the periodic boundary conditions, however, it is impossible to study fluctuations with a wavelength that is larger than the length of the box. This is most unsatisfactory for two-dimensional
systems or for systems in the neighborhood of (second-order) phase transitions, because in these cases the large-scale fluctuations constitute an interesting part of the theory. The same limitation holds in MD calculations for the time-dependent correlations. These may contain spurious contributions when local perturbations are not sufficiently damped, so that they reappear because of the periodic boundary conditions. Another problem occurring especially in small systems is that they can be locked in a small region of phase space. Consequently, it is often difficult to locate phase transitions, because the system remains in a metastable state for a very long time. A third problem is that short-range and long-range interactions have to be included via different methods.

B. The Mean Field Model

Just as the self-consistent phonon method, the mean field approximation (Kirkwood, 1940; James and Keenan, 1959) is based on the thermodynamic variation principle for the Helmholtz free energy:

\[ A_{\text{var}} = A_0 + \langle H - H_0 \rangle_0 \geq A \]  

(95)

The meaning of the symbols is explained in Section III.C [Eq. (83)]; \( H \) is the exact crystal Hamiltonian [Eq. (23)]. This time, however, we choose as the approximate Hamiltonian \( H_0 \) a sum of single-particle Hamiltonians:

\[ H_0 = \sum P H_P^{\text{MF}}(\mathbf{u}_P, \omega_P) \]  

(96)

In order to obtain the conditions on \( H_P^{\text{MF}}(\mathbf{u}_P, \omega_P) \) that guarantee that \( H_0 \) is the best possible Hamiltonian with the form of Eq. (96) in the sense that \( A_{\text{var}} \) adopts its minimum value, we vary every single-particle Hamiltonian by an arbitrary amount \( h_P(\mathbf{u}_P, \omega_P) \):

\[ H_0 \rightarrow H_0 + h = \sum P \{ H_P^{\text{MF}}(\mathbf{u}_P, \omega_P) + h_P(\mathbf{u}_P, \omega_P) \} \]  

(97)

and calculate the corresponding variation of the free energy:

\[ \Delta A_{\text{var}} = A_{\text{var}}(H_0 + h) - A_{\text{var}}(H_0) \]

\[ = A(H_0 + h) - A(H_0) \]

\[ + \text{Tr}[(H - H_0)\rho(H_0 + h) - \rho(H_0)] \]

\[ - \text{Tr}[h_\rho(H_0 + h)] \]  

(98)
This result can easily be obtained by writing the thermodynamic expectation value of an arbitrary operator \( X \) as

\[
\langle X \rangle = \text{Tr}\{X \rho(H)\} \quad (99)
\]

in terms of the density operator

\[
\rho(H) = Z^{-1} e^{-\beta H} \quad (100)
\]

with

\[
Z = \text{Tr} e^{-\beta H}
\]

To first order in the perturbation \( h \), \( \Delta A_{\text{var}} \) must be zero, while to second order it must be positive for arbitrary \( h \). In order to calculate \( \Delta A_{\text{var}} \) and the density operator on which it depends, up to the second order, we can use the perturbation expansion

\[
\exp\{-\beta(H_{p}^{\text{MF}} + h_{p})\} = \exp(-\beta H_{p}^{\text{MF}})
\]

\[
\times \sum_{n=0}^{\infty} \frac{(-1)^{n}}{n!} \int_{0}^{\beta} d\tau_{1} \cdots \int_{0}^{\beta} d\tau_{n} \text{T}[\hat{h}_{p}^{\tau_{1}} \cdots \hat{h}_{p}^{\tau_{n}}] \quad (101)
\]

with

\[
\hat{h}_{p}^{\tau} = \exp(\tau H_{p}^{\text{MF}})h_{p} \exp(-\tau H_{p}^{\text{MF}})
\]

This expansion lies also at the basis of the perturbation expansion given by Eq. (66). The time-ordering operator \( T \) orders the (imaginary) times \( \tau_{1}, \ldots, \tau_{n} \). For brevity we have momentarily stopped indicating the dependence of all quantities on the coordinates \( u_{p} \) and \( \omega_{p} \). Using the notation \( \rho_{p}^{\text{MF}} = \rho(H_{p}^{\text{MF}}) \) and \( \langle X \rangle_{\text{MF}} = \text{Tr}(X \rho_{p}^{\text{MF}}) \), we readily derive

\[
\rho(H_{p}^{\text{MF}} + h_{p}) = \rho_{p}^{\text{MF}} + \Delta \rho_{p}^{(1)} + \Delta \rho_{p}^{(2)} + \cdots \quad (103)
\]

with

\[
\Delta \rho_{p}^{(1)} = \rho_{p}^{\text{MF}}\{\beta\langle h_{p}\rangle_{\text{MF}} - \int_{0}^{\beta} d\tau_{1} \hat{h}_{p}^{\tau_{1}}\} \quad (104)
\]

The explicit expression for \( \Delta \rho_{p}^{(2)} \) will not be needed. Using the perturbation expansion (101) in Eq. (98) we arrive, after some algebra (van der Avoird \textit{et al.}, 1984), at

\[
\Delta A_{\text{var}} = \Delta A_{\text{var}}^{(1)} + \Delta A_{\text{var}}^{(2)} + \cdots \quad (105)
\]

with

\[
\Delta A_{\text{var}}^{(1)} = \sum_{p} \text{Tr}\{(T_{p} + L_{p} + V_{p}^{\text{MF}} - H_{p}^{\text{MF}}) \Delta \rho_{p}^{(1)}\} \quad (106)
\]
and

\[
\Delta A_{\text{var}}^{(2)} = \sum_p \text{Tr}\{(T_p + L_p + V_p^{\text{MF}} - H_p^{\text{MF}}) \Delta \rho_p^{(2)}\} + \frac{1}{2} \sum_{p \neq p'} \sum_{\rho} \text{Tr}\{\Delta \rho_p^{(1)} V_{pp'} \Delta \rho_{p'}^{(1)}\} + \beta^{-1} \sum_p \int_0^\beta d\tau_1 \tau_1 \langle h_p^{\tau_1} h_p \rangle_{\text{MF}} - \frac{1}{2} \beta \sum_p \langle h_p \rangle_{\text{MF}}^2
\]

(107)

The kinetic energy operators \( T_p = T(u_p) \) and \( L_p = L(\omega_p) \) are defined in Eqs. (25) and (26); the mean field potential is given by

\[
V_p^{\text{MF}} = \sum_{p \neq p'} \text{Tr}(V_{pp'}) \rho_p^{\text{MF}} = \sum_{p \neq p'} \langle V_{pp'} \rangle_{p'}
\]

(108)

From the extremum condition that \( \Delta A_{\text{var}}^{(1)} \) should be zero for arbitrary variations \( h_p \) and thus for arbitrary changes \( \Delta \rho_p^{(1)} \) in the density operator, we derive the expression for the optimized single-particle Hamiltonian

\[
H_p^{\text{MF}}(u_p, \omega_p) = T(u_p) + L(\omega_p) + \sum_{p' \neq p} \langle V_{pp'}(u_p, \omega_p; u_{p'}, \omega_{p'}) \rangle_{p'}
\]

(109)

This defines a set of equations for the mean field Hamiltonians \( H_p^{\text{MF}} \). These equations have to be solved self-consistently since the thermodynamic values within the angle brackets in (109) involve the mean field Hamiltonians \( H_p^{\text{MF}} \). In principle, all \( H_p^{\text{MF}} \) can be different; in practice, we impose symmetry relations. Therefore, we choose a unit cell, compatible with the symmetry of the lattice introduced in Section II.D, and we put \( H_p^{\text{MF}} \) equal to \( H_p^{\text{MF}} \) whenever \( P' \) and \( P \) belong to the same sublattice. Moreover, we apply unit cell symmetry that relates the mean field Hamiltonians on different sublattices. By using the symmetry-adapted functions introduced in Section II,B, the latter symmetry can be imposed as follows. We select a set of molecules constituting the asymmetric part of the unit cell. Then we assign to all other molecules \( P' \) Euler angles \( \tilde{\omega}_p \) through which the mean field Hamiltonian of some molecule \( P \) in the asymmetric part has to be rotated in order to obtain \( H_p^{\text{MF}} \). As a result, we find
If we substitute these transformation relations into Eq. (109), we observe that the latter equation involves only the mean field Hamiltonians of the molecules in the asymmetric part of the unit cell.

In order to perform the calculations in practice, we introduce a basis in which we diagonalize the mean field Hamiltonians. The density operators $\rho^\text{MF}_f$ become diagonal, too, and the calculation of the thermodynamic averages is obvious. The most convenient basis consists of the products

$$D^{(l)}_{m_1 m_2}(\omega) \Psi^{(n)}_{k, m_3}(u)$$

of Wigner functions $D^{(l)}_{m_1 m_2}(\omega)$ and three-dimensional harmonic oscillator functions

$$\Psi^{(n)}_{k, m_3}(u) = A \left( \frac{2}{u} \right)^{1/2} \Lambda^{k+1/2}_{1/2(n-k)}(A^2 u^2) S^{(k)}_m(u)$$

with

$$\Lambda^\alpha_l(t) = \left[ \Gamma(\alpha + 1) \binom{l + \alpha}{l} \right]^{-1/2} e^{-\frac{t}{2} \frac{1}{\alpha + 1}} L^\alpha_l(t)$$

The functions $S^{(k)}_m$ are tesseral (i.e., real combinations of spherical) harmonics, $L^\alpha_l$ are Laguerre functions, and $\Gamma(\alpha)$ are gamma functions (Powell and Craseman, 1961); $k$ is restricted to $0 \leq k \leq n$ and it must have the same parity as $n$. The constant $A$, in the case of a finite basis, can be used to optimize this basis. The matrix elements required in this basis can be easily computed from Eq. (14) and the relation

$$\int_0^\infty u^2 \left( \frac{u^2}{\Lambda^{k_1+1/2}_{1/2(n_1-k_1)}(u^2)} \right) \left( \frac{u^2}{\Lambda^{k_2+1/2}_{1/2(n_2-k_2)}(u^2)} \right) du = \frac{1}{2} (-1)^{a_1+a_2} \left[ \frac{\Gamma(a_1 + 1)}{\Gamma(a_1 + b_1 + 1)} \frac{\Gamma(a_2 + 1)}{\Gamma(a_2 + b_2 + 1)} \right]^{1/2}$$

$$\times \sum_{l=l_{\text{min}}}^{l_{\text{max}}} \frac{(c - b_1)(c - b_2)(c + 1)}{a_1 - l} \frac{(c + 1)}{a_2 - l} \Gamma(c + 1)$$
with

\[ a_i = \frac{1}{2}(n_i - k_i), \quad b_i = k_i + \frac{1}{2} \]

\[ c = \frac{1}{2}(k_1 + k_2 + \alpha + 1), \quad d = \max(a_1 + b_1, a_2 + b_2) - c \]

\[ l_{\text{min}} = \begin{cases} d & \text{if } c \text{ is half-integer and } d > 0, \\ 0 & \text{otherwise}, \end{cases} \quad l_{\text{max}} = \min(a_1, a_2) \]

The factor \( u^2 \) in the integrand originates from the volume element in \( u \) space. Matrix elements of the translational kinetic energy operator \( T(u_P) \) follow from the identity

\[ -\Delta(u_P) = A^2[-\Delta(Au_P) + A^2u_P^2] - A^4u_P^2 \]  

(115)

The operator between the brackets is the harmonic oscillator Hamiltonian, which has the basis functions (112) as its eigenfunctions; the remaining term is taken into account via Eq. (114). The rotational kinetic energy operator \( L(w_P) \) [Eq. (26)] can be written in terms of the shift operators \( J_\pm = J_a \mp iJ_b \), which act on the basis as

\[ J_cD_{mn}^{(l)}(\omega) = mD_{mn}^{(l)}(\omega) \]

\[ J_\pm D_{mn}^{(l)}(\omega) = \{(l \mp m)(l \pm m + 1)\}^{1/2}D_{m \pm 1, n}^{(l)}(\omega) \]  

(116)

At this point let us make a remark concerning the size of the basis. In order to obtain convergence, one must sometimes include (Briels et al., 1984) basis functions with high values of \( l \) and \( n \). High values of \( l \) are needed in particular when the orientations of the molecules are fairly well localized. This leads to a rapidly increasing size of the basis. Two measures can be taken to simplify the problem. First, one can adapt the basis of molecule \( P \) to the site symmetry at \( P \), which block-diagonalizes the secular problem. If this does not sufficiently reduce the problem, the mean field model Hamiltonian (96) can be further separated by writing

\[ H_{P}^{\text{MF}}(u_P, \omega_P) = H^T_{P}(u_P) + H^L_{P}(\omega_P) \]  

(117)

As a result, we now have two “particles” at every lattice point \( P \), one translating and one librating. Expressions for the separate mean field Hamiltonian can be derived as before. The translating particle experiences the mean field of all its neighbors, translating and librating, and of its accompanying librating particle; for the librating particle this relation holds in reverse. The advantage of this separation is that the basis to be used in any cycle of the iterative mean field calculation is either a pure translational basis or a pure rotational basis, and the secular problems are
much smaller than before. The price that we pay is the neglect of correlation between the single-particle translations and librations. This correlation is recovered in the RPA calculations described in the following section.

Once we have obtained the mean field Hamiltonians, we can calculate the thermodynamic properties of the system. The free energy can be found from Eq. (95) and other quantities follow from it:

\[ A = -k_B T \sum_p \ln Z_p^{MF} - \frac{1}{2} \sum_p \langle V_p^{MF} \rangle_p \]

\[ S = -\frac{\partial A}{\partial T} = k_B \sum_p \ln Z_p^{MF} + T^{-1} \sum_p \langle H_p^{MF} \rangle_p \]  

(118)

\[ E = A + TS = \sum_p \langle H_p^{MF} \rangle_p - \frac{1}{2} \sum_p \langle V_p^{MF} \rangle_p \]

The mean field partition function is \( Z_p^{MF} = Z(H_p^{MF}) \). In order to obtain the entropy in its final form, we have used the relation

\[ \sum_p \langle \frac{\partial H_p}{\partial T} \rangle_p = \frac{1}{2} \sum_p \frac{\partial}{\partial T} \langle V_p^{MF} \rangle_p \]  

(119)

which follows from Eq. (109).

Before we discuss the stability condition \( \Delta A_{var}^{(2)} \geq 0 \) on the mean field solution, we first describe the RPA formalism.

C. The Random Phase or Time-Dependent Hartree Approximation

The mean field model outlined in the preceding section provides us with a set of single-particle states

\[ H_p^{MF} |\psi_p^{(\alpha)}\rangle = e_p^{(\alpha)} |\psi_p^{(\alpha)}\rangle \]  

(120)

from which we construct the crystal states

\[ |\psi^{MF}_{[\alpha]}\rangle = \prod_p |\psi_p^{(\alpha_p)}\rangle \]  

(121)

For all \( \alpha_P \) equal to zero, Eq. (121) represents the ground state of the crystal. In order to keep the equations as simple as possible, we have again stopped explicitly indicating the coordinates on which all functions and operators depend. When the mean field Hamiltonian has the form of Eq. (117), the index \( P \), from now on, must be interpreted as \( P = \{n, i, K\} \),
where $K = T, L$ distinguishes between the translating and librating "particles."

The shortcoming of the mean field method is that it admits no correlation between the motions of the individual particles. This correlation can be introduced by means of the random phase approximation (RPA) or time-dependent Hartree (TDH) method. In order to formulate this method, we introduce excitation operators $(E_p^\alpha)^\dagger$, which replace $\psi_p^{(0)}$ by $\psi_p^{(\alpha)}$ when applied to the mean field ground state of the crystal; when applied to any other state, they yield zero. Then, we write the Hamiltonian as a quadratic form in the excitation operators $(E_p^\alpha)^\dagger$ and their Hermitian conjugates $E_p^\alpha$.

$$H = \sum_{pP'} \sum_{\alpha, \alpha'} \{ A_{p, p'}^{\alpha, \alpha'} (E_p^\alpha)^\dagger E_{p'}^\alpha + B_{p, p'}^{\alpha, \alpha'} (E_p^\alpha)^\dagger (E_{p'}^\alpha)^\dagger + (B_{p, p'}^{\alpha, \alpha'})^\dagger E_p^\alpha E_{p'}^\alpha \} \quad (122)$$

Linear terms are absent because of the Brillouin theorem. The coefficients $A_{p, p'}^{\alpha, \alpha'}$ and $B_{p, p'}^{\alpha, \alpha'}$ can be calculated by equating the nonzero matrix elements of the RPA Hamiltonian [Eq. (122)], in the basis of Eq. (121), to the corresponding matrix elements of the exact Hamiltonian [Eq. (23)] in the same basis. From the translational symmetry of the mean field states it follows that the $A$ and $B$ coefficients do not depend on the complete labels $P = \{ n, i, K \}$ and $P' = \{ n', i', K' \}$, but only on the sublattice labels $\{ i, K \}$ and $\{ i', K' \}$. The second ingredient of the RPA formalism is that we assume boson commutation relations for the excitation and de-excitation operators (Raich and Etters, 1968; Dunmore, 1972).

The RPA Hamiltonian [Eq. (122)] can be easily diagonalized. A partial diagonalization is already obtained by writing it in terms of operators

$$E_{i, K}^\alpha(q) = \frac{1}{\sqrt{N}} \sum_n \exp(iq \cdot R_n) E_p^\alpha \quad (123)$$

with $P = \{ n, i, K \}$, adapted to the translational symmetry of the crystal. Just as in Section III,A, the commutation relations are preserved under this transformation. The next step is to define operators $a_{i, K}^{\dagger}(q)$ that represent the exact excitation operators of the crystal, which satisfy the equations of motion

$$[H, a_{i, K}^{\dagger}(q)] = \omega_{i, K}(q) a_{i, K}^{\dagger}(q)$$
$$[H, a_{i, K}(q)] = -\omega_{i, K}(q) a_{i, K}(q) \quad (124)$$

Expressing these operators as

$$a_{i, K}^{\dagger}(q) = \sum_{\alpha, \beta, \gamma} \{ x_{\alpha, \beta, \gamma}^{i, K}(q) E_{i, K}^\alpha(q)^\dagger + y_{\alpha, \beta, \gamma}^{i, K}(q) E_{i, K}^\gamma(-q) \} \quad (125)$$
leads to the RPA eigenvalue problem for the coefficients $x_{a,i,K}$ and $y_{a,i,K}$:

$$
\begin{pmatrix}
  \chi - \Phi(q) & -\Phi(q) \\
  \Phi(q) & -\chi + \Phi(q)
\end{pmatrix}
\begin{pmatrix}
  x(q) \\
  y(q)
\end{pmatrix}
= 
\begin{pmatrix}
  x(q) \\
  y(q)
\end{pmatrix}
\omega(q)
$$

The diagonal matrix $\chi$ contains the mean field excitation energies

$$
\chi_{a,i,K;\alpha',i',K'} = \delta_{\alpha,\alpha'} \delta_{i,i'} \delta_{K,K'} [\epsilon^{(a)}_{i,i,K} - \epsilon^{(0)}_{i,i,K}]
$$

and the elements of the matrix $\Phi(q)$ are defined as

$$
\Phi_{\alpha,i,K;\alpha',i',K'}(q) = \sum_n \exp(iq \cdot R_n) \langle \psi^{(a)}_P | \psi^{(0)}_{P'} | V_{(0,i,n,i')} | P_\alpha P_\gamma | \psi^{(0)}_P | \psi^{(0)}_{P'} \rangle
$$

$$
+ \delta_{i,i'} \delta_{K,K'} \sum_n \sum_{\alpha''} \langle \psi^{(a)}_P | \psi^{(0)}_{P'} | V_{(0,i,n,i')} | Q/Q', \psi^{(0)}_P | \psi^{(0)}_{P'} \rangle
$$

with $P = \{0, i, K\}$, $P' = \{n, i', K'\}$, $Q = \{n', i'', K, K_c\}$, $P_c = \{0, i, K_c\}$ and $K_c$ is the complement of $K$ and $|\psi^{(a)}_P | \psi^{(0)}_{P'}\rangle = |\psi^{(0)}_P | \psi^{(0)}_{P'}\rangle$. When the mean field problem is separated for the translations and librations, as reflected by Eq. (117), the matrix $\Phi(q)$ will have a block structure. The blocks $\Phi^{TT}(q)$ and $\Phi^{LL}(q)$ correlate the translational and librational motions of the molecules, respectively, and the off-diagonal blocks $\Phi^{TL}(q)$ and $\Phi^{LT}(q)$ account for the translation-rotation coupling. The second term of the elements of the latter matrices, given by Eq. (128), includes the coupling between the single-particle librations and translations. The eigenvalues $\omega(q)$ in Eq. (126) provide the excitation energies of the crystal. The eigenvectors can be conceived as the polarization vectors that, in general, correspond to mixed translational–rotational modes. In using a quadratic Hamiltonian, the RPA model is similar to the harmonic model. The motions in the RPA model can be strongly anharmonic, however; they may even be hindered rotations.

The RPA formalism that we have just presented only applies at zero temperature. It is possible, however, to derive similar eigenvalue equations for the excitation frequencies $\omega(q)$ by means of the time-dependent Hartree method (Fredkin and Werthamer, 1965; Hüller, 1974; Jansen et al., 1984). The TDH equations are valid for finite temperature; in the limit of $T \rightarrow 0$ K, they become identical to the RPA equations. The TDH matrix that replaces the RPA matrix in the eigenvalue equations (126) can be written as

$$
M(q) = \begin{pmatrix}
-P & 0 \\
0 & P
\end{pmatrix}
\begin{pmatrix}
\Phi(q) - \chi & \Phi(q) \\
\Phi(q) & \Phi(q) - \chi
\end{pmatrix}
= 
\begin{pmatrix}
-P & 0 \\
0 & P
\end{pmatrix}
N(q)
$$
where the diagonal matrix $\chi$ is given by
\[
\chi_{\alpha, \beta, i, K; \alpha', \beta', i', K'} = \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} \delta_{i, i'} \delta_{K, K'} \frac{\epsilon_p^{(\alpha)} - \epsilon_p^{(\beta)}}{P_p^{(\alpha)} - P_p^{(\beta)}} \quad (\alpha > \beta) \tag{130}
\]
and the matrix $\Phi(q)$ by
\[
\Phi_{\alpha, \beta, i, K; \alpha', \beta', i', K'}(q) = \sum_n \exp(iq \cdot R_n) \langle \psi_p^{(\alpha)} | V_{\{0, i\} \{n, i'\}} | \psi_p^{(\beta)} \rangle_{P_c, P'_c} \langle \psi_p^{(\beta')} | V_{\{0, i\} \{n, i'\}} | \psi_p^{(\alpha')} \rangle_{Q_c, Q'_c} + \delta_{i, i'} \delta_{K, K'} \sum_n \sum_{i'}
\]
\[
\langle \psi_p^{(\alpha)} | V_{\{0, i\} \{n, i'\}} | \psi_p^{(\beta')} \rangle_{Q_c, Q'_c} \langle \psi_p^{(\beta')} | V_{\{0, i\} \{n, i'\}} | \psi_p^{(\alpha')} \rangle_{Q_c, Q'_c} \tag{131}
\]
while $P$ is a diagonal matrix containing population differences:
\[
P_{\alpha, \beta, i, K; \alpha', \beta', i', K'} = \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} \delta_{i, i'} \delta_{K, K'} \left[ P_p^{(\alpha)} - P_p^{(\beta)} \right] \tag{132}
\]
with
\[
P_p^{(\alpha)} = \langle \psi_p^{(\alpha)} | \rho_p^{MF} | \psi_p^{(\alpha)} \rangle = \exp(-\beta \epsilon_p^{(\alpha)}) \sum_\alpha \exp(-\beta \epsilon_p^{(\alpha)}) \tag{133}
\]
In the limit of $T \to 0$, $P^{(0)}_p = 1$ and $P^{(\beta)}_p = 0$ for $\beta > 0$; the matrix $P$ becomes the unit matrix $I$, and obviously, the TDH matrix $M(q)$ given by Eqs. (129) to (132) reduces to the RPA matrix [see Eqs. (126)–(128)].

**D. Stability Conditions for the Mean Field Solution**

Just as there exist the so-called Thouless stability conditions on the Hartree–Fock solutions in nuclear physics (Thouless, 1960, 1961; Rowe, 1970) and in quantum chemistry (Čížek and Paldus, 1971), one has stability conditions on the mean field solutions in lattice dynamics problems (Fredkin and Werthamer, 1965). The mean field solutions are obtained from the condition $\Delta A^{(1)}_{var} = 0$ (see Section IV,A). They are stable; i.e., they correspond with a local minimum in the free energy if $\Delta A^{(2)}_{var} > 0$. Substituting the mean field solution (109) into the equation (107) for $\Delta A^{(2)}_{var}$, the term with $\Delta \rho_p^{(2)}$ vanishes and we can express the stability condition as
\[
\Delta A^{(2)}_{var} = \frac{1}{2} \sum_{p \neq p'} \text{Tr}\{\Delta \rho_p^{(1)} | V_{pp'} | \Delta \rho_{p'}^{(1)}\} + \beta^{-1} \sum_p \int_0^\beta d\tau_1 \tau_1 \langle \hat{h}_p^{(1)} h_p \rangle_{MF} - \frac{1}{2} \beta \sum_p \langle h_p \rangle_{MF}^2 > 0 \tag{134}
\]
This condition must hold for arbitrary variations $h_P$, with the corresponding changes in the density operators $\Delta \rho_P^{(1)}$ as given by Eq. (104). Writing Eq. (134) in the main field basis $|\psi_P^{(a)}\rangle$ and substituting the matrix elements of Eq. (104) in this basis, we find

$$\Delta A_{\text{var}}^{(2)} = \frac{1}{2} \sum_P \sum_{\alpha,\alpha'} \sum_{\alpha,\alpha'} \sum_{p,p'} \langle \psi_P^{(a)} | \Delta \rho_P^{(1)} | \psi_P^{(b')} \rangle \langle \psi_P^{(b')} | \Delta \rho_P^{(1)} | \psi_P^{(a')} \rangle \times \left[ \langle \psi_P^{(a')} \psi_P^{(a')} \rangle V_{PP} | \psi_P^{(a)} \psi_P^{(b')} \rangle \right]$$

$$- \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{p,p'} \left[ \epsilon_P^{(a)} - \epsilon_P^{(b)} \right]$$

The matrix elements of the variations in the density operators $\Delta \rho_P^{(1)}$ can be interpreted as arbitrary variation coefficients

$$c_{\alpha,\beta,P} = \langle \psi_P^{(a)} | \Delta \rho_P^{(1)} | \psi_P^{(b)} \rangle$$

The second-order change in the free energy $\Delta A_{\text{var}}^{(2)}$ thus appears to be a quadratic form in these coefficients. If $\Delta A_{\text{var}}^{(2)}$ has to be positive for arbitrary variation coefficients $c_{\alpha,\beta,P}$, the Hessian of this form has to be positive definite. By Fourier transforming the coefficients, the Hessian can be block-diagonalized with blocks

$$\begin{pmatrix}
\Phi(q) - \chi & \Phi(q) & \Phi(q) \\
\Phi(q)^\dagger & f(q) - g & \Phi(q)^\dagger \\
\Phi(q) & \Phi(q) & \Phi(q) - \chi
\end{pmatrix}$$

which each have to be positive definite. The matrices $\chi$ and $\Phi(q)$ are defined in Eqs. (130) and (131); the other submatrices have similar definitions (van der Avoird et al., 1984), which are not relevant for the conclusion, however. Not only the matrices (137) have to be positive definite, but also all of their diagonal submatrices, in particular the matrices $N(q)$, defined in Eq. (129), which we obtain from Eq. (137) by omitting the central rows and columns. From Eq. (129) it is not difficult to demonstrate that the eigenvalues of $N(q)$ will all be positive if and only if the eigenvalues of $M(q)$, which are the RPA frequencies, are all real (van der Avoird et al., 1984). In that case the matrix $N(q)$ is positive definite. Therefore, we find the following stability condition: $\Delta A_{\text{var}}^{(2)}$ will only be positive, i.e., the mean field solution will only be stable, if the matrix $N(q)$ is positive definite. This implies that all TDH frequencies must be real. If at least one of these frequencies is complex, and one can prove that it will be purely imaginary, one finds negative eigenvalues of $N(q)$ and one can choose variations $\Delta \rho_P^{(1)}$ around the mean field solution $\rho_P^{\text{MF}}$ that make $\Delta A_{\text{var}}^{(2)}$ negative. In that case, the mean field solution does not correspond
to a local minimum in the free energy, but to a saddle point [or even a maximum if all eigenvalues of $N(q)$ would be negative]. Following the direction(s) indicated by the variations that make $\Delta A_{\text{var}}^{(2)}$ negative, one can find a mean field solution of lower free energy.

V. Molecular Motions in Solid Nitrogen

Solid nitrogen is a very suitable system to illustrate the various lattice dynamics theories and to verify how well they describe the different motions that molecules can perform in a solid. Nitrogen has ordered phases in which the molecules librate around well-defined equilibrium orientations, as well as plastic, i.e., orientationally disordered, phases. In the latter case, the x-ray and neutron diffraction studies (Streib et al., 1962; Jordan et al., 1964; Schuch and Mills, 1970; Powell et al., 1983) cannot determine the molecular orientations, and the nature of the molecular motions [i.e., (hindered) rotations or precessions or jumps between different equilibrium orientations] is still uncertain (Schuch and Mills, 1970; Press and Hüller, 1978; Powell et al., 1983). Even in the ordered phases the amplitudes of the molecular librations are not very small, however, especially near the order–disorder phase transition, where "orientational melting" takes place. The ordered $\alpha$ and $\gamma$ phases that exist at low temperature for pressures below and above 4 kbar, respectively, and the plastic $\beta$ phase that occurs above $T = 35.6$ K (at zero pressure) have been subject to many experimental investigations. The structures of these phases are shown in Fig. 1. The results prior to 1976 have been collected by Scott (1976). Additional data are still becoming available, and new phases that are stable at higher pressures have been discovered (LeSar et al., 1979; Cromer et al., 1981), for which the molecular ordering is not as yet well established. All the lattice dynamics methods that we have described in Sections III and IV have been applied to the $\alpha$ and $\gamma$ phases, the methods of Section IV also to the $\beta$ phase. In this section we discuss the most characteristic results and compare them, with some emphasis on the formalism developed by ourselves, which holds both for small- and large-amplitude motions.

A. Theory for Linear Molecules

The orientations of linear molecules, relative to the global frame, can be specified by two Euler angles $\omega = \{\theta_P, \phi_P\}$; the symmetry-adapted functions $G_m^{(\omega)}(\omega_P)$ that occur in the intermolecular potential [Eq. (15)] reduce to Racah spherical harmonics $C_m^{(\omega)}(\theta_P, \phi_P)$. If the molecules possess a center of inversion such as N$_2$ (when we disregard the occurrence of mixed isotopes $^{14}$N$^{15}$N, the natural abundance of $^{15}$N being only 0.37%).
Fig. 1. Crystal structures of (a) α-, (b) β-, and (c) γ-nitrogen, according to Scott (1976).
just the even $l$ values occur. The expression (26) for the rotational kinetic energy becomes simply

$$L(\omega_p) = BJ^2(\theta_p, \phi_p)$$

(138)

with the rotational constant $B = (2I)^{-1} = (2\mu r_0^2)^{-1}$. For $^{14}N^{14}N$ the average internuclear distance $r_0 = 1.094 \text{ Å}$, the reduced mass $\mu = 7 \text{ amu}$, and $B = 2.013 \text{ cm}^{-1}$. The Wigner $D_{nm}^{(l)}(\omega_p)$ functions in the orientational basis [Eq. (111)] can also be replaced by spherical harmonics $C_{m}^{(l)}(\theta_p, \phi_p)$, with further restrictions on $l$ depending on the nuclear permutation–inversion symmetry, which is related to the nuclear spin species. Therefore, for $^{14}N$ the nuclear spin $I = 1$ and the $^{14}N^{14}N$ molecules can be classified as ortho-$N_2$ with $I = 0$ or $I = 2$, and rotational basis functions with even $l$, and para-$N_2$ with $I = 1$ and a rotational basis with odd $l$. In lattice dynamics calculations (Dunmore, 1972; Jansen et al., 1984; van der Avoird et al., 1984), one has assumed that the crystal is composed of pure ortho-$N_2$ or pure para-$N_2$. The difference between the libron frequencies for ortho and para crystals is a measure for the quenching of the free $N_2$ rotations, i.e., the degree of orientational localization, caused by the rotational barriers from the anisotropic potential. In most cases, except for the delocalized solutions in $\beta$-nitrogen (van der Avoird et al., 1984), one has found
very small ortho–para differences, which indicate a rather strong localization.

B. Results from Harmonic and Quasi-Harmonic Models

A large majority of the lattice dynamics calculations on nitrogen have employed the harmonic model. Naturally, these calculations concern the

<table>
<thead>
<tr>
<th>TABLE IIIA</th>
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<tbody>
<tr>
<td><strong>Lattice Frequencies in α-N₂ (in cm⁻¹), T = 0 K, p = 0</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>( a (\text{Å}) )</td>
</tr>
<tr>
<td>( \Gamma(0, 0, 0) )</td>
</tr>
<tr>
<td>( { E_g } )</td>
</tr>
<tr>
<td>( T_g )</td>
</tr>
<tr>
<td>( T_g )</td>
</tr>
<tr>
<td>( A_u )</td>
</tr>
<tr>
<td>( { T_u } )</td>
</tr>
<tr>
<td>( E_u )</td>
</tr>
<tr>
<td>( T_u )</td>
</tr>
<tr>
<td>( M \left( \frac{\pi}{a}, \frac{\pi}{a}, 0 \right) )</td>
</tr>
<tr>
<td>( { M_{12} } )</td>
</tr>
<tr>
<td>( M_{12} )</td>
</tr>
<tr>
<td>( { M_{12} } )</td>
</tr>
<tr>
<td>( M_{12} )</td>
</tr>
<tr>
<td>( M_{12} )</td>
</tr>
<tr>
<td>( R \left( \frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a} \right) )</td>
</tr>
<tr>
<td>( { R_{11} } )</td>
</tr>
<tr>
<td>( R_{11} )</td>
</tr>
<tr>
<td>( R_{23} )</td>
</tr>
<tr>
<td>( R_{23} )</td>
</tr>
<tr>
<td>( R_{23} )</td>
</tr>
<tr>
<td>rms deviation of librational frequencies</td>
</tr>
<tr>
<td>rms deviation of translational frequencies</td>
</tr>
<tr>
<td>rms deviation of all lattice frequencies</td>
</tr>
</tbody>
</table>

ᵃ From Kjems and Dolling (1975).
ᵇ From Raich and Gillis (1977).
ᶜ From Luty et al. (1980).
ᵈ From Briels et al. (1984).
ordered $\alpha$ and $\gamma$ phases, although sometimes the translational vibrations in the $\beta$ phase have been considered, too, with the molecular rotations neglected. The only nontechnical difference between these harmonic treatments lies in the potentials used, which are practically always empirical model potentials mostly of the atom–atom and/or quadrupole–quadrupole type (see Section II). It is generally believed that, particularly, the phonon frequencies are very sensitive to the shape of the intermolecular potential, the translational frequencies to its distance dependence and the librational modes to its anisotropy. The experimental phonon frequencies from infrared and Raman spectroscopy (for wave vector $\mathbf{q} = 0$) and from inelastic neutron scattering (for any $\mathbf{q}$) have been used to optimize the parameters in the model potentials. As an example of the most sophisticated work of this type, we quote the paper by Raich and Gillis (1977). The results listed in the second columns of Tables IIIA and IIIIB are characteristic: fairly good agreement with experiment for the pure translational phonon frequencies and substantially worse agreement for the librational modes even after optimizing the parameters. The discrepancy has been ascribed to the strong anharmonicity and rather large amplitudes of the librations, even at the lowest temperatures. A study by Luty et al. (1980) using a nonempirical $N_2–N_2$ site–site potential obtained from quantum-chemical $ab$ initio calculations (Berns and van der Avoird, 1980) yields similar results (see the third columns of Tables IIIA, B). The overall agreement in the $ab$ initio treatment, which involves no parameter

<table>
<thead>
<tr>
<th>TABLE IIIIB</th>
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<tbody>
<tr>
<td><strong>Lattice Frequencies in $\gamma$-N$_2$ (in cm$^{-1}$), $T = 0$ K, $p = 4$ kbar</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment$^a$</th>
<th>Semiempirical harmonic$^b$</th>
<th>$Ab$ initio harmonic$^c$</th>
<th>SCP$^c$</th>
<th>RPA$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.957</td>
<td>3.940</td>
<td>4.032</td>
<td>4.100</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.109</td>
<td>5.086</td>
<td>5.000</td>
<td>5.188</td>
</tr>
<tr>
<td>$\Gamma(0, 0, 0)$</td>
<td>${E_g, \ B_{1g}, \ A_{2g}}$</td>
<td>${E_u, \ B_{1u}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Librations</td>
<td></td>
<td></td>
<td>55.0</td>
<td>50.5</td>
</tr>
<tr>
<td>Translational</td>
<td></td>
<td></td>
<td>98.1</td>
<td>74.8</td>
</tr>
<tr>
<td>vibrations</td>
<td></td>
<td></td>
<td>105.1</td>
<td>111.2</td>
</tr>
<tr>
<td>rms deviation</td>
<td></td>
<td></td>
<td>65.0</td>
<td>58.3</td>
</tr>
</tbody>
</table>

$^a$ From Thiery and Fabre (1976) and Fonré et al. (1981).
$^b$ From Raich and Gillis (1977).
$^c$ From Luty et al. (1980).
$^d$ From Briels et al. (1980).
optimization, is slightly worse. We shall illustrate, however, that this is largely due to the harmonic approximation made in the lattice dynamics calculation. We observe, at this point, a weakness of the semiempirical procedure: optimizing a parameterized potential by comparing approximate, mostly harmonic, lattice dynamics results with measured data might lead to incorrect potentials and, at the same time, partly hide the flaws of the approximate lattice dynamics model.

Harris and Coll (1972), Kobashi (1978), and Kuchta and Luty (1983) have used anharmonic perturbation theory (see Section III,B) to study the effect of the cubic and quartic anharmonicities on the libron and phonon frequencies in \( \alpha \)-nitrogen. The results are conflicting, however, and the shifts appear to depend very sensitively on the potential. Harris and Coll (1972), using only the quadrupole–quadrupole interactions, find a reduction of the libron frequencies by about 12\%, whereas Kobashi (1978), using a 12–6 atom–atom potential, finds an increase in all libron and phonon frequencies by 4 to 14 cm\(^{-1}\), i.e., 7 to 17\%. Kuchta and Luty (1983), using a perturbed uncoupled oscillator model starting from the \textit{ab initio} potential of Berns and van der Avoird (1980), obtain a decrease of the harmonic libron frequencies by 18 to 27\%. The agreement of the latter results, after the perturbation correction, with experimental data must probably be regarded as fortuitous, however, since the anharmonic corrections for the librations are too large to be treated by perturbation theory up to the second order.

A similar influence of the potential chosen occurs if one tries to calculate the anharmonic effects by the self-consistent phonon (SCP) method. The calculation by Raich \textit{et al.} (1974) is based on the atomic version of the SCP method (see Section III,C). Using an empirical 12–6 atom–atom potential, they found a consistent increase of the harmonic phonon and libron frequencies by 3 to 10\%. The calculation by Luty \textit{et al.} (1980), who use the SCP method of Wasiutynski (1976) and the \textit{ab initio} \( \text{N}_2–\text{N}_2 \) potential of Berns and van der Avoird (1980), yields a consistent lowering by about the same amount. It is striking (see Tables IIIA,B, fourth columns) that the \textit{ab initio} results for the pure translational phonon frequencies in \( \alpha \)- and \( \gamma \)-nitrogen agree remarkably well with experiment, without any parameter optimization, while the librational frequencies and those of the mixed modes are still substantially too high. Apparently the anharmonicity in the distance dependence of the intermolecular potential, which affects the translational vibrations, is very well accounted for by the SCP method. The orientational dependence of the potential is strongly anharmonic. In combination with the fairly large amplitudes of the rotational oscillations, this causes the SCP method to fail in describing the librational motions. This failure may be related to the additional approximations made in generalizing this method to molecular crystals.
Raich et al. (1974) and Goldman and Klein (1975) have applied the SCP method to the translational phonons in $\beta$-nitrogen. The molecular rotations were assumed to be completely free and the effective isotropic intermolecular potential used was a rotationally averaged, empirical atom–atom $12^{-6}$ potential. The results of such models that completely neglect any translation–rotation coupling are mainly of qualitative interest.

C. Large-Amplitude Motions in the Ordered Phases

Since it became clear from various observations that the librational motions of the molecules, even in the ordered $\alpha$ and $\gamma$ phases of nitrogen at low temperature, have too large amplitudes to be described correctly by (quasi-) harmonic models, we have resorted to the alternative lattice dynamics theories that were described in Section IV. Most of these theories have been developed for large-amplitude rotational oscillations, hindered or even free rotations, and remain valid when the molecular orientations become more and more localized.

Weis and Klein (1975) made classical molecular dynamics (MD) calculations for 250 N$_2$ molecules in a cubic box, with periodic boundary conditions. These molecules were initially arranged in the cubic Pa$3$ structure of $\alpha$-nitrogen, and they were made to interact via a $12^{-6}$ atom–atom potential. The molecular motions were mainly characterized via the calculated dynamic structure factor $S(q, \omega)$, which describes the response of the system to a transfer of momentum $q$ and energy $\hbar \omega$ (see Section IV,A). Because for given wave vector $q$ the peaks in $S(q, \omega)$ can be identified with phonons, the results of these calculations could be compared with (quasi-) harmonic lattice dynamics studies. The phonon frequencies appeared to be substantially different from the quasi-harmonic results calculated with the same atom–atom potential, and the temperature shifts of some of the peaks were much larger in the MD calculations. These differences and the corresponding peak broadenings have been ascribed by Weis and Klein to the occurrence of strongly anharmonic, large-amplitude motions that cause the breakdown of the quasi-harmonic model. At a temperature, of 35 K, close to the $\alpha$–$\beta$ phase transition point, the MD calculations even indicate the existence of “quasi-free” rotations.

Jacobi and Schneppe (1972) and Raich (1972) were the first to develop a quantum-dynamical model for the large-amplitude librations in $\alpha$-nitrogen. Their formalism is essentially described in Section IV,C. They first calculated single-molecule mean field states that may be localized as well as delocalized, depending on the height of the rotation barriers from the anisotropic potential. These states were used to construct a basis of excitonlike wave functions for the whole crystal. The final step in their calcu-
lation, the diagonalization of the full-crystal Hamiltonian in this basis, amounts to diagonalizing the upper left block of the RPA matrix, Eq. (126). Therefore, this theory is more approximate than the RPA formalism; one of the consequences is that it does not converge to the harmonic solution in the limit of an exactly harmonic crystal Hamiltonian. If the excitonlike model were applied to the translational phonons rather than to the librations, the acoustical modes would not go to zero frequency for \( q = 0 \). Employing the full RPA method, as described in Section IV,C, ensures the convergence to the correct limits; this method has been applied to the librations in \( \alpha \)-nitrogen by Dunmore (1972, 1976), Raich et al. (1974), and Mandell (1974, 1975).

All these authors have used semiempirical \( \text{N}_2\text{--N}_2 \) potentials, often simplified to the utmost by retaining only pure quadrupole–quadrupole interactions or atom–atom 12–6 interactions. Moreover, they have always fixed the molecules with their centers of mass to the lattice points, thus neglecting the translational vibrations and the effects of libron–phonon coupling. We applied the RPA formalism to \( \alpha \)- and \( \gamma \)-nitrogen (Jansen et al., 1984) by using the \textit{ab initio} potential of Berns and van der Avoird (1980). This potential was not approximated by a site–site model this time, but expanded in symmetry-adapted functions as in Section II,B. In a subsequent paper (Briels et al., 1984) we extended the theory in order to account explicitly for the translational phonons and for libron–phonon coupling after expanding the crystal Hamiltonian as in Section II,D. The extended formalism is described in Section IV,C. Since this treatment is more complete than any of the previous ones, we shall use its results as an illustration.

We have started by assuming the observed lattice symmetry and by theoretically optimizing the cell parameters for the given \textit{ab initio} potential as follows. For \( \alpha \)-nitrogen we have calculated the minimum of the free energy in the mean field approximation as a function of the cubic cell parameter \( a \). This yields the optimum value \( a = 5.699 \, \text{Å} \), experimentally (Scott, 1976) \( a = 5.644 \, \text{Å} \), and the mean field lattice cohesion energy at \( T = 0 \, \text{K} \) of \( \Delta E = 5.92 \, \text{kJ/mol} \), experimentally \( \Delta E = 6.92 \, \text{kJ/mol} \). For the \( \gamma \) phase we have calculated the free energy \( A \) for several values of the tetragonal cell parameters \( a \) and \( c \) and fitted \( A(a, c) \) by a second-order polynomial. On each curve of constant molar volume \( v = Na^2c/2 \), we have determined the optimum \( a \) and \( c \) by minimizing \( A \). Using the optimum points and the corresponding free energies, we have calculated the pressure as \( p = -\partial A/\partial v \). Thus we found at \( p = 4 \, \text{kbar} \) that \( a = 3.961 \, \text{Å} \) and \( c = 5.104 \, \text{Å} \), in excellent agreement with the experimental values \( a = 3.957 \, \text{Å} \) and \( c = 5.109 \, \text{Å} \) (Scott, 1976).

The mean field approximation yields a picture of the single-molecule
motions as determined by the anisotropic \textit{ab initio} potential. The orientational probability distributions in \(\alpha\) and \(\gamma\)-nitrogen are shown in Fig. 2a,b, respectively. We clearly observe that the librations of the molecules in the \(\alpha\) phase are localized about the cubic body diagonals, i.e., the \([1, 1, 1]\) direction and three equivalent directions. In \(\gamma\)-nitrogen the \(N_2\) molecules appear to librate about the \([1, 1, 0]\) and \([1, -1, 0]\) directions. Both these findings agree with experiment, cf. Fig. 1. For temperatures up to at least 40 K, these pictures remain qualitatively similar. The amount of delocalization is measured by the decreasing order parameter \(S = \langle P_2(\cos \theta) \rangle\) (see Fig. 3), with \(\theta\) now defined relative to the equilibrium axis. Even at \(T = 0\) K the root-mean-square amplitude of the librations is already substantial, however, about 16° in the \(\alpha\)-phase. Similar parameters, including the translational vibrations, are listed in Table IV. We observe that the molecular motions, both librational and translational, in \(\gamma\)-nitrogen at \(p = 4\) kbar are more restricted than in the \(\alpha\) phase, at zero pressure.

After calculating the ground and excited mean field states of \(\alpha\)- and \(\gamma\)-nitrogen, we have included the correlation between the molecular motions, as well as the translational–rotational coupling, by determining the eigenvalues of the RPA matrix \(M(q)\) [Eq. (129)]. The expansion of the potential in the translational displacements \((u_P)\) of the molecules [see Eq.

\[
\begin{array}{c|c|c}
\hline
\text{Table IV} & & \\
\hline
\text{Translational and Librational Amplitudes from Mean Field Calculations} & & \\
\hline
\hline
\alpha-N_2 & T = 0 K & p = 0 \\
\hline
\langle u_1^2 \rangle^{1/2} = 0.112 \text{ Å} & u_1 = u_{[1,1,1]} \\
\langle u_2^2 \rangle^{1/2} = 0.107 \text{ Å} & \\
\langle u_3^2 \rangle^{1/2} = 0.189 \text{ Å} & \\
\arccos((\cos^2 \theta)^{1/2}) = 16.1^\circ & \\
\hline
\gamma-N_2 & T = 0 K & p = 4 \text{ kbar} \\
\hline
\langle u_1^2 \rangle^{1/2} = 0.100 \text{ Å} & u_1 = u_{[1,1,0]} \\
\langle u_{2,ab}^2 \rangle^{1/2} = 0.086 \text{ Å} & u_{2,ab} = u_{[1,-1,0]} \\
\langle u_{1,c}^2 \rangle^{1/2} = 0.087 \text{ Å} & u_{1,c} = u_{[0,0,1]} \\
\langle u_3^2 \rangle^{1/2} = 0.159 \text{ Å} & \\
\arccos((\cos^2 \theta)^{1/2}) = 12.9^\circ & \\
\text{asymmetry parameter (rotation out of ab plane – rotation in ab plane):} & \\
\frac{\langle \sin^2 \theta (\sin^2 \varphi - \cos^2 \varphi) \rangle}{\langle \sin^2 \theta \rangle} = 0.05 & \\
\hline
\end{array}
\]
Fig. 2. Orientational probability distributions of the molecular axes in (a) $\alpha$-nitrogen and (b) $\gamma$-nitrogen. Contours of constant probability for the molecule in the origin, calculated in the mean field model, are plotted as functions of the polar angles ($\theta$, $\phi$) with respect to the crystal axes (Fig. 1). The angle $\theta$ increases linearly with the radius of the plots from 0 (in the center) to $\pi/2$ (at the boundary); $\phi$ is the phase angle.
Dynamics of Molecular Crystals

Fig. 3. Temperature dependence of the (mean field) order parameter in $\alpha$-$N_2$.

(40)] has been truncated at three different levels. Taking $\alpha_{\text{max}} = 2$ corresponds to a harmonic model for the translational phonons; taking $\alpha_{\text{max}} = 3$ and $\alpha_{\text{max}} = 4$ includes the cubic and quartic anharmonicities, respectively. The orientational ($\omega_p$) dependence of the \textit{ab initio} potential has always been included exactly, which is important because of the large amplitude of the librons. Some typical results are shown in Table V. The size of the anharmonic corrections to the translational phonon frequencies is comparable with that of the self-consistent phonon corrections calculated with the same \textit{ab initio} potential (Luty \textit{et al.}, 1980); the corrected frequencies agree equally well with experiment. There is an important difference, however, between our RPA formalism and the SCP method. The latter neglects those terms in the potential that depend on the odd powers of the molecular displacements. The cubic terms have sometimes been added perturbationally (Goldman \textit{et al.}, 1968; Koehler, 1969), but not so by Luty \textit{et al.} (1980). Our formalism includes the effects of the cubic terms directly in the mean field and RPA results. In $\alpha$-nitrogen, however, because of the inversion symmetry, they vanish at the mean field level and have no effect on the purely translational phonon frequencies of Table V. In the mixed phonon–libron modes the cubic corrections mostly lower the frequencies, while the quartic corrections are always positive and dominant.

We wish to emphasize that the most essential advantage of the RPA method discussed here over the previous (quasi-) harmonic treatments is the correct description of the large-amplitude libron modes and the mixed libron–phonon modes. This is reflected by the substantial anharmonic corrections in the frequencies of these modes; compare the last column of
Table V

$\alpha_{\text{max}}$ Dependence of Some RPA Lattice Frequencies for $\alpha$-N$_2$

($\alpha = 5.644 \text{ Å}, T = 0 \text{ K}$)

<table>
<thead>
<tr>
<th></th>
<th>Frequency $\omega$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_{\text{max}} = 2^a$</td>
</tr>
<tr>
<td>$\Gamma(0, 0, 0)$</td>
<td>$E_g$ 32.8</td>
</tr>
<tr>
<td></td>
<td>$T_g$ 43.4</td>
</tr>
<tr>
<td></td>
<td>$T_g$ 71.6</td>
</tr>
<tr>
<td>Librations</td>
<td>$A_u$ 42.3</td>
</tr>
<tr>
<td></td>
<td>$T_u$ 48.7</td>
</tr>
<tr>
<td>Translations</td>
<td>$E_u$ 55.7</td>
</tr>
<tr>
<td></td>
<td>$T_u$ 73.0</td>
</tr>
<tr>
<td>$M(\frac{\pi}{a}, \frac{\pi}{a}, 0)$</td>
<td>$M_{12}$ 28.8</td>
</tr>
<tr>
<td>Mixed</td>
<td>$M_{12}$ 40.4</td>
</tr>
<tr>
<td></td>
<td>$M_{12}$ 52.2</td>
</tr>
<tr>
<td></td>
<td>$M_{12}$ 60.0</td>
</tr>
<tr>
<td></td>
<td>$M_{12}$ 67.0</td>
</tr>
</tbody>
</table>

$^a$ Harmonic model for translations.

Table III with the preceding columns. The new results calculated with the \textit{ab initio} potential agree very well with the frequencies from inelastic neutron scattering (Kjems and Dolling, 1975) and from infrared and Raman spectroscopy (Thiéry and Fabre, 1976; Fondère \textit{et al.}, 1981) for all types of modes. Also the phonon dispersion relations, displayed in Fig. 4, are in good agreement with the neutron-scattering data. Since most of the lattice modes are actually mixed libron–phonon modes, this indicates that the translation–rotation coupling is correctly included in the RPA formalism.

D. The Plastic Phase and the Orientational Order–Disorder Phase Transition

Lattice dynamics calculations on the plastic $\beta$-nitrogen phase are relatively scarce because, obviously, the standard (quasi-) harmonic theory cannot be applied to this phase. Classical Monte Carlo calculations have been made by Gibbons and Klein (1974) and Mandell (1974) on a face-centered cubic ($\alpha$-nitrogen) lattice of 108 N$_2$ molecules, while Mandell has also studied a 32-molecule system and a system of 96 N$_2$ molecules on a hexagonal close-packed ($\beta$-nitrogen) lattice. Gibbons and Klein used 12–6
and 9–6 atom–atom potentials and fairly high temperatures, $T = 96$ and $192 \text{ K}$; they found only complete orientational disorder. Mandell made his $\text{N}_2$ molecules interact as pure point quadrupoles, and he showed that even the smaller 32-molecule system already yields a fairly realistic order–disorder phase transition.

Another simple, quantum-mechanical, model for the phase transition has been proposed by Raich and Etters (1972). They studied $\text{N}_2$ molecules on an fcc lattice, again interacting as pure point quadrupoles. Using a mean field model for the librations in the $\alpha$ phase, a free rotor model for $\beta$-nitrogen, and calculating the corresponding free-energy curves, they found an $\alpha$–$\beta$ phase transition at somewhat too high a temperature. This model has been refined by Raich et al. (1974) and Goldman and Klein (1975), who applied the self-consistent phonon method to the translational and librational motions in the $\alpha$ phase and to the pure translational phonons in the $\beta$ phase (cf. Section V, B). The rotational motions in $\beta$-nitrogen were still assumed to be completely free, however, and any
translation–rotation coupling was neglected. Classical molecular dynamics calculations by Klein et al. (1977, 1981) on a 288-molecule model for β-nitrogen at $T = 47$ K indicate that this coupling is probably important, since the translational phonon frequencies derived from these MD calculations, while using the same 12–6 atom–atom potential, are substantially different from the SCP results of Raich et al. (1974). The rotational motions in the β phase were found to be "quasi-free" in the classical MD model.

Finally, we discuss the mean field and RPA calculations made on β-nitrogen (van der Avoird et al., 1984) by using the *ab initio* potential of Berns and van der Avoird (1980) again. We started our calculations on this phase, just as those for α- and γ-nitrogen, by assuming the experimentally observed lattice symmetry. Thus, the two molecules in the hexagonal unit cell (see Fig. 1) were given translationally equivalent mean field solutions. The orientational probability distribution that results for the pure ortho- N$_2$ crystal is shown in Fig. 5a. The ground state of the para-N$_2$ species is twofold degenerate; the average probability distribution $\frac{1}{2}|\psi_1|^2 + \frac{1}{2}|\psi_2|^2$ is similar to Fig. 5a. This picture suggests that the orientational motions in β-nitrogen are quasi-free precessions around the crystal c axis, modulated by small sixfold barriers. In accordance with the ideas of Press and Hüller (1978) and the earlier mean field calculations by Dunmore (1976), the precession angle $\theta$ between the molecular axis and the c axis is not sharply defined, but it shows a rather broad distribution with the maximum at the "experimental" value of $\theta = 56^\circ$ (Scott, 1976).

The mean field ground state yielding this delocalized picture appeared to be unstable, however. This could be concluded from the ensuing RPA calculations yielding imaginary libron frequencies and the stability conditions in Section IV,D. We have searched for a stable mean field solution by independently varying the orientational wave functions of the two molecules in the unit cell, and we have indeed found such a solution, which is lower in (free) energy by 0.87 kJ/mol than the previous delocalized solution at $T = 0$ K. In this new solution the orientations of the N$_2$ molecules are clearly localized (see Fig. 5b). They librate about an equilibrium axis that makes an angle of 52° with the crystal c axis. The equilibrium axes for the two neighboring molecules in the hexagonal unit cell are not the same, but they are rotated through 180° about the c axis. This 180° rotation avoids the steric hindrance between neighbors that would occur when the molecules were freely precessing (Schuch and Mills, 1970) and, thus, leads to the lower free energy.

The problem with this localized, stable, mean field solution is that it has a much lower symmetry than the experimentally observed hexagonal symmetry of β-nitrogen. We have conjectured that the higher symmetry is
Fig. 5. Orientational probability distribution of the molecular axes for the delocalized (a) and localized (b) mean field states in $\beta$-nitrogen. (a) applies to both molecules in the unit cell. (b) is drawn for one molecule in the unit cell; the other molecule in the cell is rotated over $\phi = 180^\circ$. The distribution does not change qualitatively up to (at least) $T = 70$ K; it just becomes slightly wider with increasing temperature. Reading of the contour plot as in Fig. 2.
observed because of rapid jumps of the molecular axes between six localized librational states of the type found in the final mean field calculation. The six equilibrium axes will be located at $\theta = 52^\circ$ and $\phi = 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ, \text{and} \ 300^\circ$. The characteristic time for these jumps should be less than the inverse frequency of the nuclear quadrupole resonance measurements (de Reggi et al., 1969), i.e., about $10^{-7}$ sec. In order to preserve the lower energy of the stable mean field solution, the jumps of neighboring molecules must be correlated; two neighbors have the tendency to remain $180^\circ$ out of phase in their $\phi$ angles.

With the different models emerging for the molecular motions in the $\beta$ phase and the mean field model for localized, large-amplitude librations in the $\alpha$ phase (see Section V,C), we have studied the $\alpha$-$\beta$ phase transition. The calculated free-energy curves corresponding with these models are shown in Fig. 6. The free energy for the delocalized precession model of $\beta$-nitrogen decreases much more steeply, with increasing temperature, than that for $\alpha$-nitrogen. This is caused by the spectrum of the delocalized $\beta$-N$_2$ model being like a free rotor, with considerably smaller excitation

![Fig. 6. Free energy (at zero pressure) for $\alpha$-nitrogen and $\beta$-nitrogen, in different mean field models (closed lines). The dashed free rotor curve has been calculated from the isotropic ($l_1, l_2, l_3$) = (0, 0, 0) term of the ab initio potential by adding the free rotor expression for the free energy. The dashed jump model curve has been obtained from the localized mean field solution (with the full anisotropic potential) by adding an entropy term $-k_B T \ln 6$ (see the text).](image-url)
energies than the harmonic oscillatorlike spectrum of $\alpha$-N$_2$. As shown in Fig. 6, a free rotor model for $\beta$-N$_2$ yields almost the same free-energy curve as the delocalized precession model. However, both these models cannot give a free energy lower than that for $\alpha$-N$_2$, and thus a phase transition, at any reasonable temperature. On the other hand, the localized librational solution for $\beta$-N$_2$ is much lower in energy, but its free-energy curve does not sufficiently fall off with temperature to cross the $\alpha$-N$_2$ curve. Now we invoke the jumps of the molecules between the localized solutions. Ignoring, for the moment, the correlations between these jumps and assuming that each molecule has access to six localized states yields an entropy term $-k_B T \ln 6$. Adding this term to the free-energy curve of a particular localized solution leads to the curve in Fig. 6 marked "$\beta$-N$_2$ jump." This model predicts an $\alpha$-$\beta$ phase transition temperature of 34 K, very close to the experimental value $T = 35.6$ K.

Starting from the localized mean field wave functions, we have also calculated the libron frequencies in $\beta$-nitrogen via the RPA formalism. All frequencies appeared to be real, as they should be for a stable mean field solution. The infrared spectrum (Medina and Daniels, 1976) shows two very broad peaks around 25 to 36 cm$^{-1}$ and 50 to 68 cm$^{-1}$, depending on the pressures. The first one has been interpreted as a translational phonon band, the second one as a libron band. Neutron scattering (Kjems and Dolling, 1975) yields broad peaks at 25 and 64 cm$^{-1}$ attributed to translational phonons. We have calculated optical libron frequencies of 34, 41, 56, and 59 cm$^{-1}$. The observed broad peaks may well contain these libron excitations in addition to the translational phonon bands. We assign the broadening of these peaks to the occurrence of more or less random transitions, classically called jumps, between the different localized libron states.

In summary, we think that our calculations suggest a model with localized librations and 60° jumps for the orientational motions in $\beta$-nitrogen. This model gives a reasonable account of the $\alpha$-$\beta$ phase transition and the libron spectrum of $\beta$-N$_2$. A dynamical model for the 60° jumps, which must include strong short-range pair correlations, is still lacking, however. Possibly this correlation can be introduced by using Jastrow functions (van Kranendonk, 1983).

VI. Dynamics and Magnetism of Solid Oxygen

Oxygen, with its $^3\Sigma_g^-$ ground state, is one of the few stable molecules with a nonvanishing electronic spin momentum. The potential between O$_2$ molecules is not only determined by the usual van der Waals interactions occurring between closed shell molecules, but it contains, moreover, the
coupling between the electronic spins. In addition to their positional and orientational coordinates, the O₂ molecules have an extra degree of freedom: the orientations of their triplet spin momenta. Consequently, in the solid we must consider the molecular motions, translational and rotational, as well as the spin dynamics.

This extra degree of freedom makes solid O₂ one of the most interesting molecular crystals. Even at low pressure one finds three different phases: the α phase between 0 and 23.8 K, the β phase between 23.8 and 43.8 K, and the γ phase between 43.8 K and the melting point at 54.4 K. These phases have structural as well as magnetic order. The α and β phases are orientationally ordered; the γ phase is plastic. The α phase is antiferromagnetic, with the usual (spin up, spin down) two-sublattice structure; α-oxygen is the only homogeneous antiferromagnet known. The β phase probably has short-range antiferromagnetic order with a three-sublattice 120° spin arrangement. The γ phase is paramagnetic, just like liquid oxygen. Both in the α and β phases the molecules are packed in layers, the a–b planes, with their axes perpendicular to these planes (see Fig. 7). In the β phase this packing is hexagonal; in the monoclinic α phase the hexagons are slightly distorted by a contraction in the a direction and a dilation in the b direction. This distortion is driven by the magnetic coupling: the α–β phase transition is called magnetoelastic. The spins in the α phase are preferentially directed in the ±b directions.

![Fig. 7. Crystal structures of (a) α-oxygen and (b) β-oxygen, according to De Fotis (1981).](image)
The excitations in such a magnetic solid are not only due to the lattice vibrations, phonons, and librions, but also to the spin waves; the corresponding quasi-particles are called magnons. The magnetic excitations in $\alpha$-O$_2$ have been directly observed by infrared and Raman spectroscopy and by inelastic neutron scattering. In general, they determine, of course, the magnetic properties of the system, susceptibilities, spin flop processes, etc. They also affect other properties, though, such as the specific heat and the thermal expansion coefficients. For the experimental and theoretical work prior to 1981 we refer to De Fotis’s (1981) review, which begins by stating that “the magnetic, structural, thermodynamic and spectroscopic properties of the condensed phases of oxygen have been under study for nearly a century. Yet important aspects of their behavior remain poorly understood.” Work by Slyusarev et al. (1980, 1981), Gaididei and Loktev (1981), Stephens et al. (1983), Meier et al. (Meier et al., 1982; Meier and Helmholdt, 1984; Meier, 1984), Etters et al. (Etters et al., 1983; Helmy et al., 1984), and van der Avoird et al. (van Hemert et al., 1983; Wormer and van der Avoird, 1984; Jansen and van der Avoird, 1985) has provided additional information.

A. Lattice Dynamics and Spin Wave Calculations

Until very recently, the lattice vibrations in solid O$_2$ and its magnetic properties have always been treated separately. As far as the packing in the crystal and the lattice vibrations are concerned, one can consider the O$_2$ molecules as resembling N$_2$. An important quantitative difference lies in the O$_2$ molecule’s quadrupole moment, however, which is about four times smaller than that of N$_2$ (in absolute value). This smaller quadrupole moment, together with the exchange coupling between the open-shell O$_2$ molecules (see the subsequent discussion), probably explains why the packing in the ordered $\alpha$ and $\beta$ phases of solid O$_2$ (see Fig. 7) is very different from the ordered N$_2$ structures (see Fig. 1) (English and Venables, 1974; English et al., 1974). The lattice dynamics calculations that have been made for $\alpha$- and $\beta$-oxygen (Kobashi et al., 1979; Etters et al., 1983; Kuchta, 1985) are very similar to the standard harmonic calculations made on solid nitrogen (see Section V); they have used empirical atom–atom 12–6 or exp $-6$ potentials. The calculated optical libron frequencies are generally in reasonable agreement with the experimental data. One important observation could not be explained by these calculations, however, In $\beta$-oxygen there is a degenerate optical ($\mathbf{q} = \mathbf{0}$) libron mode of $E_g$ symmetry with a frequency of about 50 cm$^{-1}$. This mode corresponds with the in-phase librations of all O$_2$ molecules around the crystal a and b axes, and the degeneracy occurs because of the equivalence of these axes in the hexagonal $\beta$ phase. When the hexagonal sym-
metry is distorted by going through the $\beta-\alpha$ phase transition, this mode will be split, in principle. The librations around the monoclinic $b$ axis in $\alpha$-$O_2$ have $A_g$ symmetry; those around the $a$ axis have $B_g$ symmetry. The splitting actually observed by Raman spectroscopy is so large, however, that it cannot be explained by any of the lattice dynamics calculations. The experimental spectrum of $\alpha$-$O_2$ shows two peaks at 43 and 79 cm$^{-1}$, whereas the lattice dynamics calculations yield a splitting of about 10 cm$^{-1}$ at most. The latter result is not surprising in view of the small structural distortion that accompanies the $\beta-\alpha$ phase transition. Most authors have assumed, therefore, that the $A_g$ and $B_g$ modes remain very nearly degenerate in $\alpha$-$O_2$ and that the higher-frequency peak represents a two-libron, two-phonon, or libron-magnon transition. Experiments by Bier and Jodi (1984) indicate, however, that the mode at 43 cm$^{-1}$ is probably the $B_g$ mode and the mode at 79 cm$^{-1}$ the $A_g$ mode. We shall give an explanation of this phenomenon in the next section.

The magnetic properties of $\alpha$-$O_2$, which is the most extensively studied phase, have always been interpreted on the basis of the following phenomenological spin Hamiltonian:

$$H_{\text{spin}} = -\frac{1}{2} \sum_{p \neq p'} 2J_{pp'} S_p \cdot S_{p'} + \sum_{p'} (A S_{x,p}^2 + B S_{y,p}^2)$$  \hspace{1cm} (139)$$

where $z$ is the preferred magnetization axis, the $b$ axis, the $x$ axis is the orientation of the molecular axes (i.e., the crystallographic $c^*$ direction), and the $y$ axis coincides with the crystal $a$ axis. The first term in this Hamiltonian is the Heisenberg exchange coupling between the triplet $O_2$ molecules. The dominant, intersublattice exchange coupling is antiferromagnetic, i.e., $J_{pp} < 0$, and it occurs between a given molecule and its four nearest neighbors in the $a$-$b$ plane. In the more recent work, moreover, the in-plane intrasublattice coupling with the two next-nearest neighbors and the interplanar coupling with four additional neighbors have been included. The interplanar coupling was found (Burakhovich et al., 1977; Stephens et al., 1983) to be very weak, which makes $\alpha$-oxygen, and $\beta$-oxygen, a quasi-two-dimensional magnetic system. The single-particle term $A S_x^2$ is due to the intramolecular spin–orbit and spin–spin interactions; the free-molecule value of $A$ is equal to 3.96 cm$^{-1} = 5.72$ K. This term tends to keep the directions of the molecular spin momenta perpendicular to the molecular axes, such that in $\alpha$- and $\beta$-oxygen the spins will lie in the $a$-$b$ plane. The additional single-particle term $B S_y^2$ is then added ad hoc in order to impose the observed in-plane anisotropy that forces the spins to lie parallel to the $b$ axis. Classical dipole models yielding the preferred magnetization axis and the order of magnitude of the empirical
$B$ values suggest that the term $BS^2$ actually represents the magnetic dipole–dipole interactions between the molecular spin moments.

With the use of the phenomenological spin Hamiltonian [Eq. (139)], mean field and spin-wave calculations have been made that yield the observed magnetic, optical, and thermodynamic properties. The antiferromagnetic spin-wave calculations are mostly based on the RPA method outlined in Section IV,C. The formalism is very simple in this case, because the basis for every molecule consists only of the three triplet spin states. By taking the mean field ground state on each molecule and the first excited state, which provides the single magnon states, the RPA equations can be solved exactly for the magnon frequencies. The calculated properties have been compared with experimental data and the coupling constants $J$, $A$, and $B$ in the Hamiltonian (139) have thus been determined empirically. The situation is not very satisfactory, however, since the various semiempirical studies on $\alpha$-O$_2$ have yielded substantially different sets of coupling constants, depending on the type of experimental data fitted. The discrepancies have been pointed out most clearly by De Fotis (1981), but also the more recent studies still yield rather different $J$, $A$, and $B$ values. Moreover, most of the empirical $A$ and $B$ values in solid O$_2$ deviate considerably from the values corresponding with the free-molecule zero-field splitting and the magnetic dipole moment, respectively. This is surprising since we expect the distortions of the molecular electronic charge distributions, due to the weak van der Waals interactions in the solid, to be minor.

B. The Complete Crystal Hamiltonian and the Coupling between Lattice Vibrations and Spin Dynamics

In a recent paper (Jansen and van der Avoird, 1985), two of us have proposed replacing the phenomenological spin Hamiltonian (139) by a spin Hamiltonian from first principles. By this qualification we mean that our Hamiltonian can be derived directly from the known properties of the O$_2$ molecules and their interactions. Such a Hamiltonian, which applies not only to $\alpha$-O$_2$, but also to any of the condensed phases, looks as follows:

$$H_{\text{spin}} = -\frac{1}{2} \sum_{p \neq p'} \sum_{m} 2J_{pp'}(\omega_p, \omega_{p'}, r_{pp'})S_p \cdot S_{p'}$$

$$+ \sum_{p} \sum_{m} (-1)^m A_{-m}(\omega_p)[S_p \otimes S_p]^{(2)}_m$$

$$+ \frac{1}{2} \sum_{p \neq p'} \sum_{m} (-1)^m T_{-m}(r_{pp'})[S_p \otimes S_{p'}]^{(2)}_m$$

(140)
The irreducible tensor product between two (spherical) vectors is defined in Eq. (37). An important feature of this Hamiltonian is that it explicitly describes the dependence of the coupling "constants" $J$, $A_m$, and $T_m$ on the distance vectors $r_{pp'}$ between the molecules and on the orientations $\omega_p = \{\theta_p, \phi_p\}$ of their axes, in contrast with the phenomenological Hamiltonian (139). Another important difference with the latter is that the *ad hoc* single-particle spin anisotropy term $BS^*_J$, which probably stands implicitly for the magnetic dipole-dipole interactions, has been replaced by a two-body operator that correctly represents these interactions. The distance and orientational dependence of the coupling parameters $J$, $A_m$, and $T_m$ has been obtained as follows.

The Heisenberg exchange coupling parameter $J$ is a scalar quantity; its dependence on $r_{pp'}$, $\omega_p$, and $\omega_p$ is described by expanding it in symmetry-adapted angular functions, just as the intermolecular potential in Eq. (15). The distance-dependent expansion coefficients have been explicitly obtained from *ab initio* quantum-chemical calculations (van Hemert *et al.*, 1983; Wormer and van der Avoird, 1984). These coefficients could be represented by steeply decaying exponential functions of the distance. The *ab initio* calculations refer to (O$_2$)$_2$ dimers with the triplet O$_2$ spins coupled to a singlet, a triplet, or a quintet. The exchange splitting between the dimer spin states has been obtained from a second-quantized hole-particle formalism, generalized to nonorthogonal orbitals (Wormer and van der Avoird, 1984), It was found that this exchange splitting could indeed be represented accurately by a Heisenberg effective spin Hamiltonian. The coupling parameter $J$ appeared to depend very sensitively on the distance between the O$_2$ molecules and, particularly, on their orientations (see Fig. 8). In Fig. 9 we have plotted the dependence of $J$ on the librational coordinates in $\alpha$-oxygen.

The molecular spin–anisotropy term, the second term in Eq. (140), depends on the angle between the O$_2$ spin momentum $S_p$ and the molecular axis. With respect to the global frame, this dependence can be expressed as in Eq. (140) with the second-rank tensor

$$A_m(\omega_p) = \frac{1}{3} A \sqrt{30} C_m^{(2)}(\theta_p, \phi_p)$$

(141)

The constant $A = 3.96$ cm$^{-1}$ has been obtained from the free-molecule zero-field splitting (Mizushima, 1975) and $C_m^{(2)}$ is a Racah spherical harmonic with $l = 2$. The tensor that describes the interaction between the magnetic dipole moments $g_e \mu_B S_p$, where $g_e$ equals 2.0023 and $\mu_B$ is the Bohr magneton, can be written immediately as

$$T_m(r_{pp'}) = -g_e^2 \mu_B^2 \sqrt{30} r_{pp'}^{-3} C_m^{(2)}(\hat{r}_{pp'})$$

(142)

In summing this term over the lattice, in the calculations described subsequently, the Ewald method (Born and Huang, 1954) had to be invoked.
Fig. 8. Orientational dependence of the average (spin-independent) exchange interaction energy $\overline{\Delta E} = V(\omega_p, \omega_p', r_{pp'})$ and the Heisenberg exchange coupling constant $J(\omega_p, \omega_p', r_{pp'})$ in the $O_2-O_2$ dimer at $r_{pp'} = 6$ bohrs. The full lines represent the results of all-electron calculations; the dashed line refers to a four-electron model. The multipole contributions to $\overline{\Delta E}$ are now drawn explicitly because they are negligible at $r_{pp'} = 6a_0$.

Since the $O_2$ molecule carries a triplet spin momentum, the spin Hamiltonian (140) has to be added to the Hamiltonian (23), which contains the kinetic energies and the spin-independent part of the intermolecular $O_2-O_2$ potential, in order to obtain the crystal Hamiltonian for solid $O_2$. The spin-independent $O_2-O_2$ potential can be partly extracted from the ab initio calculations on the $(O_2)_2$ dimer by averaging the calculated interac-
Fig. 9. Variation of the (intersublattice) exchange coupling parameter $J$ between the nearest neighbors in solid $\alpha$-$\text{O}_2$ along some normal coordinates of libration. The labels $L_a$ and $L_b$ refer to librations around the crystal $a$ and $b$ axes, respectively; see Fig. 7. The plus and minus signs denote in-phase and out-of-phase librations of the molecules on different sublattices.

The approximate solutions for the complete crystal Hamiltonian, which describe the coupled lattice vibrations (phonons, librons, mixed modes) and spin waves (magnons), can be obtained very elegantly via the mean field and RPA methods described in Sections IV,B and IV,C. This has
actually been done by Jansen and van der Avoird (1985) for α- and β-oxygen. All they had to add to the formalism applied by Briels et al. (1984) to solid nitrogen, was to multiply the basis \((111)\) by the triplet spin functions

\[
\Theta_{M_S}(\sigma_P) \quad \text{with} \quad S = 1 \quad \text{and} \quad M_S = 1, 0, -1
\]

to add a spin term \(H^S_P(\sigma_P)\) to the mean field Hamiltonian (117) and to extend the particle label \(P = \{n, i, K\}\) in the RPA Hamiltonian (122) to translations, librations, and spin "motions": \(K = \{T, L, S\}\). This extension leads to extra blocks in the RPA eigenvalue equations (126) that correlate the spin excitations and couple them to the phonons and librons.

In principle, one can obtain mixed phonon–libron–magnon modes. Such modes are not found in solid oxygen, however. The bilinear coupling terms between the lattice modes and the single-magnon spin modes vanish from the RPA Hamiltonian (122) because of symmetry. The excitations are either pure lattice vibrations, of (mixed) phonon–libron type, or pure magnons. The effective Hamiltonian for the lattice modes is obtained from the complete Hamiltonian by spin averaging Eq. (140), i.e., replacing \(S_P\) by \(\langle S_P \rangle\), and adding it to Eq. (23). The amplitude of the librations, 11° in α-oxygen at \(T = 0\) K, appears to be substantially smaller than in solid nitrogen. This agrees with the experimental data (Cahill and Leroi, 1969). The effective spin Hamiltonian is given by Eq. (140) with the coupling constants \(\langle J(\omega_P, \omega_P', \mathbf{r}_{PP'})\rangle\), \(\langle A_m(\omega_P)\rangle\), and \(\langle T_m(\mathbf{r}_{PP'})\rangle\) averaged over the translations and librations. Proceeding in this way, several of the problems outlined in Section VI,A can be solved.

The problem of the splitting of the \(E_g\) libron in β-oxygen into an \(A_g, B_g\) doublet in α-oxygen appears to have the following explanation. Given the small structural distortion at the β-α phase transition, this splitting is indeed far too large to be obtained from lattice dynamics calculations employing the usual spin-independent Hamiltonian (23). The spin orderings in β and α-oxygen are very different, however, yielding a strong discontinuity of \(\langle S_P \rangle \cdot \langle S_{P'} \rangle\) at the β-α transition. More precisely, one finds for the 120° spin arrangement in β-O\(_2\) that \(\langle S_P \rangle \cdot \langle S_{P'} \rangle = -0.5\) and for the antiferromagnetic ordering in α-O\(_2\) that \(\langle S_P \rangle \cdot \langle S_{P'} \rangle = -1\) for nearest neighbors. Introducing these values into the effective Hamiltonian for the lattice modes, the Heisenberg coupling parameter \(J(\omega_P, \omega_P', \mathbf{r}_{PP'})\) in Eq. (140) gets a very different weight in the β and α phases. We have mentioned already that this parameter is extremely anisotropic, and thus it has a strong influence on the librational motions (see Fig. 9). The \(A_g\) mode in α-O\(_2\) indeed obtains a much higher frequency than the \(E_g\) mode in β-O\(_2\), while the \(B_g\) mode is somewhat lowered. Using the anisotropic \(J(\omega_P, \omega_P', \mathbf{r}_{PP'})\) from \textit{ab initio} calculations (Wormer and van der Avoird, 1984) gives
quantitative agreement with the experimental splitting and shifts. Omitting the Heisenberg term yields a small splitting, just as in the earlier lattice dynamics calculations. This confirms the crucial role of this term in the libron-splitting mechanism.

Jansen and van der Avoird (1985) have also made spin-wave calculations as described earlier. The RPA equations with the effective spin Hamiltonian (140), averaged over the translations and librations, could be solved analytically for any wave vector $\mathbf{q}$. The optical ($\mathbf{q} = 0$) magnon frequencies emerging from these calculations are 6.3 and 20.9 cm$^{-1}$, in reasonable agreement with the experimental values 6.4 and 27.5 cm$^{-1}$. This agreement is very satisfactory if we realize that the spin Hamiltonian has been obtained from first principles, with none of its parameters fitted to the magnetic data.* We conclude that the RPA model, both for the lattice modes and the spin waves, when based on a complete crystal Hamiltonian from first principles, yields a realistic description of several properties of solid O$_2$ that were not well understood before.

Appendix

In this article we have used some of the concepts of quantum-statistical mechanics. These concepts can, of course, be found in the textbooks (Ter Haar, 1966; Feynman, 1972; McQuarrie, 1976), but the ideas that are most relevant to this paper are summarized in this appendix. In particular, we prove the thermodynamic variation principle, which has been applied several times.

In quantum-statistical physics, just as in the classical counterpart, one introduces a density operator $\rho$ such that the average value of any mechanical observable $X$ can be calculated as

$$\langle X \rangle = \text{Tr}(\rho X) \quad (A.1)$$

Depending on the boundary conditions imposed on the system and on the specific form of $\rho$, several ensembles are distinguished. Most often the system is assumed to have constant volume $V$ and the density operator is chosen to be

$$\rho = e^{\beta(A-H)} \quad (A.2)$$

* Actually, the long-range dispersion term in the spin-independent potential of Eq. (23), which affects the lattice vibrations and thus the averaged coupling parameters in Eq. (140), has been fitted to obtain the best lattice constants in $\alpha$-O$_2$. The magnetic data, and the libron splitting discussed, are very insensitive to this term, however.
The corresponding ensemble is therefore called canonical. The constant $A$ is chosen such that $\text{Tr}(\rho) = 1$, from which it follows that $\rho$ can be interpreted as defining a probability distribution over the eigenstates of the Hamiltonian $H$. It is easy to demonstrate that

$$A = -\beta^{-1} \ln Z$$  \hspace{1cm} (A.3)

with $Z = \text{Tr}(e^{-\beta H})$ and $\beta^{-1} = k_B T$, $k_B$ being the Boltzmann constant. The quantity $A$ corresponds with the Helmholtz free energy of the system.

The thermodynamic variation principle reads

$$A \leq A_0 + \langle H - H_0 \rangle_0$$  \hspace{1cm} (A.4)

with the free energy $A_0$ and the average $\langle \cdot \rangle_0$ referring to an approximate Hamiltonian $H_0$. The inequality holds for any $H_0$. In the classical limit it is a simple consequence of Jensen’s inequality known from integration theory (Rudin, 1966). In the quantum-mechanical case, its proof is more elaborate (Girardeau and Mazo, 1973; Feynman, 1972). Here we reproduce the proof of Girardeau and Mazo and define

$$Z(\lambda) = \text{Tr}(e^{X + \lambda Y})$$  \hspace{1cm} (A.5)

We need the derivatives of this quantity with respect to $\lambda$. The derivatives of an exponential operator are given by the rule

$$\frac{d}{d\lambda} e^{H(\lambda)} = e^{H(\lambda)} \int_0^1 dx e^{-xH(\lambda)} \frac{dH(\lambda)}{d\lambda} e^{xH(\lambda)}$$  \hspace{1cm} (A.6)

This rule is proved by writing

$$\frac{d}{d\lambda} e^{yH(\lambda)} = e^{yH(\lambda)} F(y)$$

and demonstrating, via some simple differentiations, that

$$\frac{dF(y)}{dy} = e^{-yH(\lambda)} \frac{dH(\lambda)}{d\lambda} e^{yH(\lambda)}$$

Since

$$\lim_{y \to 0} F(y) = 0$$

it follows that

$$F(y) = \int_0^y dx e^{-xH(\lambda)} \frac{dH(\lambda)}{d\lambda} e^{xH(\lambda)}$$
which, for \( y = 1 \), proves the rule (A.6). Applying this rule, with \( H(\lambda) = X + \lambda Y \), and using the invariance of the trace with respect to cyclic permutations of the operators, one finds for the derivatives of the quantity \( Z(\lambda) \) defined by Eq. (A.5) that

\[
Z'(\lambda) = \text{Tr}(Ye^{X+\lambda Y}) \quad \text{(A.7)}
\]

\[
Z''(\lambda) = \text{Tr} \left( Y \frac{d}{d\lambda} e^{X+\lambda Y} \right) \quad \text{(A.8)}
\]

Applying the rule (A.6) to Eq. (A.8) and using the cyclic invariance of the trace again, it follows for Hermitian operators \( X \) and \( Y \) that

\[
Z''(\lambda) = \int_0^1 dx \, \text{Tr}\{C(x)C(x)\} \quad \text{(A.9)}
\]

with

\[
C(x) = e^{\frac{1}{2}x(X+\lambda Y)}Ye^{\frac{1}{2}(1-x)(X+\lambda Y)}
\]

Knowing the derivatives of the quantity \( Z(\lambda) \), we can expand it as a Taylor series:

\[
Z(\lambda) = Z(0) + \lambda Z'(0) + \frac{1}{2} \lambda^2 Z''(\lambda')
\]

for some \( \lambda' \) lying in the interval \( 0 \leq \lambda' \leq \lambda \). Since the second derivative, expressed as in Eq. (A.9), must satisfy the relation

\[
Z''(\lambda) \geq 0 \quad \text{(A.10)}
\]

we find the inequality

\[
Z(1) \geq Z(0) + Z'(0) \quad \text{(A.11)}
\]

When choosing

\[
X = -\beta H_0 - \beta \langle H - H_0 \rangle_0, \quad Y = -\beta (H - H_0) + \beta \langle H - H_0 \rangle_0
\]

it can be shown, using Eq. (A.7), that \( Z'(0) = 0 \), and the inequality (A.11) becomes

\[
\text{Tr}[\exp(-\beta H)] = \text{Tr}[\exp(X + Y)] \geq \text{Tr}[\exp(X)] \geq \text{Tr}[\exp(-\beta H_0)] \exp(-\beta \langle H - H_0 \rangle_0) \quad \text{(A.12)}
\]

Taking the logarithm of this inequality and multiplying by \( -\beta^{-1} \) yields the thermodynamic variation principle, Eq. (A.4).

When the free energy \( A \) is given as a function of its characteristic variables, viz., \( T \) and \( V \), it is possible to calculate all thermodynamic properties of the system. We list, for instance, the...
(entropy) \[ S = -\left(\frac{\partial A}{\partial T}\right)_V \]

(energy) \[ E = A + TS \]

(pressure) \[ p = -\left(\frac{\partial A}{\partial T}\right)_T \]

(specific heat) \[ C_v = T \left(\frac{\partial S}{\partial T}\right)_V = -T \left(\frac{\partial^2 A}{\partial T^2}\right)_V \]

\[ C_p = T \left(\frac{\partial S}{\partial T}\right)_p = C_v + \alpha_p^2 \frac{TV}{kT} \]

(thermal expansion coefficient) \[ \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \]

(compressibility) \[ \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \]

For details we refer the reader to the textbooks mentioned.

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