Ab initio description of large amplitude motions in solid N$_2$. I. Librons in the ordered $\alpha$ and $\gamma$ phases

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Starting from an ab initio intermolecular potential, we have calculated the mean field states for the librations in the ordered $\alpha$ and $\gamma$ phases of solid N$_2$, using a basis of spherical harmonics up to $l_{\text{max}} = 12$. The correlation between the mean field solutions was then taken into account via a libron model based on the random-phase approximation or time-dependent Hartree method. The calculated librational frequencies are rather accurate, showing that the discrepancies in earlier results with the ab initio potential are mainly due to the breakdown of (quasi-)harmonic models for the librations, even in the ordered phases.

I. INTRODUCTION

Solid nitrogen under its own vapor pressure can exist in two phases, the low temperature $\alpha$ phase and the high temperature $\beta$ phase. The $\alpha$–$\beta$ phase transition occurs at temperature $T_{\alpha\beta} = 35.6$ K. Above 4 kbar a third phase is known, the $\gamma$ phase, and at still higher pressures, above 49 kbar, a new phase ($\delta$) has recently been found$^{1,2}$ and another phase ($\epsilon$) has been predicted.$^3$ In these papers we shall look at the $\alpha$, $\beta$, and $\gamma$ modifications which have been extensively studied experimentally. The $\alpha$ and $\gamma$ phases are ordered solids in which the molecules perform oscillations around their equilibrium positions and equilibrium orientations; especially the angular oscillations have considerable amplitudes. In the disordered $\beta$ phase the angular motions are even more violent such that the orientational distribution function is expected to be almost constant for all angles. A schematic drawing of the structures of these phases is given in Figs. 1(a), (b), and (c). For more information on the results of experimental and theoretical work on solid nitrogen prior to 1976 we refer to the review of Scott.$^4$

In the following we report the results of a new theoretical study of the molecular motions in solid nitrogen. There are two main reasons which make a study like this highly interesting.

(i) The starting point of any study of the dynamics of molecular crystals is the description of the intermolecular potential. Normal practice is to introduce a model description of this potential in which several parameters are free to be chosen. Next the dynamics calculations are performed for different values of the model parameters, and finally these parameters are fixed by a minimization of the difference between the calculated and observed properties of the crystals, such as structures and phonon frequencies. Much work has been done$^5-7$ on the choice of the model potentials and there exist now several models which seem to do their job reasonably well. A great disadvantage of the procedure described above, however, is that the final parameters depend largely on the approximations made in the dynamics calculations. The model potentials thus obtained may be satisfactory for representing the (solid state) data to which they have been fitted, but in the cases where this has been investigated, they did not yield other (gas phase and liquid state) properties very well. It is therefore of great value that, for nitrogen, we can use a potential which was obtained from quantum chemical calculations,$^8,9$ independent of any dynamics study. This potential has now been tested in several bulk properties: virial coefficients,$^10$ transport properties, Rayleigh linewidths, and rotational relaxation coefficients$^11$ of gaseous N$_2$ and liquid state properties,$^12$ which are generally found to be quite accurate. It has been used in self-consistent phonon (SCP) calculations on solid N$_2$ with good results for the static properties and excellent agreement with experiment for the translational phonon frequencies. The librational phonon frequencies came out about 30% too high, but this was believed to be due mainly to the failure of the dynamical (SCP) model to account for the strongly anharmonic librations. In the present paper we investigate these librations.

(ii) In most molecular crystals the molecules are trapped in deep potential wells. The lattice dynamics calculations can be done within the harmonic approximation, and they are by now fairly standard.$^5$ In some cases anharmonic effects appear to be important and these are most often introduced perturbatively.$^5$ At higher temperatures, however, especially in the neighborhood of phase transitions, molecular motions are so violent that perturbation calculations do not seem to be of much value. (Moreover, in view of the fact that the perturbation series for a quartic anharmonic oscillator has a vanishing range of convergence,$^{14}$ one should be very careful with lattice dynamics perturbation calculations.) In solid nitrogen, especially in the $\beta$ phase, but, to a lesser degree also in $\alpha$ and $\gamma$ nitrogen, the molecules perform angular motions which are intermediate between harmonic librations and free rotations. The study of molecular motions in this region is far from standard, and poses a challenging problem.

In this paper we confine ourselves to the pure rotational motions of the molecules. In a harmonic approximation this would be possible exactly at certain points in the Brillouin zone. In general the decoupling of the translational and the rotational motions can only be justified approximately. Examples of systems in which it has been successfully applied are the methane and deuterated methane crystals$^{15-17}$ and the hydrogen crystals.$^{18-20}$ Also in the case of nitrogen decoupling has been applied previously.$^{21-24}$ In a forthcoming
paper we will describe the coupled rotational-translational motions of the molecules.

Let us briefly outline the theoretical model that we have used. In contrast with the SCP scheme\textsuperscript{5,25} which is essentially a (quasi-)harmonic model, we approach the solution from the side of freely rotating molecules. Using free rotor states as a basis we construct states for each particle, which describe its rotational motion and which effectively contain the influence of all neighboring molecules. Thus it is possible to retain the full anharmonic potential, without any further approximation. After we have constructed the single particle states, we use these states to build the states of the whole crystal and we calculate the corresponding energies. Again it is possible to include the full potential without further approximation. The approximation in the above procedure is introduced by employing only part of the single particle states. The above procedure is not at all new but it has not been applied very extensively, and never with an \textit{ab initio} potential. Moreover, we shall extend the existing theory, by looking at the stability conditions for the mean field solutions (in paper II) and by including explicitly the translational coupling (in paper III). Therefore we give in Sec. II the formulas that we have programmed; references to the original literature can also be found in this section.

II. MODEL AND THEORETICAL METHODS

A. The Hamiltonian

The system we are concerned with consists of a periodic crystal of librating molecules with their centers of mass fixed at the equilibrium positions, the lattice sites \( P \). After the introduction of a suitably chosen unit cell for the "center of mass crystal," the position vector of \( P = \{n, z\} \) can be written as \( R_{P} = R_{n} + r \), where \( n \) represents the three indices of the unit cell to which \( P \) belongs, \( R_{n} \) the position vector of the origin of this unit cell, and \( r \) the position vector of \( P \) relative to this origin. The orientation of a molecule at position \( P \) will be described by the polar angles \( \Theta_{P} = (\theta_{P}, \phi_{P}) \) of its molecular axis. The intermolecular energy of two molecules at positions \( P \) and \( P' \), respectively can then be written as

\[
\Phi(R_{PP'}, \Theta_{P}, \Theta_{P'}) = \sum_{l} \sum_{m} \Phi_{l}(R_{PP'}) \sum_{m} \left( \begin{array}{ccc}
  l_{1} & l_{2} & l_{3} \\
  m_{1} & m_{2} & m_{3}
\end{array} \right)
\times C^{(l)}_{m_{1}}(\Theta_{P}) C^{(l)}_{m_{2}}(\Theta_{P'}) C^{(l)}_{m_{3}}(\hat{R}_{PP'}).
\]

Here, \( R_{PP'} = R_{P} - R_{P'} \) and \( \hat{R}_{PP'} \) is the unit vector along \( R_{PP} \); \( l \) and \( m \) denote the index sets \( \{l_{1}, l_{2}, l_{3}\} \) and \( \{m_{1}, m_{2}, m_{3}\} \), respectively; \( C^{(l)}_{m}(\Theta) \) is a Racah spherical harmonic\textsuperscript{26} and the symbol following the second summation sign is a 3-j coefficient. The coefficients \( \Phi_{l}(R_{PP'}) \) are related to the \textit{ab initio} calculated coefficients \( V_{l_{1}l_{2}l_{3}}(R_{PP'}) \) of Berns and van der Avoird\textsuperscript{9} by

\[
\Phi_{l}(R_{PP'}) = |(2l_{1} + 1)(2l_{2} + 1)(2l_{3} + 1)|^{1/2} V_{l_{1}l_{2}l_{3}}(R_{PP'}). \]

In general they satisfy several symmetry relations\textsuperscript{27,28} which in the case of homonuclear diatomic molecules imply that only coefficients with \( l_{1}, l_{2}, \) and \( l_{3} \) even can be nonzero.

We write the crystal Hamiltonian as a sum of one-particle terms and two-particle terms plus a constant:
\[ H = U^c + \sum_p L_p(\Omega_p) + \frac{1}{2} \sum_{p \neq p'} \Phi_{pp'}(\Omega_p,\Omega_{p'}) , \]  

where

\[ L_p(\Omega_p) = B | \mathbf{J}(\Omega_p) |^2 + \sum_{n,m} V_n^m(P)C_m^l(\Omega_p) , \]

\[ \Phi_{pp'}(\Omega_p,\Omega_{p'}) = \sum_{l,m} C_{m}^{(l)}(\Omega_p)X_{m,n}^{(l)}(P,P')C_{m'}^{(l)}(\Omega_{p'}) . \]

The primes at the summation signs in Eqs. (3a) and (3b) indicate that the value \( l = 0 \) should be omitted from the summations (this convention is used throughout this paper). \( \mathbf{J}(\Omega_p) \) is the angular momentum vector operator associated with the molecule at position \( P \), and \( B \) its rotation constant. Because we assume that the centers of mass of the molecules are fixed to their equilibrium positions, the first term in Eq. (3a) represents the complete kinetic energy of the molecule at position \( P \). The constant \( U^c \) and the coefficients \( V_m^l(P) \) and \( X_{m,n}^{(l)}(P,P') \) are given by

\[ U^c = \frac{1}{2} \sum_{p \neq p'} \frac{\varphi_{0,0}(R_{pp'})}{p} + \sum_p U_p , \]

\[ V_m^l(P) = (2l + 1)^{-1/2}(1 - 1)^l \sum_{p \neq p'} \frac{\varphi_{l,0}(R_{pp'})}{p}C_m^{(l)}(\hat{R}_{pp'}) \ast , \]

\[ X_{m,n}^{(l)}(P,P') = \sum_{l,m_n} \varphi_{l}(R_{pp'}) \left( \begin{array} {ccc} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array} \right) C_{m_n}^{(l)}(\hat{R}_{pp'}) . \]

The quantities are invariant under any lattice translation of the center of mass crystal; in fact in the nitrogen crystals \( U_p \) and \( V_m^l(P) \) are also independent of the sublattice index \( i \), so that we can omit the label \( P \). Finally, because we neglect the translational displacements, many terms will cancel in Eq. (4b) at points of high site symmetry. For example, in \( \alpha - N_2 \) the \( l = 2,0,2 \) and \( l = 2,0,2 \) terms drop out completely.

**B. The mean field approximation**

The mean field approximation\(^\text{15,17,29}^\) is based on the Gibbs–Bogoliubov inequality\(^\text{10,31}^\),

\[ A_{\text{var}} = A_0 + \langle H - H_o \rangle_{\Omega_p} - A \]

where \( H_0 \) can be any Hamiltonian. \( \langle X \rangle_0 \) is the thermodynamic average of the operator \( X \) over the eigenstates of \( H_o \), i.e., \( \langle X \rangle_0 = +^\text{1} \text{Tr} X \exp\{ - \beta H_0 \} \) with \( Z_0 = \text{Tr} \exp\{ - \beta H_0 \} \) as usual (\( k_B T \) is Boltzmann's constant); \( A_0 = - k_B T \ln Z_0 \) and \( A \) is the free energy of the system with Hamiltonian \( H \). The approximation then consists of letting \( H_0 \) be a sum of one-particle operators

\[ H_0 = \sum_p H_{\text{MF}}(\Omega_p) , \]

such that \( A_{\text{var}} \) is stable against all variations of \( H_{\text{MF}}(\Omega_p) \). This leads to the coupled set of equations

\[ H_{\text{MF}}(\Omega_p) = L(\Omega_p) + \sum_{p \neq p'} \langle \Phi_{pp'}(\Omega_p,\Omega_{p'}) \rangle_p . \]

Here \( \langle X \rangle_p \) denotes the thermodynamic average of \( X \) over the eigenstates of \( H_{\text{MF}}(\Omega_p) \). The Eqs. (7) have to be solved self-consistently. In principle, \( H_{\text{MF}} \) can be different for every \( P \). In practice, of course, one imposes symmetry relations on the solutions of Eq. (7). This means that one chooses a unit cell, compatible with the symmetry of the center of mass crystal, and then puts \( H_{\text{MF}} \) equal to \( H_{\text{MF}} \) for all \( P \) and \( P' \) for which \( R_{pp'} \) is equal to a lattice vector. Next, one introduces unit cell symmetry, also compatible with the symmetry of the center of mass crystal, such that the mean field Hamiltonians on different sublattices are related.

In this paper we restrict ourselves to those solutions of Eq. (7) that have the experimentally observed symmetry. As a result we have, in all cases, only one independent molecule per unit cell, whose mean field is given by

\[ \Phi_{\text{MF}}(\Omega_p) = \sum_{k,n} F_{n}^{(k)}(P)C_{m}^{(n)}(\Omega_p) , \]

\[ F_{n}^{(k)}(P) = \sum_{p} X_{m,n}(P,P')(C_{m}^{(n)})_p . \]

The molecular field acting on a molecule at position \( P' \) is then completely determined by the symmetry of the unit cell, and can be obtained by a rotation of the mean field of the independent molecule over the Euler angles \( \omega_{p'} = (\alpha_{p'},\beta_{p'},\gamma_{p'}) \). As a result, the mean field of the molecule at \( P' \), when measured in a coordinate frame which is rotated over the Euler angles \( \omega_{p'} \) relative to the laboratory frame, is given by \( \Phi_{\text{MF}}(\Omega_{p'}) \), where \( \hat{\Omega}_{p'} \) denotes the polar angles of the molecule at \( P \) relative to the rotated coordinate frame. Because in all cases the Euler angles are such that \( L(\Omega_{p'}) \) is invariant under the corresponding transformation, the mean field Hamiltonian at \( P' \) is given by \( H_{\text{MF}}(\hat{\Omega}_{p'}) \). From this we conclude that the thermodynamic average of \( C_{m}^{(n)}(\hat{\Omega}_{p'}) \) is equal to \( \langle C_{m}^{(n)} \rangle_p \), and therefore that

\[ \langle C_{m}^{(n)} \rangle_p = \sum_{m} \langle C_{m}^{(k)} \rangle_{p} D_{m,n}^{(k)}(\omega_{p'}) . \]

For the Euler angles and the Wigner matrices \( D_{m,n}^{(k)}(\omega) \) we use the conventions of Edmonds.\(^\text{26}^\) Introducing Eq. (9) into Eq. (8b), we find

\[ F_{n}^{(k)}(P) = \sum_{k,n} Y_{m,n}^{(k)}(P)(C_{m}^{(n)})_p , \]

\[ Y_{m,n}^{(k)}(P) = \sum_{p \neq p'} \sum_{m} X_{m,n}^{(k)}(P,P')D_{m,n}^{(k)}(\omega_{p'}) . \]

Equations (7), (8a), and (10) constitute the set of equations that we shall solve self-consistently. In order to calculate \( \langle C_{m}^{(n)} \rangle_p \), we first diagonalize \( H_{\text{MF}}(\Omega_p) \), and then perform the averaging in the obvious way. The diagonalization gives us eigenfunctions of the mean field Hamiltonian, which will be used in the next section. In order to perform the diagonalization in practice we must introduce a basis; the most convenient basis for the current problem is the basis of tesseral harmonics because the mean field Hamiltonian is real and symmetric in this basis.
Once we have obtained the mean field Hamiltonians we can calculate the thermodynamic properties\(^7\) of the system. The free energy is found from Eqs. (5) and (6), and other quantities follow from it:

\[
A = -k_B T \sum_P \ln Z_{\text{MF}}^P + \sum_P U_P - \frac{1}{2} \sum_P \langle \Phi_{\text{MF}}^P \rangle ,
\]

\[
S = -\frac{\partial A}{\partial T} = k_B T \sum_P \ln Z_{\text{MF}}^P + \frac{1}{T} \sum_P \langle H_{\text{MF}}^P \rangle ,
\]

\[
E = A + TS = \sum_P U_P + \sum_P \langle H_{\text{MF}}^P \rangle - \frac{1}{2} \sum_P \langle \Phi_{\text{MF}}^P \rangle .
\]

In order to get the entropy in its final form [Eq. (11b)] we have made use of \(\Sigma_P \langle \partial H_{\text{MF}}^P / \partial T \rangle_P = \frac{1}{2} \Sigma_P \partial / \partial T \langle \Phi_{\text{MF}}^P \rangle_P\), which follows from Eq. (7).

C. Simple libron theory

The mean field treatment described above provides us with a set of single particle states \(|\psi_{\text{MF}}^P(\Omega_c)\rangle\) and corresponding single particle energies \(\epsilon_{\text{MF}}\) given by

\[
H_{\text{MF}}^P(\Omega_c)|\psi_{\text{MF}}^P(\Omega_c)\rangle = \epsilon_{\text{MF}}|\psi_{\text{MF}}^P(\Omega_c)\rangle,
\]

where all mean field Hamiltonians have the same symmetry, and therefore all energies are independent of \(P\). Because \(H_{\text{MF}}^P(\Omega_c)\) depends on the temperature \(T\), the states and energies also depend on \(T\). From the single particle states we now obtain mean field states for the crystal:

\[
|\Psi_{\text{MF}}\rangle = \prod_{\alpha} \rho_{\alpha} |\psi_{\text{MF}}^\alpha(\Omega_{\alpha})\rangle |\psi_{\text{MF}}^\beta(\Omega_{\beta})\rangle ...|\psi_{\text{MF}}^N(\Omega_{\alpha})\rangle,
\]

where \(Z\) is the number of molecules in the unit cell and \(N\) the number of unit cells. In the construction of these states we have taken into account the complete anisotropy and anharmonicity of the Hamiltonian. The mean field states do not show, however, any correlation between the motion of different molecules. The simplest way to obtain "correlated states" is by diagonalization of the full Hamiltonian in the subspace spanned by the mean field states \(|\psi_{\text{MF}}^\alpha(\Omega_{\alpha})\rangle\) (at \(T = 0\) K) with at most one \(\alpha\) different from zero, where \(|\psi_{\text{MF}}^\alpha(\Omega_{\alpha})\rangle\) denotes the ground state at position \(P\). It is not difficult to show that the Brillouin theorem is valid in this case [i.e., when \(T = 0\) K]:

\[
\langle \Psi_{\text{MF}}^0 | H | \Psi_{\text{MF}}^\alpha \rangle = 0.
\]

Here \(|\Psi_{\text{MF}}^0\rangle\) denotes the mean field ground state of the crystal and \(|\Psi_{\text{MF}}^\alpha \rangle\) a crystal state with an excitation to the single particle state \(\alpha\) at position \(P\). From this theorem it follows that the ground state remains unchanged and that we can find the excitation energies of the crystal from a diagonalization of \(\tilde{H} = H - \langle \Psi_{\text{MF}}^0 | H | \Psi_{\text{MF}}^\alpha \rangle\) in a basis of excited states. In order to diagonalize \(\tilde{H}\), we adapt this basis to the translation symmetry of the crystal, i.e., we take basis functions

\[
|\Psi_{\beta}^\gamma\rangle = \frac{1}{\sqrt{N}} \sum_{\alpha} e^{i q_{\alpha} R_{\alpha}} |\psi_{\text{MF}}^\alpha(\Omega_{\alpha}[\gamma])\rangle.
\]

In this basis \(\tilde{H}\) is diagonal in \(q\), and its elements are

\[
\langle \Psi_{\beta}^\gamma | H | \Psi_{\alpha}^\delta \rangle = \delta_{\alpha,\gamma} \epsilon_{\beta} - \epsilon_{\alpha} + \Phi(q)_{\alpha,\beta},
\]

\[
\Phi(q)_{\alpha,\beta} = \sum_n e^{i q_{\alpha} R_{n}} \langle \psi_{\text{MF}}^\alpha(\Omega_{\alpha}[\beta]) | \psi_{\text{MF}}^\beta(\Omega_{\alpha}[\beta]) | \rangle.
\]

In the derivation of this result we have used the translational symmetry, and the fact that at \(T = 0\) the ground state average is equivalent to the thermodynamic average, which allowed us to substitute Eq. (7). In the sum in Eq. (16b) the self-interaction \(\Phi_{\alpha,\alpha}\) must be put equal to zero. Introducing Eq. (13b) into Eq. (16b) we find

\[
\Phi(q)_{\alpha,\beta} = \sum_{\Omega_{\alpha},\Omega_{\beta}} \sum_{\Omega_{\alpha},\Omega_{\beta}} \langle \psi_{\text{MF}}^\alpha(\Omega_{\alpha}) | \psi_{\text{MF}}^\alpha(\Omega_{\beta}) | \rangle Z^\Omega_{\alpha,\beta}(q)_{\alpha,\beta}.
\]

D. The random phase or time-dependent Hartree approximation

A shortcoming of the theory described in the preceding subsection is the absence of correlation between the molecular motions in the ground state. The simplest theory which incorporates correlation effects into the ground state is based on the random phase approximation. In this approximation,\(^{21,23,24}\) the Hamiltonian is written as a quadratic form in the excitation operators \((E_{\alpha}^\alpha)^\dagger\) and their Hermitian conjugates \(E_{\alpha}^\alpha\); the operator \((E_{\alpha}^\alpha)^\dagger\) excites a molecule at position \(P\) from its mean field ground state to the excited state \(\alpha\). Linear terms are absent because of the Brillouin theorem, Eq. (14). Because the Hamiltonian contains all quadratic terms, certain matrix elements between states that differ in two excitations are taken into account, and this will affect the ground state. The next step is to restrict \(\alpha\) to a few excited mean field states on each molecule and to approximate the commutators of \((E_{\alpha}^\alpha)^\dagger\) and \((E_{\alpha}^\alpha)^\dagger\) as boson commutators. In Dunmore’s application of the random-phase approximation to \(\alpha-N_2\) only the lowest (twofold degenerate) excited mean field state was included\(^{23,24}\); we investigate the effect of the higher states. Finally, the quadratic boson Hamiltonian is diagonalized which leads to the elementary excitations of the crystal.

It is well known\(^{22,23}\) in the case of many-fermion systems, that the equations which result from the random phase approximation can be derived in many alternative ways. In our case too, the final equations can be found\(^{34}\) in several ways. In an Appendix we shall give a derivation by means of the time-dependent Hartree (TDH) method.\(^{16,35,36}\) We do this because the TDH formulas are related to the stability conditions for the mean field solutions which we investigate in paper II and, moreover, because we wish to generalize the theory, in paper III, in order to attack the problem of rotation-translation coupling.
With any lattice Hamiltonian it is possible to label the states and corresponding energies with a vector \( \mathbf{q} \) from the first Brillouin zone. The result of the Appendix is that the

\[
M(q) = \begin{pmatrix}
    A - B(q) & -B(q) \\
    B(q) & A + B(q)
\end{pmatrix}
\begin{pmatrix}
P & O \\
O & P
\end{pmatrix}
\begin{pmatrix}
    \chi - \Phi(q) \\
    -\Phi(q)
\end{pmatrix}
\]

It is not difficult to demonstrate that to every positive eigenvalue there corresponds a negative eigenvalue of the same absolute value; this is related to the fact that with any excitation \( E_{a}(q) - E_{b}(q) \) there is a deexcitation \( E_{b}(q) - E_{a}(q) \). Moreover, it is not difficult to prove\(^3\) that the squares of the \( A^{(k)}(q) \) are determined by the symmetric generalized eigenvalue problem:

\[
[\chi - 2\Phi(q)]\mathbf{c} = [A^{(k)}(q)]^{2}\mathbf{P}\mathbf{c} - \chi\mathbf{P}\mathbf{c}
\]

with \( \Phi(q)_{\alpha,\alpha',\tau} \) given by Eq. (16b). The diagonal matrices \( \mathbf{P} \) and \( \chi \) are defined by

\[
\begin{align*}
P_{\alpha,\alpha',\tau} &= \delta_{\alpha,\alpha'}\delta_{\tau,\tau'}(P^{(0)}_{\alpha} - P^{(0)}_{0}) , \\
\chi_{\alpha,\alpha',\tau} &= \delta_{\alpha,\alpha'}\delta_{\tau,\tau'}(\epsilon^{(0)}_{\alpha} - \epsilon^{(0)}_{0})/P^{(0)}_{\alpha} - P^{(0)}_{0} ,
\end{align*}
\]

and the matrices \( \mathbf{A} \) and \( \mathbf{B} \) by

\[
\begin{align*}
\mathbf{A} &= \mathbf{P}\chi , \\
\mathbf{B}(q) &= \mathbf{P}\Phi(q) .
\end{align*}
\]

In the limit \( T \to 0 \), the occupation numbers \( P(0) \) and \( P(\alpha) \) are 1 and 0, respectively, and Eqs. (19) and (21a) and (21b) are identical to the RPA equation. For \( T > 0 \), there is a slight difference between the time-dependent Hartree method and the RPA method.

There exists a simple relation between the RPA results and the results of Raichs libron theory (see Sec. II C). In the limit \( T \to 0 \), the left upper matrix \( \mathbf{A} - \mathbf{B}(q) \) of \( \mathbf{M}(q) \), with \( \mathbf{A} \) and \( \mathbf{B}(q) \) given by Eqs. (21a) and (21b) is identical to the matrix defined by Eqs. (16a) and (16b). If one restricts the basis to the first excited mean field level for each particle, \( \mathbf{A} \) is a constant times the unit matrix. In that case, one finds\(^34\) the following simple relation:

\[
A^{(k)}(q) = [2(\epsilon^{(1)} - \epsilon^{(0)})\delta_{\alpha}(q) - (\epsilon^{(1)} - \epsilon^{(0)})^{2}]^{1/2}
\]

between the RPA excitation energies \( A^{(k)}(q) \) and the excitation energies \( \delta_{\alpha}(q) \) obtained by means of the simple libron theory of Sec. II C.

\[
S_{\alpha m}(\Omega) = \left\{ \frac{2l + 1}{8\pi} \right\}^{1/2} \left\{ (-1)^{m} C_{m}^{(l)}(\Omega) + C_{m}^{(l)}(\Omega) \right\} , \quad m > 0 ,
\]

\[
S_{\alpha 0}(\Omega) = \left\{ \frac{2l + 1}{4\pi} \right\}^{1/2} C_{m}^{(l)}(\Omega) , \quad m = 0 ,
\]

\[
S_{\alpha m}(\Omega) = -i \left\{ \frac{2l + 1}{8\pi} \right\}^{1/2} \left\{ (-1)^{m} C_{-m}^{(l)}(\Omega) - C_{m}^{(l)}(\Omega) \right\} , \quad m < 0 ,
\]

Matrix elements are easily obtained by use of\(^26\)

\[
\int \frac{d\Omega}{4\pi} C_{m_{1}}^{(l_{1})}(\Omega) C_{m_{2}}^{(l_{2})}(\Omega) C_{m_{3}}^{(l_{3})}(\Omega) = \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ m_{1} & m_{2} & m_{3} \end{pmatrix} .
\]

**II. RESULTS AND DISCUSSION**

**A. General remarks**

We have performed our calculations with the \textit{ab initio} calculated potential of Berns and van der Avoird.\(^7\) The coefficients in the spherical expansion of this potential are given by

\[
\varphi_{i}(R) = C_{i}^{\text{mult}} R^{-(l_{i} + l_{i} + 1)} + C_{i}^{(6)} R^{-6} + C_{i}^{(8)} R^{-8} + C_{i}^{(10)} R^{-10} .
\]

For the sake of completeness we have reproduced in Table I the coefficients which together specify the potential.

In order to solve the mean field equation we have imposed the experimentally observed symmetry on the solutions. A schematic drawing of the crystal structures is given in Fig. 1. As to the choice of the cell parameters, let us make a few remarks. In a combined mean field treatment of the translational and rotational degrees of freedom, which will be given in paper III, one can vary the cell parameters in order to obtain the free energy \( A \) as a function of \( V \) and \( T \).

Using the thermodynamic data of the vapor, which are easy to calculate, one can then calculate the cell parameters of the crystal along the solid-vapor equilibrium line. These cell parameters should actually be used in a study of the dynamics of the crystals, i.e., in the formulas which eventually yield the libron frequencies. Since we treat only the rotational degrees of freedom in the present paper, however, this procedure would lead to too small values of the cell parameters, and it would be unreasonable to compare the calculated libron frequencies with the experimental ones. Therefore, we have chosen to effectively average over the translational phonons by using the experimental cell parameters, which are given in Fig. 1.

We have performed the mean field calculations not in the usual basis of spherical harmonics, but in a basis of tesseral harmonics, because then the mean field Hamiltonian is real and symmetric. The tesseral harmonics are defined as

\[
\begin{align*}
Jansen, Briels, and van der Avoird: Large amplitude motions in solid N_{2} .
\end{align*}
\]
TABLE I. Expansion coefficients of the \textit{ab initio} $N_2-N_2$ potential.

\begin{tabular}{c c c c c c c c c c}
\hline
$l_1$ & $l_2$ & $l_3$ & $C_{l_1}^{\text{exp}}$ & $C_{l_2}^{\text{exp}}$ & $C_{l_3}^{\text{exp}}$ & $C_{l_1}^{\text{mff}}$ & $C_{l_2}^{\text{mff}}$ & $C_{l_3}^{\text{mff}}$ & $C_{l_1}^{\text{corr}}$ \\
\hline
0 & 0 & 0 & 44.258 & -4.231 \times 10^{-3} & -2.946 \times 10^{-4} & -2.239 \times 10^{-5} & 44.258 & -4.231 \times 10^{-3} & -2.946 \times 10^{-4} & -2.239 \times 10^{-5} \\
0 & 0 & 2 & 197.31 & 2.774 \times 10^{-2} & -5.457 \times 10^{-4} & 1.829 \times 10^{-5} & 2.774 \times 10^{-2} & -5.457 \times 10^{-4} & 1.829 \times 10^{-5} \\
0 & 0 & 4 & 38.781 & 4.710 & -14.731 & -1.862 \times 10^{-5} & 4.710 & -14.731 & -1.862 \times 10^{-5} \\
0 & 0 & 6 & 76.213 & 1.851 \times 10^{-3} & -5.457 \times 10^{-4} & 1.829 \times 10^{-5} & 1.851 \times 10^{-3} & -5.457 \times 10^{-4} & 1.829 \times 10^{-5} \\
4 & 0 & 0 & 3.045 & 0.045 & -0.121 & -0.121 & 0.045 & -0.121 & -0.121 \\
4 & 0 & 2 & 0.972 & -2.946 \times 10^{-4} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & -2.946 \times 10^{-4} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
4 & 0 & 4 & 38.407 & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} \\
4 & 0 & 6 & 5.057 & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
4 & 2 & 0 & 5.057 & 0.266 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & 0.266 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
4 & 2 & 2 & 13.263 & 2.814 \times 10^{-5} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & 2.814 \times 10^{-5} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
4 & 2 & 4 & 38.407 & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} \\
4 & 2 & 6 & 5.057 & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
6 & 0 & 0 & 0.045 & 0.045 & -0.121 & -0.121 & 0.045 & -0.121 & -0.121 \\
6 & 0 & 2 & 0.972 & -2.946 \times 10^{-4} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & -2.946 \times 10^{-4} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
6 & 0 & 4 & 38.407 & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} \\
6 & 0 & 6 & 5.057 & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
6 & 2 & 0 & 5.057 & 0.266 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & 0.266 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
6 & 2 & 2 & 13.263 & 2.814 \times 10^{-5} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & 2.814 \times 10^{-5} & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
6 & 2 & 4 & 38.407 & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} & 2.255 \times 10^{-4} & 1.829 \times 10^{-5} & 1.829 \times 10^{-5} \\
6 & 2 & 6 & 5.057 & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} & -0.121 & -2.239 \times 10^{-5} & -2.239 \times 10^{-5} \\
\hline
\end{tabular}

*In kJ mol
$^{-1}$
.

\*In kJ mol
$^{-1}$
 nm
$^{-1}
$.

\*In kJ mol
$^{-1}$
 nm
$^{-3}$.

\*In kJ mol
$^{-1}$
 nm
$^{-5}$.

\*In kJ mol
$^{-1}$
 nm
$^{-10}$.

We have always assumed that the crystal was composed of either \textit{ortho} molecules only, or \textit{para} molecules only. In those cases the basis was restricted to tesseral harmonics with even or odd $l$, respectively. All functions were included up to $l_{\text{max}} = 10/9$ inclusive for \textit{ortho/para} $\alpha$-nitrogen, and to $l_{\text{max}} = 12/11$ for \textit{ortho/para} $\gamma$-nitrogen. This was always sufficient\cite{37} to have the ground state energy converged to within 0.5 cm$^{-1}$ and the first excited state to within 1 cm$^{-1}$.

In \textit{ortho} we have extended the lattice summations over six shells. This means that we have neglected the potential for all values of the intermolecular distance beyond 9.87 Å. The same interaction radius has been used in $\beta$ and $\gamma$ nitrogen. In Dunmore's calculations\cite{23,24} on $\alpha$-$N_2$ he has assumed that the effective lattice potential has cylindrical symmetry around the molecular equilibrium axes (the body diagonals of the cubic unit cell, see Fig. 1). We have not made this assumption, but we have found that the only noncylindrical $C^m_{\mu}(Q_p)$ contributions to the potential [see Eq. (8a)] which are not vanishing because of the symmetry, i.e., the $m = \pm 3$ (in a local frame with the Z axis along the body diagonal), have actually very small effects on the final results.

Finally, we have used the value $B = 24.080$ 977 J mol
$^{-1}$
 = 2.012 986 4 cm$^{-1}$
 for the rotation constant of $N_2$.

\section*{B. Mean field results}

In Fig. 2 we have presented the single particle excitation energies obtained from the mean field calculations. Although the mean field excitation energies do not readily compare with the excitation energies of the whole crystal, the mean field spectra nevertheless give some interesting information on the average motions of the individual molecules. Additional information can be obtained from the probability densities which we have calculated from the mean field wave functions and presented in Fig. 3. In the following we shall discuss these results for each modification separately. The thermodynamic properties and the $\alpha$-$\beta$ phase transition will be discussed in paper II.

In \textit{ortho} the single particle energy levels group together in such a way that the spectrum becomes very similar to that of a two-dimensional harmonic oscillator. This is true for the \textit{ortho} as well as for the \textit{para} species. Moreover, the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.pdf}
\caption{Calculated mean field levels for the librations in $\alpha$ and $\gamma$ nitrogen.}
\end{figure}
This suggestion is confirmed by the probability densities in Fig. 3(a). This figure pertains to the ortho species at temperature \( T = 0 \) K; analogous figures for nonzero temperatures below 40 K, and also those for para-nitrogen are qualitatively similar. We clearly observe that the orientations of the molecules are localized around the \([1, 1, 1]\) axes, which is in agreement with the experimental findings [see Fig. 1(a)]. Because of the special way of plotting, i.e., \( \theta \) being proportional to the radius of the representation point, we also see clearly the symmetry of the density as a function of \( \theta \) and \( \phi \). An interesting quantity, measuring the amount of delocalization, is the order parameter \( S = \langle P_2(\cos \theta) \rangle \) where \( \theta \) is now taken relative to the equilibrium \([1, 1, 1]\) axes and the brackets denote a thermodynamic average. At \( T = 0 \) K we find \( S = 0.885 \), which should be compared with the experimental result \( S_{\text{exp}} = 0.863 \). The fact that our value is somewhat larger than the experimental one means that our ground state wave function is not sufficiently delocalized. Previous mean field calculations,\(^{38}\) using only quadrupole–quadrupole interactions, also led to too large a value of \( S \) (\( S = 0.890 \)).

In Fig. 4 we have plotted the variation of the order parameter \( S \) with the temperature. The calculated variation is mainly caused by the changes in the occupation numbers of the mean field levels; these levels themselves change only very little. We observe that the calculated order parameter does not fall off sufficiently with increasing temperature as compared with the experimental one. This result is typical for mean field calculations.\(^{3,4,38,39}\)

Also in \( \gamma \)-nitrogen the mean field single particle excitation energies for the ortho and para species are almost identical; the small differences in the higher part of the spectrum are due to the fact that the energy levels here are not yet converged to their correct position \( (l_{\text{max}} = \infty) \). The spectrum, in both cases, resembles that of a system of two independent harmonic oscillators with slightly different frequencies \( (\omega_1 = 72.1, \omega_2 = 81.3 \text{ cm}^{-1}) \). Again this suggests that the molecules perform small oscillations around their equilibrium orientations which, as can be seen from Fig. 3(b), are directed along the local \([1, 1, 0]\) axes, in agreement with ex-
periment. Looking at Fig. 1(c), we might guess that the smaller oscillation frequency pertains to an oscillation in the (a,b) plane, while the larger one pertains to an oscillation perpendicular to this plane. By inspection of the vectors corresponding to the mean field energy levels we have found that this guess is consistent with the wave functions of the first two excited states but not with those of the higher levels. The order parameter for the ground state equals 0.921, which indicates that the molecules in γ-nitrogen are slightly more localized than those in α-nitrogen. The mean field results and the corresponding orientational probability distributions for the β phase will be discussed in paper II.

C. Libron frequencies

In Tables II and III we have collected the librational phonon frequencies in α and γ nitrogen, respectively. We have included in these tables the results of previous harmonic and self-consistent phonon (SCP) calculations\(^1\) which were based on the same \textit{ab initio} potential.\(^2\) These calculations have used a site-site representation of this potential, whereas we now have employed the potential in the form of a spherical expansion [see Eqs. (1) and (23) and Table I]; the differences between these two representations are small, however.\(^3\) Also included are the results of simple one-dimensional model calculations\(^4\) which correct the SCP results for the strong anharmonicity of the librational potential. Furthermore, we compare some values from harmonic\(^5\) and libron model\(^23,24\) calculations based on the best available semiempirical potentials. Going downwards in these tables, we observe a systematic improvement in the results of different dynamical models based on the same \textit{ab initio} potential: harmonic, SCP, Raich’s libron model, and RPA (or time-dependent Hartree) libron model. The results of the RPA model, and already those of Raich’s libron model, are substantially better than those of the SCP model. The one-dimensional model results\(^6\) have indicated already that this is due to the failure of the SCP model (or any other quasiharmonic model) in describing large amplitude orientational oscillations. The libron results practically do not change when higher excited mean field states are included; apparently it is sufficient to take only the lowest two excited states for each particle into account (corresponding with the two angular degrees of freedom). This might be different, however, when the mean field excitation energies are lower and the states are more delocalized, as one expects in the β phase. Our best results, the RPA libron results, are considerably better also than the results of the harmonic calculations,\(^6\) and comparable with the best libron results,\(^23,24\) using optimized empirical potentials. In the \textit{ab initio} potential which we have used no fitting of the parameters to any solid state data has been involved, however.

### Table II. Librational frequencies in α-nitrogen (in cm\(^{-1}\)). \(T = 0 \text{ K.}\)

<table>
<thead>
<tr>
<th>(\Gamma: \mathbf{q} = (0,0,0))</th>
<th>(E_s)</th>
<th>(T_s)</th>
<th>(T_s^\prime)</th>
<th>(R_s^\prime)</th>
<th>(R_{,T^\prime})</th>
<th>rms deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment (Ref. 44)</td>
<td>32.3</td>
<td>36.3</td>
<td>59.7</td>
<td>43.6</td>
<td>47.2</td>
<td>12.3</td>
</tr>
<tr>
<td>Harmonic (Ref. 13)</td>
<td>40.8</td>
<td>50.7</td>
<td>74.3</td>
<td>55.6</td>
<td>58.3</td>
<td>9.7</td>
</tr>
<tr>
<td>SCP (Ref. 13)</td>
<td>39.5</td>
<td>48.5</td>
<td>70.3</td>
<td>52.7</td>
<td>55.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Raich’s libron (this work)*</td>
<td>34.5</td>
<td>41.8</td>
<td>71.7</td>
<td>48.0</td>
<td>51.0</td>
<td>5.2</td>
</tr>
<tr>
<td>RPA (this work)</td>
<td>30.7</td>
<td>41.0</td>
<td>68.5</td>
<td>47.9</td>
<td>51.0</td>
<td>6.1</td>
</tr>
<tr>
<td>One-dimensional model (Ref. 40)</td>
<td>30.1</td>
<td>43.3</td>
<td>67.2</td>
<td>47.0</td>
<td>52.8</td>
<td>0.9</td>
</tr>
<tr>
<td>One-dimensional model (Ref. 41)</td>
<td>32.0</td>
<td>37.2</td>
<td>61.0</td>
<td>49.4</td>
<td>52.8</td>
<td>6.2</td>
</tr>
</tbody>
</table>

\(^*\)Results for \(l_{\text{max}} = 10\) and 2 excited mean field states per molecule, for five excited states the frequencies are 34.4, 41.1, and 69.3 cm\(^{-1}\).

### Table III. Librational frequencies in γ-nitrogen (in cm\(^{-1}\)). \(T = 0 \text{ K.}\)

<table>
<thead>
<tr>
<th>(\Gamma: \mathbf{q} = (0,0,0))</th>
<th>(E_s)</th>
<th>(B_{1g})</th>
<th>(A_{2g})</th>
<th>rms deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment (Ref. 43)</td>
<td>55.0</td>
<td>98.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harmonic (Ref. 13)</td>
<td>57.9</td>
<td>86.5</td>
<td>109.7</td>
<td>8.5</td>
</tr>
<tr>
<td>SCP (Ref. 13)</td>
<td>56.5</td>
<td>85.2</td>
<td>107.1</td>
<td>9.2</td>
</tr>
<tr>
<td>Raich’s libron (this work)</td>
<td>64.3</td>
<td>101.6</td>
<td>129.0</td>
<td>7.0</td>
</tr>
<tr>
<td>RPA (this work)*</td>
<td>63.8</td>
<td>99.6</td>
<td>119.9</td>
<td>6.3</td>
</tr>
<tr>
<td>One-dimensional model (Ref. 40)</td>
<td>56.5</td>
<td>87.6</td>
<td>104.6</td>
<td>7.5</td>
</tr>
<tr>
<td>Harmonic (Ref. 6)</td>
<td>50.5</td>
<td>74.8</td>
<td>105.1</td>
<td>16.8</td>
</tr>
</tbody>
</table>

\(^*\)Results for \(l_{\text{max}} = 12\) and 2 excited mean field states included per molecule. For \(l_{\text{max}} = 10\) and 2 excited states the frequencies are 64.9, 101.9, and 122.7 cm\(^{-1}\) and for \(l_{\text{max}} = 10\) and 5 excited states: 64.7, 101.9, and 122.7 cm\(^{-1}\).
IV. CONCLUSION

From the results discussed in the previous section we can observe that the libron models presented in this paper, when applied with the \textit{ab initio} \( \text{N}_2-\text{N}_2 \) potential of Berns and van der Avoird,\(^9\) yield very good agreement with the experimental data for \( \alpha \) and \( \gamma \) nitrogen. Assuming the center of mass lattice without predetermined orientations of the \( \text{N}_2 \) molecules, the experimentally observed structures come out of mean field calculations. The collective orientational oscillations of the molecules ( librational phonons or librions) around these equilibrium structures are described by means of the libron models. The frequencies emerging from these libron models are very accurate indeed, for all the measured points\(^{32,43}\) where the translational phonons may be considered to be decoupled from the librations, because of the symmetry. This leads to the following conclusions:

(i) The \textit{ab initio} \( \text{N}_2-\text{N}_2 \) potential of Berns and van der Avoird is quite realistic, also in its orientational dependence (anisotropy). Its distance dependence has already been tested in SCP calculations\(^{13}\) which gave accurate results for the translational phonon frequencies.

(ii) The libron model works very well, at least for the pure librational motions in the ordered molecular solids, \( \alpha \) and \( \gamma \) nitrogen. In the next paper (II) we look at orientationally disordered solids, \( \beta \) nitrogen, and in a subsequent paper (III), at the effect of translational-rotational coupling which should be included at least for those lattice vibrations where no decoupling occurs due to symmetry. Actually, this decoupling holds only for some specific points in the Brillouin zone. In calculating observable properties as thermodynamic averages one should (numerically) integrate over the complete zone, including all the mixed mode points.

ACKNOWLEDGMENTS

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APPENDIX

In this Appendix we briefly present the time-dependent Hartree theory for the dynamics of molecular crystals which can be used to derive Eqs. (19) and (20). It starts by applying a small perturbation \( \lambda h (t) \) to the crystal. The Hamiltonian of the system is then

\[ H(t) = H + \lambda h(t) , \]

where \( H \) is given by Eq. (2). We write the statistical density operator \( D(t) \) as

\[ D(t) = D + \lambda A(t) , \]

where \( D = \exp(-\beta H)/Z \) is the time-independent canonical density operator. The time evolution of \( D(t) \) is given by the Liouville equation, which to first order in \( \lambda \) reads

\[ i \hbar A(t) = [h (t), D] + [H, A(t)] . \]

We solve this equation by taking its Fourier transform; for \( \tilde{A}(\omega) = \int d^3 t e^{i \omega t} A(t) \) we obtain:

\[ \tilde{A}(\omega) = \sum_{\alpha, \beta} \left[ \langle \psi_{\alpha} | \left[ \hat{h}(\omega), D \right] | \psi_{\beta} \rangle \langle \psi_{\beta} | \psi_{\alpha} \rangle \right] . \]

Here \( \tilde{h}(\omega) = \int d^3 t e^{i \omega t} h(t) \) and \( | \psi_{\alpha} \rangle \) is an exact eigenstate of \( H \) with corresponding eigenvalue \( E_{\alpha} \). The important point now is that \( \tilde{A}(\omega) \) has singularities for those values of \( \omega \) which are equal to some energy difference \( (E_{\alpha} - E_{\beta})/\hbar \); we shall approximately calculate these singularities for the case that either \( E_{\alpha} \) or \( E_{\beta} \) is the ground state energy.

We use a perturbation of the form \( h(t) = \sum_{\rho} h_{\rho}(\Omega_{\rho}, t) \), and we write the statistical density operator in the time-dependent Hartree approximation

\[ D(t) = \prod_{\rho} d_{\rho}(\Omega_{\rho}, t) , \]

\[ d_{\rho}(\Omega_{\rho}, t) = d_{\rho}^{MF}(\Omega_{\rho}) + \lambda \delta_{\rho}(\Omega_{\rho}, t) . \]

Here \( d_{\rho}^{MF}(\Omega_{\rho}) \) is the time-independent mean field single particle density operator: \( \exp(-\beta H^{MF}(\Omega_{\rho}))/Z^{MF} \), with \( H^{MF}(\Omega_{\rho}) \) given by Eq. (7). As a result, in the limit \( \lambda \to 0 \), the system is described by the mean field approximation. To first order in \( \lambda \) we get

\[ \tilde{A}(\omega) = \sum_{\rho} d^{MF}(\Omega_{\rho}) \delta_{\rho}(\Omega_{\rho}, \omega) d_{\rho}^{ZF}(\Omega_{\rho}) , \]

where \( \delta_{\rho}(\Omega_{\rho}, \omega) = \int d^3 t \delta_{\rho}(\Omega_{\rho}, t) \). It follows that \( \tilde{A}(\omega) \) has singularities at the values of \( \omega \) where \( \delta_{\rho}(\Omega_{\rho}, \omega) \) has singularities.

In order to calculate the singular points of \( \delta_{\rho}(\Omega_{\rho}, \omega) \) we write down the Liouville equation to the first order in \( \lambda \), and perform the trace over all one-particle Hilbert spaces except for that of molecule \( \rho \):

\[ i \hbar \{ H^{MF}(\Omega_{\rho}) \} \sum_{\rho'} d^{MF}(\Omega_{\rho}) \delta_{\rho'}(\Omega_{\rho}, t) \cdots d_{\rho}^{ZF}(\Omega_{\rho}) = i \hbar \delta_{\rho}(\Omega_{\rho}, t) \]

\[ = \{ H^{MF}(\Omega_{\rho}) \} d^{MF}(\Omega_{\rho}) + \{ H^{MF}(\Omega_{\rho}), \delta_{\rho}(\Omega_{\rho}, t) \} + \{ \Phi_{\rho}(\Omega_{\rho}, t), d_{\rho}^{MF}(\Omega_{\rho}) \} + \{ h_{\rho}(\Omega_{\rho}, t), d_{\rho}^{MF}(\Omega_{\rho}) \} , \]

\[ \Phi_{\rho}(\Omega_{\rho}, t) = \sum_{\rho'} \{ H^{MF}(\rho) \} \delta_{\rho'}(\Omega_{\rho}, t) \Phi_{\rho'}(\Omega_{\rho}, \rho_{\rho}) . \]

The superscripts of the trace operators are self-explanatory. In the first step we have made use of \( \text{Tr} \, \delta_{\rho}(\Omega_{\rho}, t) = 0 \), which follows from Eq. (A5b). Verification of the last step in Eq. (A7a) is somewhat tedious but straightforward. The first commuta-
tor following the last equal sign in Eq. (A7a) is of course equal to zero. The next step is to Fourier transform Eqs. (A7a) and (A7b) and to calculate the matrix elements \( \langle \psi^{(0)}_p | \delta_p(\omega) | \psi^{(1)}_p \rangle \); the operator then follows from

\[
\delta_p(\Omega_p, \omega) = \sum_{\alpha, \beta} |\psi^{(0)}_p|^{2} \langle \psi^{(0)}_p | \delta_p(\omega) | \psi^{(1)}_p \rangle \langle \psi^{(1)}_p | \psi^{(0)}_p \rangle .
\]

Because all manipulations are fairly elementary, and moreover are essentially identical to those of Hüller,\(^{16}\) we just give the final result:

\[
\langle \psi^{(0)}_p | \delta_p(\omega) | \psi^{(1)}_p \rangle = \sum_{\alpha} \sum_{\lambda} \frac{B^{(K)}_{\alpha, \beta, p}(q)}{\hbar \omega - A^{(K)}(q)} .
\]

The precise form of \( B^{(K)}_{\alpha, \beta, p}(q) \) is not important; suffice it to say that it originates from the last commutator in Eq. (A7a). \( A^{(K)}(q) \) are the eigenvalues of a matrix \( \mathbf{M}(q) \) with elements

\[
M_{\alpha, \beta, \alpha', \beta'}(q) = \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} \delta_{\epsilon^{(\alpha)} - \epsilon^{(\beta)}} - \left( P^{(\alpha)} - P^{(\beta)} \right) \sum_n e^{in\mathbf{R}_0 \cdot \mathbf{q}} \langle \psi^{(0)}_{|0|, \alpha} | \psi^{(1)}_{|1|, \beta} \rangle \langle \mathbf{P}_{|0|, |n\mathbf{r}|} | \psi^{(1)}_{|1|, |n\mathbf{r}|} \rangle ,
\]

where \( P^{(\alpha)} = \langle \psi^{(0)}_{|0|} | d^{(\alpha)}_\mathbf{q} | \psi^{(0)}_{|0|} \rangle \). From Eqs. (A4), (A6), (A8), and (A9) we conclude that the eigenvalues \( A^{(K)}(q) \) provide the approximate energy differences \( E^{(\alpha)} - E^{(\beta)} \). It is clear from Eq. (A10) that the rows of \( \mathbf{M}(q) \) for which \( \epsilon^{(\alpha)} = \epsilon^{(\beta)} \) are identically zero. We shall omit these rows and the corresponding columns, because we are only interested in the eigenvalues \( A^{(K)}(q) \) that are not trivially equal to zero (the zeros correspond to the diagonal terms in Eq. (A4)). Finally, if we use the fact that the mean field states are real, we can arrange the indices such that \( \mathbf{M}(q) \) has the structure given in Eq. (19).