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# ***Ab initio* description of large amplitude motions in solid N<sub>2</sub>. III. Libron-phonon coupling**

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A new lattice dynamics scheme is proposed for handling librons, anharmonic translational vibrations, and translational-rotational coupling in molecular crystals. This scheme is an extension of earlier libron models which describe large amplitude librations or hindered rotations. The formalism is based on expanding the intermolecular potential in the molecular displacement coordinates, including cubic and quartic terms, while retaining the exact orientational dependence. Closed expressions are obtained via spherical tensor methods. After constructing separate mean field states for the molecular rotations and translations, using bases of tesseral harmonics and 3D harmonic oscillator functions, respectively, the intermolecular correlations are taken into account and simultaneously the translational-rotational coupling, by solving the equations of motion for the crystal according to the time-dependent Hartree or random-phase approximation. Application of the formalism to the ordered  $\alpha$  and  $\gamma$  phases of solid nitrogen, using an *ab initio* potential, gave very satisfactory results.

## **I. INTRODUCTION**

As explained in any textbook, the basic tool in solid state physics is the use of wave functions, or operators in the equations of motion method, which are adapted to the translational symmetry of the lattice. In the usual harmonic lattice dynamics treatments<sup>1</sup> the adaptation to this symmetry is easy and the original problem reduces to a set of smaller problems, one for every wave vector  $\mathbf{q}$  in the first Brillouin zone. If the symmetry adaptation is applied to only part of the problem, however, as in perturbational treatments of anharmonic effects,<sup>1,2</sup> multiple sums over the Brillouin zone will inevitably appear. These multiple summations in  $\mathbf{q}$  space restrict the calculation of perturbation terms to a few of the lowest orders and, therefore, make the theory inapplicable to strongly anharmonic systems.

In papers I and II of this series,<sup>3,4</sup> we describe a lattice dynamics theory for molecular crystals which avoids multiple sums in  $\mathbf{q}$  space, because the wave functions are adapted to the translational symmetry of the crystal only in the final stage. Thus, we were able to treat the librations in the ordered  $\alpha$  and  $\gamma$  phases of solid nitrogen and even the reorientations of the molecules in the plastic  $\beta$  phase, without making any approximation to the strongly anharmonic potential. Just as in all previous, semiempirical, libron treatments,<sup>5-8</sup> the molecular centers of mass in our calculations were assumed to be fixed on the lattice sites. This assumption implies the decoupling of the librons and the translational phonons. In principle, one could still take the latter into account by using a translationally averaged potential for the librations; in practice, this has not been done explicitly.

The coupling between librons and phonons, i.e., rotational-translational coupling, is quite important, however. All lattice modes are actually mixed, except those at high symmetry points in the Brillouin zone of crystals with specific space groups. For calculating thermodynamic properties, which involves summation over the complete Brillouin zone, all these mixed modes must be included. It has been shown in more empirical models<sup>9-12</sup> that rotational-translational cou-

pling can lead to interesting phenomena such as ferroelastic phase transitions in KCN and *s*-triazine crystals.

In this paper we present a new formalism for the calculation of the coupled libron-phonon modes in molecular crystals. This formalism combines our previous treatment<sup>3,4</sup> of large amplitude librons with the explicit handling of the translational lattice modes. It is applied to solid nitrogen, again, using the anharmonic anisotropic *ab initio* potential.<sup>13</sup> Since the translational phonons are fairly well described by the harmonic model already (and even better by the quasi-harmonic self-consistent phonon model<sup>14</sup>), we required our formalism to be exact for harmonic lattice Hamiltonians. This implies, in the general case of translations and librations, that it includes at least the translational-rotational coupling which is naturally present in the harmonic model. Our formalism goes beyond the harmonic approximation, however, even for the translational phonons, by including all terms in the potential which are cubic and quartic in the molecular displacements. The orientational dependence of the potential is represented exactly, as in papers I and II. The above requirements are met by the following scheme. First, we treat the anharmonic anisotropic lattice Hamiltonian, which depends on the translational and orientational coordinates of the molecules, in a mean field calculation for the translations and reorientations of each molecule, separately. Then, we construct wave functions as products of mean field ground states and one excited mean field function, adapted to the translational symmetry. The coupling between these wave functions is handled within the time-dependent Hartree (TDH) or random-phase approximation (RPA).

For the harmonic approximation to the lattice Hamiltonian the mean field states are the ground and first excited harmonic oscillator states with frequencies determined by the self forces. It has been demonstrated<sup>15,16</sup> that the TDH/RPA equation of motion is exact in this case. Moreover, it has been proved<sup>15,16</sup> that the TDH/RPA frequencies will be zero for uniform translations of the whole system, which implies in case of crystals that the acoustical phonon modes will correctly tend to zero frequency for wave vector zero.

This condition is not satisfied by the simpler forms of the equation of motion based on the Tamm-Dancoff approximation,<sup>15</sup> which have been used in lattice dynamics also.<sup>6</sup>

If we would separately couple the translational and/or rotational motions of the individual molecules, obtain solutions adapted to the lattice symmetry, and then introduce translational-rotational coupling, we would still be hindered by the problem of multiple sums in  $\mathbf{q}$  space mentioned at the start. Instead, we have chosen to couple all mean field translational and rotational excited states simultaneously by means of the TDH/RPA scheme, applying the translational symmetry reduction directly to the full TDH problem.

## II. THEORY

In part A of this section we consider the intermolecular potential and bring it into a form which is suitable for the subsequent treatment. In part B we deal with the translational part of the problem, including the basis functions and the matrix elements. Finally, in part C we combine the results of subsection B with those of paper I, in order to describe the coupled rotational-translational motions.

### A. The potential

As in our first paper, we associate each molecule in the crystal with a lattice point  $P = \{\mathbf{n}, i\}$ , with position vector  $\mathbf{R}_P = \mathbf{R}_n + \mathbf{r}_i$ , where  $\mathbf{R}_n$  is the position vector of the origin of the unit cell  $\mathbf{n}$  and  $\mathbf{r}_i$  the position of  $P$  relative to this origin ( $i = 1, 2, \dots, Z$ , where  $Z$  is the number of molecules per unit cell). The molecules are now supposed to oscillate and librate with their centers of mass remaining in the neighborhood of the points  $P$ ; the position vectors of their mass centers relative to these points are denoted by  $\mathbf{u}_P$ . The orientations of the (linear) molecules with respect to a fixed lattice frame will be described by the polar angles  $\Omega_P = \{\theta_P, \varphi_P\}$  of their axes. The potential energy between two molecules associated with  $P$  and  $P'$ , respectively, can then be written as

$$\Phi(\mathbf{U}_{PP'}, \Omega_P, \Omega_{P'}) = \sum_{\mathbf{l}} \varphi_{\mathbf{l}}(\mathbf{U}_{PP'}) \sum_{\mathbf{m}} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \times C_{m_1}^{(l_1)}(\Omega_P) C_{m_2}^{(l_2)}(\Omega_{P'}) C_{m_3}^{(l_3)}(\hat{\mathbf{U}}_{PP'}). \quad (1)$$

Here,  $\mathbf{U}_{PP'} = (\mathbf{R}_{P'} + \mathbf{u}_{P'}) - (\mathbf{R}_P + \mathbf{u}_P) = \mathbf{R}_{PP'} + \mathbf{u}_{P'} - \mathbf{u}_P$  and  $\hat{\mathbf{U}}_{PP'}$  is the unit vector along  $\mathbf{U}_{PP'}$ . The angular functions  $C_m^{(l)}$  are Racah spherical harmonics<sup>17</sup> and the larger brackets denote a Wigner 3- $j$  symbol;  $\mathbf{l} = \{l_1, l_2, l_3\}$  and  $\mathbf{m}$

$= \{m_1, m_2, m_3\}$ . The *ab initio* N<sub>2</sub>-N<sub>2</sub> potential has actually been represented in this form.<sup>13</sup>

The potential given by Eq. (1) depends on the translational degrees of freedom  $\mathbf{u}_P$  and  $\mathbf{u}_{P'}$  in a very intricate way. In order to make this dependence explicit, which is required for the subsequent theory, we expand the factors that contain these variables in a Taylor series

$$\varphi_{\mathbf{l}}(\mathbf{U}_{PP'}) C_{m_3}^{(l_3)}(\hat{\mathbf{U}}_{PP'}) = \sum_{\alpha_1, \alpha_2} \frac{(-\mathbf{u}_P \cdot \nabla)^{\alpha_1}}{\alpha_1!} \frac{(\mathbf{u}_{P'} \cdot \nabla)^{\alpha_2}}{\alpha_2!} \times \varphi_{\mathbf{l}}(\mathbf{R}_{PP'}) C_{m_3}^{(l_3)}(\hat{\mathbf{R}}_{PP'}). \quad (2)$$

The simplest way to evaluate this expansion is by means of the so-called gradient formula<sup>17</sup> in spherical tensor form:

$$\mathbf{u}_P \cdot \nabla F(\mathbf{R}_{PP'}) C_{m_3}^{(l_3)}(\hat{\mathbf{R}}_{PP'}) = u_P \sum_k A_{lk}(R) F(\mathbf{R}_{PP'}) \times \{C^{(1)}(\hat{\mathbf{u}}_P) \otimes C^{(k)}(\hat{\mathbf{R}}_{PP'})\}_{m_3}^{(l_3)}, \quad (3)$$

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

$$A_{lk}(R) = -\delta_{k,l-1} \left[ \frac{l(2l-1)}{2l+1} \right]^{1/2} \left( \frac{d}{dR} + \frac{l+1}{R} \right) + \delta_{k,l+1} \left[ \frac{(l+1)(2l+3)}{2l+1} \right]^{1/2} \left( \frac{d}{dR} - \frac{l}{R} \right) \quad (4)$$

while the tensor product between curly brackets is given by

$$\{C^{(l_1)}(\hat{\mathbf{u}}_P) \otimes C^{(l_2)}(\hat{\mathbf{R}}_{PP'})\}_{m_3}^{(l_3)} = (-1)^{l_1+l_2+m_3} \times \sum_{m_1, m_2} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \times C_{m_1}^{(l_1)}(\hat{\mathbf{u}}_P) C_{m_2}^{(l_2)}(\hat{\mathbf{R}}_{PP'}). \quad (5)$$

Using Eq. (3) several times we can write Eq. (2) as

$$\varphi_{\mathbf{l}}(\mathbf{U}_{PP'}) C_{m_3}^{(l_3)}(\hat{\mathbf{U}}_{PP'}) = \sum_{\mathbf{k}} \sum_j {}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'}, \mathbf{u}_P, \mathbf{u}_{P'}) \times \{ \{C^{(k_1)}(\hat{\mathbf{u}}_P) \otimes C^{(k_2)}(\hat{\mathbf{u}}_{P'})\}^{(j)} \otimes C^{(k_3)}(\hat{\mathbf{R}}_{PP'}) \}_{m_3}^{(l_3)}. \quad (6)$$

The angular independent factors are given by

$${}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'}, \mathbf{u}_P, \mathbf{u}_{P'}) = \sum_{\alpha_1, \alpha_2} \frac{(-\mathbf{u}_P)^{\alpha_1}}{\alpha_1!} \frac{(\mathbf{u}_{P'})^{\alpha_2}}{\alpha_2!} \times {}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'} | \alpha_1, \alpha_2). \quad (7)$$

So it is our task to calculate the coefficients  ${}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'} | \alpha_1, \alpha_2)$ . We do this via the following recursion relation:

$$\begin{aligned} & \mathbf{u}_P \cdot \nabla \sum_{\mathbf{k}} \sum_j {}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'} | \alpha_1, \alpha_2) \{ \{C^{(k_1)}(\hat{\mathbf{u}}_P) \otimes C^{(k_2)}(\hat{\mathbf{u}}_{P'})\}^{(j)} \otimes C^{(k_3)}(\hat{\mathbf{R}}_{PP'}) \}_{m_3}^{(l_3)} \\ &= u_P \sum_{\mathbf{k}} \sum_j {}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'} | \alpha_1 + 1, \alpha_2) \{ \{C^{(k_1)}(\hat{\mathbf{u}}_P) \otimes C^{(k_2)}(\hat{\mathbf{u}}_{P'})\}^{(j)} \otimes C^{(k_3)}(\hat{\mathbf{R}}_{PP'}) \}_{m_3}^{(l_3)} \end{aligned} \quad (8)$$

and an analogous formula to raise the index  $\alpha_2$ . Using the gradient formula and the expansion of a product of two spherical harmonics<sup>17</sup> we find that the left-hand side of Eq. (8) is given by

$$\begin{aligned} & u_P \sum_{\mathbf{k}} \sum_{\mathbf{n}} C_{n_1}^{(k_1)}(\hat{\mathbf{u}}_P) C_{n_2}^{(k_2)}(\hat{\mathbf{u}}_{P'}) C_{n_3}^{(k_3)}(\hat{\mathbf{R}}_{PP'}) (2k_1 + 1) \sum_{k'_1, k'_3} \sum_j A_{k'_1 k'_3}(R_{PP'}) {}^j W_{\mathbf{k}}^{(l)}(\mathbf{R}_{PP'} | \alpha_1, \alpha_2) \begin{pmatrix} 1 & k'_1 & k_1 \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \sum_{n'_1, n'_3} \sum_{\nu, \mu'} \begin{pmatrix} 1 & k'_1 & k_1 \\ \nu & n'_1 & -n_1 \end{pmatrix} \begin{pmatrix} 1 & k'_3 & k_3 \\ \nu & -n'_3 & n_3 \end{pmatrix} \begin{pmatrix} k'_1 & k_2 & j' \\ -n'_1 & -n_2 & \mu' \end{pmatrix} \begin{pmatrix} j' & k'_3 & l_3 \\ \mu' & n'_3 & -m_3 \end{pmatrix} (-1)^{\nu+n'_1}. \end{aligned} \quad (9)$$

The last sum in this expression can be evaluated using standard angular momentum techniques,<sup>17,18</sup> it is equal to

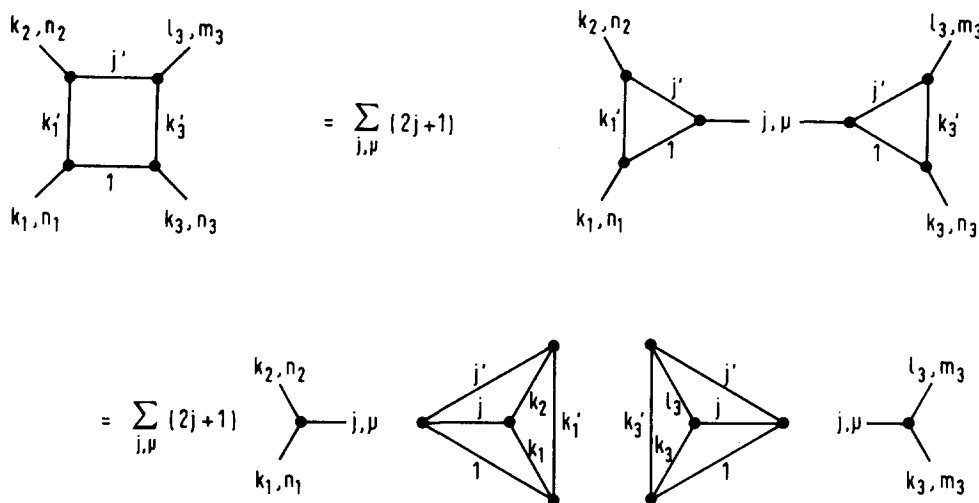


FIG. 1. Recoupling scheme for expansion of the potential [Eqs. (9) and (10)].

$$\sum_{j\mu} (2j+1) (-1)^{\mu+m_3} \begin{pmatrix} k_1 & k_2 & j \\ n_1 & n_2 & -\mu \end{pmatrix} \begin{pmatrix} j & k_3 & l_3 \\ \mu & n_3 & -m_3 \end{pmatrix} \left\{ \begin{matrix} k_1 & k_2 & j \\ j' & 1 & k_1' \end{matrix} \right\} \left\{ \begin{matrix} j & k_3 & l_3 \\ k_3' & j' & 1 \end{matrix} \right\} (-1)^{k_1+j+l_3} \quad (10)$$

The symbols between curly brackets are 6-*j* coefficients. In Fig. 1 we have given the graphical representation of this summation according to the conventions of Brink and Satchler.<sup>18</sup> Introducing the last two results into Eq. (8) we find

$${}^j W_{\mathbf{k}}^{(l)}(R_{PP'} | \alpha_1 + 1, \alpha_2) = (-1)^{k_2+k_3+l_3} (2j+1)(2k_1+1) \sum_{k_1', k_3'} \sum_j \begin{pmatrix} 1 & k_1' & k_1 \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} k_1 & k_2 & j \\ j' & 1 & k_1' \end{matrix} \right\} \left\{ \begin{matrix} j & k_3 & l_3 \\ k_3' & j' & 1 \end{matrix} \right\} A_{k_3' k_3}(R_{PP'}) \\ \times {}^j W_{k_1', k_3', k_3}^{(l)}(R_{PP'} | \alpha_1, \alpha_2). \quad (11)$$

In the same way a recursive relation raising the index  $\alpha_2$  by one unit can be derived. In the actual calculations it is most convenient to first raise one of the indices  $\alpha_1$  or  $\alpha_2$  to its final value, while keeping the other one equal to zero, and then to raise the second index. This greatly simplifies the recursive relations, because, e.g., when  $\alpha_2 = 0$ , then  $k_2 = 0$  and the first 6-*j* coefficient in Eq. (11) becomes a simple square root; moreover  $j' = k_1'$  and  $j = k_1$  so that the sum over  $j'$  in Eq. (11) contains only one term.

While the sums over  $\mathbf{k}$  and  $j$  in Eqs. (6) and (7) are bounded for given  $\alpha_1$  and  $\alpha_2$ , the sums over the latter indices must, in principle, be extended to infinity. In testing our programs we have found that generally good results can be obtained with  $\alpha_1 + \alpha_2 \leq \alpha_{\max} = 4$ . Indeed, taking  $R_{PP'}$  equal to the nearest neighbor distance in  $\alpha$ -N<sub>2</sub>, and  $u_P$  and  $u_{P'}$  as large as 8% of this value we found the exact value of the potential within 1%, when using  $\alpha_{\max} = 4$ .

Introducing Eqs. (6) and (7) into Eq. (1) we find with a slight change of notation:

$$\Phi_{PP'}(\mathbf{u}_P, \Omega_P; \mathbf{u}_{P'}, \Omega_{P'}) = \sum_{\Lambda_1, \Lambda_2} (u_P)^{\alpha_1} C_{n_1}^{(k_1)}(\hat{\mathbf{u}}_P) C_{m_1}^{(l_1)}(\Omega_P) X_{\Lambda_1, \Lambda_2}(P, P') C_{m_2}^{(l_2)}(\Omega_{P'}) C_{n_2}^{(k_2)}(\hat{\mathbf{u}}_{P'}) (u_{P'})^{\alpha_2}, \quad (12)$$

which is in the required form. Here  $\Lambda_1$  and  $\Lambda_2$  are composite indices and

$$X_{\Lambda_1, \Lambda_2}(P, P') = \frac{(-1)^{\alpha_1}}{\alpha_1!} \frac{1}{\alpha_2!} \sum_{k_3, l_3, j} {}^j W_{\mathbf{k}}^{(l)}(R_{PP'} | \alpha_1, \alpha_2) (-1)^{k_1+k_2+k_3+j} \\ \times \sum_{n_3, m_3, \mu} (-1)^{m_3+\mu} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} k_1 & k_2 & j \\ n_1 & n_2 & -\mu \end{pmatrix} \begin{pmatrix} j & k_3 & l_3 \\ \mu & n_3 & -m_3 \end{pmatrix} C_{m_3}^{(k_3)}(\hat{\mathbf{R}}_{PP'}). \quad (13)$$

Construction of the crystal Hamiltonian is now straightforward; the result is given below in Eq. (19). For convenience we do not separate the one and two particle terms in the potential, as we did in paper I. Of course this does not change the physics of our model, the only result being that the mean field energies are shifted by a constant, temperature dependent, amount.

## B. Translational motions

When we disregard the orientations of the molecules for the moment, we can write the crystal Hamiltonian as

$$H = \sum_P T(\mathbf{u}_P) + \frac{1}{2} \sum_{P \neq P'} \Phi_{PP'}(\mathbf{u}_P, \mathbf{u}_{P'}), \quad (14a)$$

$$T(\mathbf{u}_P) = -\frac{\hbar^2}{2M} \Delta(\mathbf{u}_P), \quad (14b)$$

$$\Phi_{PP'}(\mathbf{u}_P, \mathbf{u}_{P'}) = \sum_{\lambda_1, \lambda_2} (u_P)^{\alpha_1} C_{n_1}^{(k_1)}(\hat{\mathbf{u}}_P) X_{\lambda_1, \lambda_2}(P, P') \\ \times C_{n_2}^{(k_2)}(\hat{\mathbf{u}}_{P'}) (u_{P'})^{\alpha_2}. \quad (14c)$$

Here  $\lambda_i$  is the composite index  $\{\alpha_i, k_i, n_i\}$ . Treating this Hamiltonian first within the mean field approximation, in other words approximating the crystal as a generalized Einstein

crystal, we find that we must solve the coupled set of equations

$$H_P^{\text{MF}}(\mathbf{u}_P) = T(\mathbf{u}_P) + \sum_{P' \neq P} \langle \Phi_{PP'}(\mathbf{u}_P, \mathbf{u}_{P'}) \rangle_{P'} \\ = T(\mathbf{u}_P) + \Phi_P^{\text{MF}}(\mathbf{u}_P), \quad (15)$$

where  $\langle X \rangle_{P'}$  denotes the thermodynamic average of  $X$  over the eigenstates of  $H_{P'}^{\text{MF}}(\mathbf{u}_{P'})$ . In order to solve these equations, just as in paper I, we impose the experimentally observed symmetry on the solutions. As a result,  $H_P^{\text{MF}} = H_{P'}^{\text{MF}}$  when  $\mathbf{R}_{PP'}$  is equal to a primitive lattice vector, and otherwise we can use

$$\langle C_n^{(k)} \rangle_{P'} = \sum_m \langle C_m^{(k)} \rangle_P D_{m,n}^{(k)}(\omega_{P'}), \quad (16)$$

for some set of Euler angles  $\{\omega_{P'}\}$ . In our case, moreover,  $\langle (u_P)^\alpha \rangle_P = \langle (u_{P'})^\alpha \rangle_{P'}$  for all  $P$  and  $P'$ .

We have solved the mean field equations (15) in a basis

$$\frac{1}{4\pi} \int d\Omega_u C_{m_1}^{(l_1)}(\hat{u}) C_{m_2}^{(l_2)}(\hat{u}) C_{m_3}^{(l_3)}(\hat{u}) = \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (18a)$$

$$\int_0^\infty u^2 du A_{(1/2)(n_1-l_1)}^{l_1+(1/2)}(u^2) \frac{u^\alpha}{u} A_{(1/2)(n_2-l_2)}^{l_2+(1/2)}(u^2) \\ = \frac{1}{2} (-1)^{a_1+a_2} \left[ \frac{\Gamma(a_1+1)}{\Gamma(a_1+b_1+1)} \frac{\Gamma(a_2+1)}{\Gamma(a_2+b_2+1)} \right]^{1/2} \sum_{l=l_{\min}}^{l_{\max}} \binom{c-b_1}{a_1-l} \binom{c-b_2}{a_2-l} \binom{c+1}{l} \Gamma(c+1);$$

$$a_i = \frac{1}{2}(n_i - l_i), \quad b_i = l_i + \frac{1}{2}, \quad c = \frac{1}{2}(l_1 + l_2 + \alpha + 1), \quad d = \max(a_1 + b_1, a_2 + b_2) - c,$$

$$l_{\min} = \begin{cases} d & \text{if } c \text{ is half-integer and } d > 0 \\ 0 & \text{otherwise} \end{cases}, \quad l_{\max} = \min(a_1, a_2). \quad (18b)$$

Equation (18b) has been derived using the results of Tennyson and Sutcliffe<sup>20</sup>; the factor  $u^2$  in this equation originates from the volume element in  $\mathbf{u}$  space. Matrix elements of the kinetic energy operator are calculated most easily by writing  $-\Delta(\mathbf{u}) = A^2[-\Delta(A\mathbf{u}) + A^2u^2] - A^4u^2$ ; the matrix elements of the operator in square brackets, which is the harmonic oscillator Hamiltonian, are simply equal to  $\delta_{l_1l_2} \delta_{m_1m_2} \delta_{n_1n_2} (2n_1 + 3)$ , while those of the remaining part can be calculated using Eq. (18b).

The final step is to construct correlated crystal states by using a restricted basis of mean field crystal states and solving the TDH equations. These equations are completely analogous to those given in Secs. II C and II D of paper I, and will not be repeated here.

### C. The coupled rotational-translational problem

The Hamiltonian for the coupled problem reads

$$H = \sum_P \{ T(\mathbf{u}_P) + L(\Omega_P) \} \\ + \frac{1}{2} \sum_{P \neq P'} \sum \Phi_{PP'}(\mathbf{u}_P, \Omega_P; \mathbf{u}_{P'}, \Omega_{P'}). \quad (19)$$

Here  $T(\mathbf{u}_P)$  and  $L(\Omega_P)$  represent the kinetic energy operators of the translational and the rotational motions, respectively. The potential has been given in Eq. (12).

Now there are two possible ways to apply the mean field

of 3D harmonic oscillator functions<sup>19</sup>

$$\Psi_{l,m}^{(n)}(\mathbf{u}_P) = A [2/u_P]^{1/2} A_{(1/2)(n-l)}^{l+(1/2)}(A^2u_P^2) S_m^{(l)}(\hat{u}_P), \quad (17a)$$

$$A_k^\alpha(t) = \left[ \Gamma(\alpha+1) \binom{k+\alpha}{k} \right]^{-1/2} e^{-t/2} t^{\alpha/2} L_k^\alpha(t). \quad (17b)$$

Here  $L_k^\alpha(t)$  denotes the Laguerre function and  $\Gamma(k)$  the Gamma function;  $l < n$ , and  $l$  and  $n$  have the same parity. The angular functions  $S_m^{(l)}$  are tesseral harmonics. The constant  $A$  is just a scaling constant, which in the case of an infinite basis has no influence. In practice, however, we restrict ourselves to a finite basis  $n \leq n_{\max}$  and use  $A$  to optimize this basis. If  $H_P^{\text{MF}}(\mathbf{u}_P)$  would have a purely harmonic spectrum, we should use  $A = \{M\omega\}^{1/2}$ , with  $\omega$  being the oscillator frequency. We have therefore chosen  $A = \{M(\epsilon^{(1)} - \epsilon^{(0)})\}^{1/2}$ , where  $\epsilon^{(i)}$  is the  $i$ th mean field energy. In some cases we have tested this choice by optimizing  $A$  and it turned out that  $A$  did not appreciably change, nor did the physical results.

Matrix elements in this basis are easily obtained using

approximation to this Hamiltonian, which correspond to writing the variational Hamiltonian  $H_0$  to be used in the Gibbs–Bogoliubov inequality, in either one of the forms

$$H_0 = \sum_P H_P^{\text{MF}}(\mathbf{u}_P, \Omega_P), \quad (20a)$$

$$H_0 = \sum_P \{ H_P^T(\mathbf{u}_P) + H_P^L(\Omega_P) \}. \quad (20b)$$

The first possibility has the advantage of including the correlation between the one-particle rotational and translational motions. From a practical point of view, however, it has the drawback of requiring a huge basis of product functions  $C_{m_1}^{(l_1)}(\Omega) \Psi_{l_2, m_2}^{(n)}(\mathbf{u})$  in order to yield reasonably converged mean field states. We therefore choose to write  $H_0$  as in Eq. (20b). Introducing this Hamiltonian into the Gibbs–Bogoliubov inequality, and optimizing the free energy (see papers I and II) we find the mean field equations

$$H_P^T(\mathbf{u}_P) = T(\mathbf{u}_P) + \sum_{P' \neq P} \langle \Phi_{PP'}(\mathbf{u}_P, \Omega_P; \mathbf{u}_{P'}, \Omega_{P'}) \rangle_{P'}^{L_P} \\ = T(\mathbf{u}_P) + \Phi_P^T(\mathbf{u}_P), \quad (21a)$$

$$H_P^L(\Omega_P) = L(\Omega_P) + \sum_{P' \neq P} \langle \Phi_{PP'}(\mathbf{u}_P, \Omega_P; \mathbf{u}_{P'}, \Omega_{P'}) \rangle_{P'}^{T_P} \\ = L(\Omega_P) + \Phi_P^L(\Omega_P). \quad (21b)$$

Here  $\langle X \rangle_{P'}^{L_P}$  denotes the thermodynamic average of  $X$  over the states of  $H_P^T(\mathbf{u}_P) + H_P^L(\Omega_P)$  and over those of  $H_P^L(\Omega_P)$ . An analogous definition holds for  $\langle X \rangle_{P'}^{T_P}$ . In order

to solve these coupled equations, we impose, in the usual way, the experimentally observed symmetry on the solutions and proceed iteratively. A useful test on the final solutions follows from  $\langle \Phi_P^T(\mathbf{u}_P) \rangle^{T_P} = \langle \Phi_P^L(\Omega_P) \rangle^{L_P}$ .

Our final task is to calculate the fundamental excitation energies of the crystal. To this end we apply the TDH for-

malism as in paper I. The time dependent perturbation is now  $h(t) = \sum_P \{ h_P^T(\mathbf{u}_P, t) + h_P^L(\Omega_P, t) \}$  and the perturbed density operator is written as  $D(t) = \Pi_P d_P^T(\mathbf{u}_P, t) d_P^L(\Omega_P, t)$ . Performing exactly the same steps as in paper I, we find that the excitation energies are equal to the positive eigenvalues of the matrix

$$M_{\alpha, \beta, i, \alpha', \beta', i'}^{K, K'}(\mathbf{q}) = \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} \delta_{i, i'} \delta_{K, K'} (\epsilon_K^{(\alpha)} - \epsilon_K^{(\beta)}) - (P_K^{(\alpha)} - P_K^{(\beta)}) \sum_n e^{i\mathbf{q} \cdot \mathbf{R}_n} \langle \alpha_P^K \beta_{P'}^{K'} | \text{Tr}_{K_c, K_c'}^{(P, P')} (d_P^{K_c} d_{P'}^{K_c'} \Phi_{P, P'}) | \beta_P^K \alpha_{P'}^{K'} \rangle - (P_K^{(\alpha)} - P_K^{(\beta)}) \delta_{i, i'} \delta_{K', K_c} \sum_Q \langle \alpha_P^K \beta_{P'}^{K'} | \langle \Phi_{PQ} \rangle_Q | \beta_P^K \alpha_{P'}^{K'} \rangle, \quad \text{with } P = \{\mathbf{n}, i\} \text{ and } P' = \{0, i'\}. \quad (22)$$

Here  $K$  is equal to either  $T$  or  $L$ , and  $K_c$  is the complement of  $K$ ; the same holds for  $K'$ .  $\epsilon_K^{(\alpha)}$  is the mean field translational energy of the state  $|\alpha_P^K(\mathbf{u}_P)\rangle$ , which is an eigenstate of  $H_P^T(\mathbf{u}_P)$ ; an analogous definition holds for  $\epsilon_K^{(\beta)}$ . Finally,  $P_K^{(\alpha)} = \langle \alpha_P^K | d_P^K | \alpha_P^K \rangle$  are occupation numbers corresponding with the mean field density operators  $d_P^K$ . As in paper I, we omit the rows and columns for which  $\epsilon_K^{(\alpha)} = \epsilon_K^{(\beta)}$  and we order the mean field states according to whether  $\epsilon_K^{(\alpha)} > \epsilon_K^{(\beta)}$  or  $\epsilon_K^{(\alpha)} < \epsilon_K^{(\beta)}$ . If we assume that all mean field states are real, the matrix  $M$  has the simple structure

$$M(\mathbf{q}) = \begin{pmatrix} A^{TT} - B^{TT}(\mathbf{q}) & -B^{TL}(\mathbf{q}) & -B^{TT}(\mathbf{q}) & -B^{TL}(\mathbf{q}) \\ -B^{TL}(\mathbf{q})^\dagger & A^{LL} - B^{LL}(\mathbf{q}) & -B^{TL}(\mathbf{q})^\dagger & -B^{LL}(\mathbf{q}) \\ B^{TT}(\mathbf{q}) & B^{TL}(\mathbf{q}) & -A^{TT} + B^{TT}(\mathbf{q}) & B^{TL}(\mathbf{q}) \\ B^{TL}(\mathbf{q})^\dagger & B^{LL}(\mathbf{q}) & B^{TL}(\mathbf{q})^\dagger & -A^{LL} + B^{LL}(\mathbf{q}) \end{pmatrix}. \quad (23)$$

Here  $A^{KK'}$  is the diagonal matrix with elements  $\delta_{\alpha, \alpha'} \delta_{\beta, \beta'} \delta_{i, i'} \delta_{K, K'} (\epsilon_K^{(\alpha)} - \epsilon_K^{(\beta)})$  and the matrices  $B^{KK'}(\mathbf{q})$  follow from Eq. (22). We notice that the correlation which we lost by choosing Eq. (20b) instead of Eq. (20a) will partly be recovered by the last term in Eq. (22). This term couples the rotations and translations on the same molecule. The only  $B$  matrix in which this term appears is  $B^{TL}(\mathbf{q})$ . In the actual calculations we have restricted the mean field basis to the ground states, the lowest three excited levels, for the translations and two excited levels for the librations. These numbers correspond with the degrees of freedom. As a result, in Eq. (23),  $\beta$  is always equal to zero, i.e., it represents the ground state, and  $\alpha$  is not. All calculations are performed for zero temperature, although the formalism holds for  $T > 0$  as well.

### III. CALCULATIONS AND RESULTS

The formalism described in the preceding section has been implemented in a computer program and applied to the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases of solid nitrogen. The structure of these phases has been described in papers I and II, and we have used the same *ab initio* potential.<sup>13</sup> First, we have performed the mean field calculations for the molecular librations and translational vibrations, separately, by an iterative procedure which alternately uses Eqs. (21a) and (21b). For the disordered  $\beta$  phase we met the following problem: The delocalized mean field solution for the molecular reorientations which corresponds with the observed hexagonal lattice symmetry is not stable, i.e., it does not represent a minimum in the free energy (see paper II). The stable solution, which we have found also, corresponds with localized librations of the molecules around one of six equivalent axes which make an angle of 52° with the crystal  $c$  axis; for the two molecules in the hexagonal unit cell equilibrium axes are rotated over 180° about the  $c$  axis. Although we expect that the experimentally

observed lattice symmetry can be restored by allowing rapid jumps of the molecules between these six localized librational solutions, the lower symmetry of the stable mean field solution makes it impossible to use our libron-phonon formalism as such. Indeed, we find that in the mean field of the “broken symmetry” librational solution, the mean field equilibrium positions of the molecules tend to shift away from the hexagonal lattice sites. Thus, the symmetry of the translational mean field solution becomes lower than the experimentally observed symmetry, as well. In order to cure this problem one would have to extend our formalism with a dynamical model for the symmetry-restoring molecular jumps.

For the ordered  $\alpha$  and  $\gamma$  phases we have not experienced such difficulties, however, and the stable mean field solutions obtained correspond with the observed space groups of the lattices. We have even determined theoretically optimized unit cell parameters in the following manner. For the  $\alpha$  phase, which exists in equilibrium with nitrogen vapor of very low pressure (practically  $p = 0$ ), we have calculated the minimum of the Helmholtz free energy  $A$ , as a function of the cubic cell parameter  $a$ . The free energy is defined as in paper I, but now we have included the translational vibrations as well. This yielded the optimum cell parameter  $a = 5.699$  Å (experimentally<sup>21</sup>  $a = 5.644$  Å) and the mean field lattice cohesion energy at  $T = 0$  K:  $\Delta E = 5.92$  kJ/mol, including zero point motions (experimentally  $\Delta E = 6.92$  kJ/mol). For the  $\gamma$  phase which is stable above  $p = 4$  kbar, 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 quadratic function. Each point  $(a, c)$  corresponds with molar volume  $v = Na^2c/2$  and on each curve of constant  $v$  we can determine the optimum  $a$  and  $c$  by minimizing  $A$ . Using these optimum points and the corresponding free energies we have calculated the pressure  $p = -\partial A / \partial v$ . Thus we have found, at  $p = 4$  kbar, that  $a = 3.961$  Å,  $c = 5.104$  Å in very

good agreement with the experimental values<sup>21</sup>  $a = 3.957 \text{ \AA}$ ,  $c = 5.109 \text{ \AA}$ .

Having calculated the ground and excited mean field states of  $\alpha$  and  $\gamma$  nitrogen, we have included the intermolecular correlations as well as translational-rotational coupling, by determining the eigenvalues of the TDH matrix  $M(q)$  [Eq. (23)]. In practice, we have solved the generalized Hermitean eigenvalue problem [paper I, Eq. (20)], which yields the squares of the TDH frequencies. We have tested the convergence of the frequencies with respect to the expansion length of the potential  $\alpha_{\max}$  and the sizes of the bases used for the translational modes,  $n_{\max}$  and for the librations  $l_{\max}$ . Characteristic results are given in Tables I and II. For  $\alpha_{\max} = 2$  only those terms in the potential which are harmonic in the molecular displacements are included, for  $\alpha_{\max} = 3$  also all cubic terms and for  $\alpha_{\max} = 4$  all quartic terms, as well, cf. Eq. (12). The orientational dependence of the potential as given by the spherical expansion [Eqs. (1) and (12)] is always fully taken into account. For some points in the Brillouin zone the effect of the cubic terms vanishes and the anharmonic quartic corrections to the translational frequencies are due to the quartic terms only. This is related to the inversion symmetry of the crystal; it occurs at the same points, such as the  $\Gamma$  point (see Table I), where the translational and librational modes are decoupled. In other points, such as the  $M$  point, the cubic corrections are nonzero but they are smaller than the quartic corrections. This may suggest that even higher terms could be important. We believe, however, that this is not the case, since the potential is represented to 1% accuracy by the terms with  $\alpha_1 + \alpha_2 \leq 4$  for molecular displacements as large as  $0.3 \text{ \AA}$ . The actual rms displacements emerging from our calculations are only about  $0.1 \text{ \AA}$  (see Table III).

The size of the anharmonic corrections to the translational frequencies is comparable, for  $\alpha$  and  $\gamma$  nitrogen, to the SCP corrections.<sup>14</sup> This is not undesirable since the SCP method appeared to work very well for the translational lattice modes in solid nitrogen.<sup>14</sup> There is an important difference, however, between our formalism and the SCP method.<sup>22</sup> The latter method neglects those terms in the potential

TABLE I.  $\alpha_{\max}$  dependence of some TDH lattice frequencies for  $\alpha$ -N<sub>2</sub> ( $a = 5.644 \text{ \AA}$ ,  $T = 0 \text{ K}$ ).

$\alpha_{\max} =$	Frequencies $\omega(\text{cm}^{-1})$		
	2	3	4
	(harmonic model)		
$\Gamma(0,0,0)$			
$E_g$	32.8	32.8	32.8
$T_g$	43.4	43.4	43.4
$T_g$	71.6	71.6	71.5
$A_u$	42.3	42.3	50.6
$T_u$	48.7	48.7	52.7
$E_u$	55.7	55.7	60.2
$T_u$	73.0	73.0	79.4
$M(\pi/a, \pi/a, 0)$			
$M_{12}$	28.8	25.7	28.8
$M_{12}$	40.4	38.5	41.5
$M_{12}$	52.2	51.7	53.3
$M_{12}$	60.0	61.2	63.7
$M_{12}$	67.0	68.6	72.0

TABLE II.  $l_{\max}$  and  $n_{\max}$  dependence of the free energy and the mean field excitation frequencies for  $\alpha$ -N<sub>2</sub> ( $\alpha_{\max} = 4$ ,  $a = 5.699 \text{ \AA}$ ,  $T = 0 \text{ K}$ ).

$l_{\max}$ (basis size $L$ )	$n_{\max}$ (basis size $T$ )	$A(\text{kJ/mol})$	$\omega_L(\text{cm}^{-1})$	$\omega_T(\text{cm}^{-1})$
6(28)	3(20)	-5.8979	57.07	48.63
	4(35)	-5.8980	57.07	48.63
	5(56)	-5.8980	57.07	48.62
8(45)	3(20)	-5.9172	51.09	48.25
	4(35)	-5.9172	51.10	48.26
	5(56)	-5.9172	51.10	48.24
10(66)	3(20)	-5.9188	50.22	48.20
	4(35)	-5.9188	50.22	48.20
	5(56)	-5.9188	50.23	48.20

which depend on odd powers of the molecular displacements, for any type of crystal and any point in the Brillouin zone. Our formalism includes the cubic terms, at those points where they do not vanish by symmetry. This is related to the occurrence of excited harmonic oscillator functions in the translational basis [Eq. (17)] with both even and odd  $n$ .

Table II illustrates that the excitation frequencies are quite well converged already for a translational basis with  $n_{\max} = 3$ . In our further calculations we have included all basis functions up to  $n_{\max} = 5$ , inclusive. The convergence of the librational frequencies is comparable with the pure libron calculations in paper I. In the final calculations we have used  $l_{\max} = 10$  for  $\alpha$ -N<sub>2</sub> and  $l_{\max} = 12$  for  $\gamma$ -N<sub>2</sub>, just as in paper I. We did not find any significant differences in the lattice frequencies between *ortho*-N<sub>2</sub> and *para*-N<sub>2</sub> solids, i.e., even  $l$  and odd  $l$  bases.

Table III lists the rms displacements of the molecules, as obtained from the mean field solutions and similar quantities for the angular oscillations. The amplitude of the motions in the  $\gamma$  phase are smaller than those in the  $\alpha$  phase. The librational amplitudes are considered in both phases even at  $T = 0 \text{ K}$ , while it should be remembered that the mean field model still has the tendency to underestimate such ampli-

TABLE III. Translational and librational amplitudes from mean field calculations.

$\alpha$ -N <sub>2</sub>	$T = 0 \text{ K}$	$p = 0$
	$\langle u_{\parallel}^2 \rangle^{1/2} = 0.112 \text{ \AA}$	$u_{\parallel} = u_{[1,1,1]}$
	$\langle u_{\perp}^2 \rangle^{1/2} = 0.107 \text{ \AA}$	
	$\langle u^2 \rangle^{1/2} = 0.189 \text{ \AA}$	
	$\arccos(\langle \cos^2 \theta \rangle^{1/2}) = 16.1^\circ$	
$\gamma$ -N <sub>2</sub>	$T = 0 \text{ K}$	$p = 4 \text{ kbar}$
	$\langle u_{\parallel}^2 \rangle^{1/2} = 0.100 \text{ \AA}$	$u_{\parallel} = u_{[1,1,0]}$
	$\langle u_{\perp}^2 \rangle^{1/2} = 0.086 \text{ \AA}$	
	$\langle u_{lc}^2 \rangle^{1/2} = 0.087 \text{ \AA}$	
	$\langle u^2 \rangle^{1/2} = 0.159 \text{ \AA}$	$u_{lc} = u_{[0,0,1]}$
	$\arccos(\langle \cos^2 \theta \rangle^{1/2}) = 12.9^\circ$	
asymmetry parameter (rotation out of $ab$ -plane rotation in the $ab$ plane:		
$\frac{\langle \sin^2 \theta (\sin^2 \varphi - \cos^2 \varphi) \rangle}{\langle \sin^2 \theta \rangle} = 0.05$		

TABLE IV. Lattice frequencies in  $\alpha$ -N<sub>2</sub> (in cm<sup>-1</sup>)  $T = 0$  K,  $p = 0$ .

		Experiment (Ref. 24)	Semiempirical harmonic (Ref. 27)	SCP (Ref. 14)	TDH(libron) (Ref. 3)	TDH (This work)	TDH (This work)
	$a(\text{\AA})$	5.644	5.644	5.796	5.644	5.644	5.699
Librations	$\Gamma(0,0,0)$						
	$E_g$	32.3	37.5	39.5	30.7	32.8	31.0
	$T_g$	36.3	47.7	48.5	41.0	43.4	41.0
	$T_g$	59.7	75.2	70.3	68.5	71.5	68.0
Translational vibrations	$A_u$	46.8	45.9	48.8		50.6	47.2
	$T_u$	48.4	47.7	48.4		52.7	48.8
	$E_u$	54.0	54.0	53.5		60.2	55.6
	$T_u$	69.4	69.5	72.0		79.4	73.1
	$M(\pi/a, \pi/a, 0)$						
	$M_{12}$	27.8	29.6	32.5		28.8	27.6
	$M_{12}$	37.9	40.6	43.3		41.5	39.1
	$M_{12}$	46.8	51.8	54.0		53.3	50.2
	$M_{12}$	54.9	59.0	58.5		63.7	59.1
	$M_{12}$	62.5	66.4	64.9		72.0	66.5
Translational vibrations	$R(\pi/a, \pi/a, \pi/a)$						
	$R_1^-$	33.9	34.4	34.2		37.0	34.4
	$R_{23}^-$	34.7	35.7	35.9		38.4	35.8
	$R_{23}^-$	68.6	68.3	71.0		78.4	72.3
Librations	$R_1^+$	43.6	50.7	52.7	47.9	50.7	47.9
	$R_{23}^+$	47.2	57.8	55.7	51.0	53.6	50.8
rms deviation of librational frequencies			10.6	9.7	5.2	7.5	5.0
rms deviation of translational frequencies			0.6	1.6		6.5	2.1
rms deviation of all lattice frequencies			6.1	6.0		6.7	3.4

tudes, i.e., to overestimate the order parameters.<sup>23</sup>

The final frequencies from TDH calculations are given in Tables IV and V for different wave vectors  $\mathbf{q}$ . The dispersion relations along some symmetry directions in the Brillouin zone are displayed in Fig. 2. We have not tried to apply the equivalent of Raich's libron theory<sup>6</sup> to the translational modes since this model which is based on the Tamm-Dancoff approximation, yields acoustical phonon branches which do not converge to zero frequency for  $\mathbf{q} \rightarrow 0$ . The TDH or RPA model does show the correct limiting behavior, in this respect, but only if it is applied exactly,<sup>15</sup> and we had to use a translational basis, which is not too small, in order to approach this limit.

The confrontation of these final results with the experimental data<sup>24-26</sup> is very satisfactory, especially if we remember that the *ab initio* potential has not been adapted in order to improve the agreement, in contrast with most semiempiri-

cal calculations. Particularly, the libron frequencies are substantially improved with respect to earlier harmonic and SCP calculations<sup>14</sup> using the same *ab initio* potential and also with respect to semiempirical harmonic calculations.<sup>27</sup> This was already achieved by our previous libron calculations,<sup>3</sup> but the present formalism yields the frequencies of the translational and mixed modes, also in good agreement with experiment. The complete phonon dispersion curves in Fig. 2 are very close to the curves obtained from inelastic neutron scattering.<sup>24</sup>

#### IV. CONCLUSIONS

We have developed a formalism for quantitative lattice dynamics calculations on molecular crystals which is applicable to strongly anharmonic systems. It does not start from the usual harmonic model. For the orientational oscillations

TABLE V. Lattice frequencies in  $\gamma$ -N<sub>2</sub> (in cm<sup>-1</sup>)  $T = 0$  K,  $p = 4$  kbar.

		Experiment (Refs. 25 and 26)	Semiempirical harmonic (Ref. 27)	SCP (Ref. 14)	TDH(libron) (Ref. 3)	TDH (This work)	TDH (This work)
	$a(\text{\AA})$	3.957	3.940	4.100	3.957	3.957	3.961
	$c(\text{\AA})$	5.109	5.086	5.188	5.109	5.109	5.104
	$\Gamma(0,0,0)$						
Librations	$E_g$	55.0	50.5	56.5	63.8	67.5	67.6
	$B_{1g}$	98.1	74.8	85.2	99.6	104.2	103.3
	$A_{2g}$		105.1	107.1	119.9	125.1	124.4
Translational vibrations	$E_u$	65.0	58.3	69.3		65.0	65.2
	$B_{1u}$		103.1	107.4		115.8	114.9
rms deviation			14.2	7.9	6.3	8.0	7.9



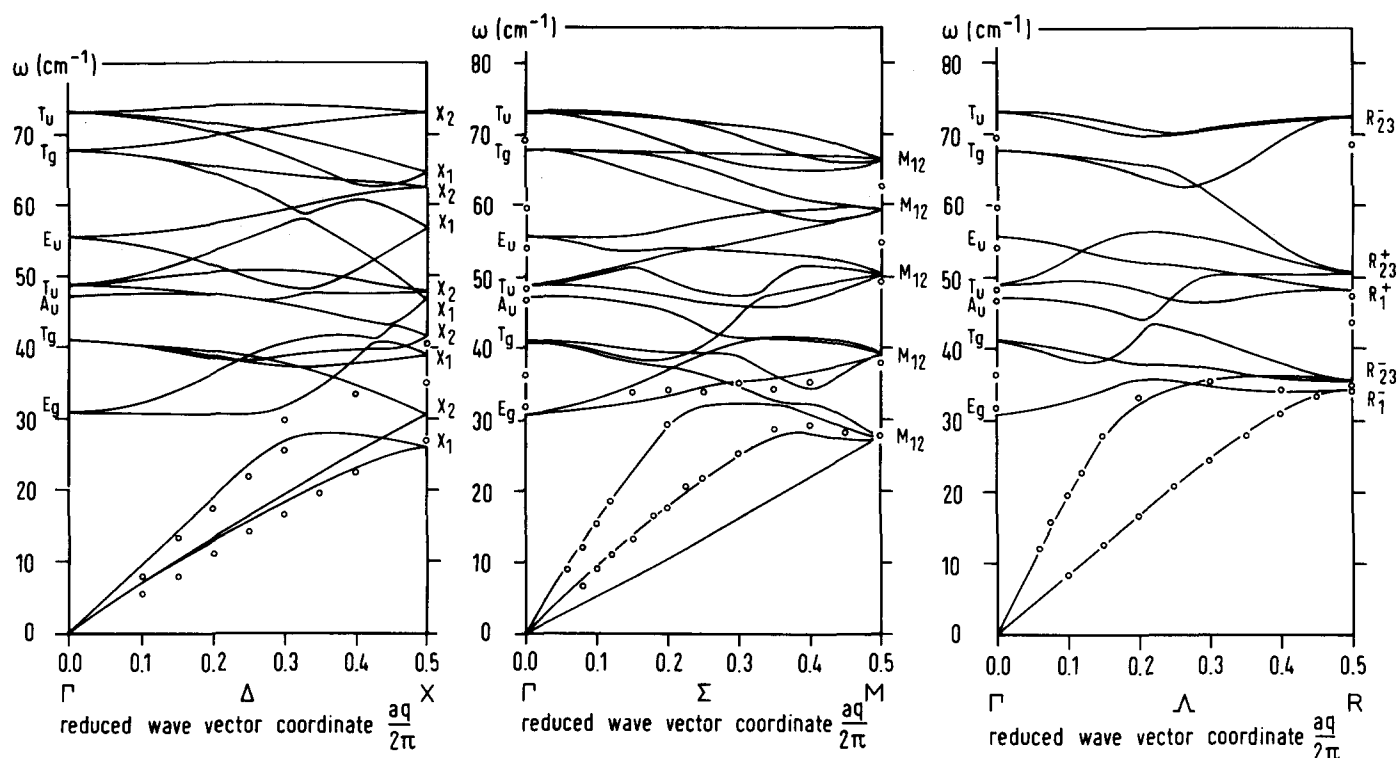


FIG. 2. Calculated (TDH) dispersion curves for  $\alpha$ -N<sub>2</sub>, for phonon-libron modes (a)–(c) propagating along the [001], [110], and [111] directions. The circles correspond with inelastic neutron scattering data measured at  $T = 15$  K (Ref. 24).

of the molecules we do not even require small amplitudes; the model is appropriate for free or hindered molecular rotations occurring in plastic phases. Only when the orientational disorder in such phases is associated with jumps of the molecules between different orientations, the formalism is not applicable as such.

The model has been applied to solid nitrogen, using an *ab initio* potential, with the results, lattice constants, and phonon-libron frequencies, in good agreement with experiment. The observation that this agreement became systematically better with improvements of the lattice dynamics model indicates that the *ab initio* potential used should be fairly realistic.

Although the formalism is certainly more complicated than the standard harmonic model, computation times for crystals of linear molecules, using extensive lattice sums, are still modest on modern computers. This is promising in view of possible extension of our formalism to crystals of nonlinear molecules. We can borrow several results from a recent dynamical model for van der Waals complexes comprising two nonlinear molecules.<sup>28</sup> The spherical harmonics  $C_m^{(l)}(\theta, \varphi)$  should be replaced by rotation functions  $D_{km}^{(l)}(\psi, \theta, \varphi)$  both in the potential [Eq. (1)] and in the basis for the molecular reorientations. The matrix elements over such functions are hardly more complicated but the dimension of the summations will be extended.

The formalism requires the potential to be given in the form of a spherical expansion [Eq. (1)]. Most semiempirical potentials are not in this form, but often they are described by an atom-atom potential model. Such atom-atom or site-site potentials can be expanded in the form of Eq. (1) or its

generalization to nonlinear molecules,<sup>29,32</sup> using closed expressions for the  $r^{-n}$  terms<sup>30–32</sup> and for the  $\exp(-ar)$  terms.<sup>32</sup>

Finally, we observe that the TDH/RPA formalism bases on mean-field states, which we have used for phonons and librions and their coupling, is similar to the spin-wave methods<sup>33–35</sup> applied to magnons. We are trying to extend our model to the coupling between phonons, librions, and magnons in solid oxygen. *Ab initio* calculations of the structure dependence of the Heisenberg exchange coupling between oxygen molecules<sup>36,37</sup> indicate that this coupling may have significant effects on several observed phenomena.

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<sup>1</sup>S. Califano, V. Schettino, and N. Neto, *Lattice Dynamics of Molecular Crystals*, Lecture Notes in Chemistry (Springer, Berlin, 1981), Vol. 26.

<sup>2</sup>T. H. K. Barrow and M. L. Klein, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1.

<sup>3</sup>A. P. J. Jansen, W. J. Briels, and A. van der Avoird, *J. Chem. Phys.* (to be published).

<sup>4</sup>A. van der Avoird, W. J. Briels, and A. P. J. Jansen, *J. Chem. Phys.* (to be published).

<sup>5</sup>M. J. Mandell, *J. Low Temp. Phys.* **17**, 169 (1974); **18**, 273 (1975).

<sup>6</sup>J. C. Raich, *J. Chem. Phys.* **56**, 2395 (1972).

<sup>7</sup>P. V. Dunmore, *J. Chem. Phys.* **57**, 3348 (1972); *Can. J. Phys.* **55**, 554 (1977).

- <sup>8</sup>T. N. Antsygina, V. A. Slyusarev, Yu. A. Freiman, and A. I. Erenburg, *Sov. J. Low Temp. Phys.* **8**, 99, 149 (1982).
- <sup>9</sup>J. C. Raich, H. Yasuda, and E. R. Bernstein, *J. Chem. Phys.* **78**, 6209 (1983).
- <sup>10</sup>A. I. M. Rae, *J. Phys. C* **15**, 1883 (1982); **15**, L287 (1982).
- <sup>11</sup>T. Luty and A. van der Avoird, *Chem. Phys.* **83**, 133 (1984).
- <sup>12</sup>B. de Raedt, K. Binder, and K. H. Michel, *J. Chem. Phys.* **75**, 2977 (1981); K. H. Michel and J. Naudts, *ibid.* **68**, 216 (1978).
- <sup>13</sup>R. M. Berns and A. van der Avoird, *J. Chem. Phys.* **72**, 6107 (1980).
- <sup>14</sup>T. Luty, A. van der Avoird, and R. M. Berns, *J. Chem. Phys.* **73**, 5305 (1980).
- <sup>15</sup>D. J. Rowe, *Nuclear Collective Motion* (Methuen, London, 1970).
- <sup>16</sup>D. R. Fredkin and N. R. Werthamer, *Phys. Rev. A* **138**, 1527 (1965).
- <sup>17</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1957).
- <sup>18</sup>D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon, Oxford, 1975).
- <sup>19</sup>J. L. Powell and B. Craseman, *Quantum Mechanics* (Addison-Wesley, Reading, 1961).
- <sup>20</sup>J. Tennyson and B. T. Sutcliffe, *J. Chem. Phys.* **77**, 4061 (1982).
- <sup>21</sup>T. A. Scott, *Phys. Rep.* **27**, 89 (1976).
- <sup>22</sup>N. R. Werthamer, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, London, 1976), Vol. I, p. 265.
- <sup>23</sup>H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University, Oxford, 1971).
- <sup>24</sup>J. K. Kjems and G. Dolling, *Phys. Rev. B* **11**, 1639 (1975).
- <sup>25</sup>M. M. Thiéry and D. Fabre, *Mol. Phys.* **32**, 257 (1976).
- <sup>26</sup>F. Fondère, J. Obriot, Ph. Marteau, M. Allavina, and H. Chakroun, *J. Chem. Phys.* **74**, 2675 (1981).
- <sup>27</sup>J. C. Raich and N. S. Gillis, *J. Chem. Phys.* **66**, 846 (1977).
- <sup>28</sup>G. Brocks, A. van der Avoird, B. T. Sutcliffe, and J. Tennyson, *Mol. Phys.* **50**, 1025 (1983).
- <sup>29</sup>A. van der Avoird, P. E. S. Wormer, F. Mulder, and R. M. Berns, *Topics Current Chem.* **93**, 1 (1980).
- <sup>30</sup>R. A. Sack, *J. Math. Phys.* **5**, 260 (1964).
- <sup>31</sup>J. Downs, K. E. Gubbins, S. Murad and C. G. Gray, *Mol. Phys.* **37**, 129 (1979).
- <sup>32</sup>W. J. Briels, *J. Chem. Phys.* **73**, 1850 (1980).
- <sup>33</sup>C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
- <sup>34</sup>D. C. Mattis, *The Theory of Magnetism I* (Springer, Berlin, 1981).
- <sup>35</sup>Yu. B. Gaididei and V. M. Loktev, *Sov. Phys. Solid State* **16**, 2226 (1975).
- <sup>36</sup>M. C. van Hemert, P. E. S. Wormer, and A. van der Avoird, *Phys. Rev. Lett.* **51**, 1167 (1983).
- <sup>37</sup>P. E. S. Wormer and A. van der Avoird, *J. Chem. Phys.* **81**, 1929 (1984).