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Ab initio description of large amplitude motions in solid N₂. II. Librons in the \( \beta \)-phase and the \( \alpha - \beta \) phase transition

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Using an ab initio pair potential, we have performed mean field and time-dependent Hartree calculations for the reorientational motions in disordered \( \beta \)-nitrogen, in a basis of tesseral harmonics. The results show that orientationally localized librational solutions with neighboring molecules rotated over 180° around the crystal \( c \) axis are energetically more favorable than (nearly) free precession of the molecules. The experimental symmetry can be obtained by allowing rapid jumps between six equivalent localized states; such a jump model predicts the \( \alpha - \beta \) phase transition at the correct temperature.

I. INTRODUCTION

In the preceding paper 1 we have described a model for the librations in the ordered \( \alpha \) and \( \gamma \) phases of solid N₂. In contrast with the more common (quasi-) harmonic models, this “libron” model holds even for the larger amplitude librations. In the present paper we apply it to the \( \beta \) phase of solid nitrogen where the molecules are orientationally disordered.

Two pictures have been accepted for \( \beta \)-nitrogen and it was not possible from the experimental data2-6 (x-ray diffraction, neutron scattering, nuclear magnetic resonance, and nuclear quadrupole resonance) to discriminate between these pictures. In both pictures the molecular centers are located on a hexagonal lattice with a \( c/a \) ratio close to the ideal hexagonal close packed value. There are two molecules in the unit cell and the space group is \( P 6_{3}/mmc \) [see Fig. 1(b) of paper I]. In the first picture the \( N_2 \) molecules are freely precessing around the crystal \( c \) axis with an angle of 56° ± 2.5° between the molecular axes and the \( c \) axis. In the second picture the nitrogen atoms are randomly distributed among 24 equivalent positions of the space group \( P 6_{3}/mmc \), with the same angle of about 56° between the molecular axes and the \( c \) axis. It has been pointed out,4 on the basis of the overlap between specific molecular density contours, that there will probably be some hindrance between neighboring molecules at specific precession angles. This would prevent completely free precessions.

Theoretical treatments of the lattice dynamics in \( \beta \)-nitrogen are not very numerous. This is obviously due to the fact that it is impossible to apply the standard harmonic model. Some authors9,10 have assumed that the intermolecular potential may be averaged over freely rotating \( N_2 \) molecules. This yields an effective isotropic potential between \( N_2 \) pseudoatoms, which was used in a self-consistent phonon calculation of the translational lattice modes. The reorientational contributions to the free energy were then superimposed, using a free rotor or 12-fold jump model.9 Explicit treatments of the reorientational motions on the basis of an anisotropic potential have been given by Mandell11—a classical Monte Carlo simulation with a pure quadrupole–quadrupole interaction—by Klein et al.12,13—a classical molecular dynamics calculation with atom–atom plus quadrupole–quadrupole potential—and by Dunmore.14 The latter, quantum mechanical mean-field calculation is similar to the first part of our study and will be discussed below. Optical (infrared, Raman)15 and inelastic neutron scattering5,6 studies of the phonon spectrum of \( \beta \)-\( N_2 \) are rather scarce as well.

In the present paper we first present a mean-field solution for the reorientational motions in \( \beta \)-\( N_2 \) which has the experimentally observed symmetry. When we tried to treat the correlations between the molecular reorientations by means of the time-dependent Hartree (TDH) or the random phase approximation (RPA), the libron frequencies came out purely imaginary, however. It is demonstrated in Sec. II, that this implies the instability of the mean-field solution. So, we have looked for a stable mean-field solution of lower symmetry and calculated the libron frequencies (in Sec. III). Next we discuss the \( \alpha - \beta \) phase transition and the physical picture that emerges for the reorientational motions in \( \beta \)-nitrogen.

II. STABILITY CONDITIONS FOR THE MEAN-FIELD MODEL

It has been demonstrated by Fredkin and Werthamer16 that the stability of the solutions of the mean-field (MF) or time-independent Hartree equations for lattice dynamics is related to the eigenvalues of the time-dependent Hartree equations. For zero temperature the latter are identical to the RPA equations (see paper I). Imaginary eigenfrequencies of the TDH equations imply that the original MF solution does not correspond to a local minimum of the free energy. The result in the Appendix of Ref. (16) is a generalization to nonzero temperature of the stability conditions for Hartree–Fock solutions in many-fermion systems.17–20 We give a slightly different proof which follows closely the presentation of the theory in paper I.

We start with the thermodynamic variation principle for the Helmholtz free energy:

\[
A_{\text{var}} = A_0 + \langle H - H_0 \rangle_0 \Delta A,
\] (1)
where $H$ is the exact lattice Hamiltonian (omitting the constant term from paper I):

$$H = \sum_p L_p(\Omega_p) + \frac{1}{2} \sum_{p'p''} \Phi_{p',p''}(\Omega_p, \Omega_{p''})$$

and $H_0$ may be any Hamiltonian. The thermodynamic expectation value $(X)_0$ is defined as

$$(X)_0 = \text{Tr}(D_0X), \tag{3}$$

where $D_0 = Z_0^{-1} e^{-\beta H_0}$ is the density operator associated with the approximate Hamiltonian $H_0$ and $A_0$ is the corresponding free energy:

$$A_0 = -\beta^{-1} \ln Z_0. \tag{4}$$

The partition function reads

$$Z_0 = \text{Tr}(e^{-\beta H_0})$$

and

$$\beta = (k_B T)^{-1}. \tag{5}$$

The exact quantities are given by

$$A = -\beta^{-1} \ln \int e^{-\beta H}$$

and

$$H^\text{MF}(\Omega_p) - H^\text{MF}(\Omega_p) + h_p(\Omega_p). \tag{9}$$

In order to derive the effect of such variations on the free energy, we use the following well-known expansion:

$$e^{-\beta H^\text{MF} + h} = e^{-\beta H^\text{MF}} T \exp \left[ -\int_0^\beta d\beta_1 \tilde{h}_p(\beta_1) \right]$$

$$= e^{-\beta H^\text{MF}} \left[ 1 - \int_0^\beta d\beta_1 \tilde{h}_p(\beta_1) + \int_0^\beta d\beta_1 \int_0^{\beta_1} d\beta_2 \tilde{h}_p(\beta_1) \tilde{h}_p(\beta_2) - \ldots \right] \tag{10}$$

with

$$\tilde{h}_p(\beta) = e^{\beta H^\text{MF}} h_p e^{-\beta H^\text{MF}}, \tag{11}$$

where $T$ is the Dyson time-ordering operator, acting here on the inverse temperatures $\beta_1, \beta_2, \text{etc}$. In order to simplify the notation we have stopped indicating the dependence of all quantities on $\Omega_p$. Expanding the logarithm in Eq. (4) we obtain for the first order variation in $A_0$:

$$A^{(1)}_0 = -\beta^{-1} \sum_p \left( \int_0^\beta d\beta_1 \tilde{h}_p(\beta_1) \right)_p$$

$$= \sum_p \langle h_p \rangle_p. \tag{12}$$

The single-particle expectation value is defined as

$$\langle x_p \rangle_p = \text{Tr}(d_p^\text{MF} x_p), \tag{13}$$

with $d_p^\text{MF}$ given by Eq. (8).

The same variation (9) of $H^\text{MF}_p$ by $h_p$ makes the corresponding density operator vary as

$$d_p = e^{-\beta(H^\text{MF}_p + h_p)/T} \left( e^{-\beta H^\text{MF}_p + h_p} \right)$$

$$= d_p^\text{MF} + \delta^{(1)}_p + \ldots \tag{14}$$

with

$$\delta^{(1)}_p = -d_p^\text{MF} \left( \int_0^\beta d\beta_1 \tilde{h}_p(\beta_1) - \beta \langle h_p \rangle_p \right). \tag{15}$$

It is easy to verify that $\text{Tr}(d_p^\text{MF}) = 0$. The same result holds for the higher order terms, so that the density operator remains normalized, $\text{Tr}(d_p^\text{MF}) = 1$, in every order. For the first order variation of $A_{\text{var}}$ we find the following expression:

$$A^{(1)}_{\text{var}} = A^{(1)}_0 + \sum_p \text{Tr}(\delta^{(1)}_p L_p) + \sum_{p',p''} \text{Tr}(d_p^\text{MF} \delta^{(1)}_p d_{p''}^\text{MF} \Phi_{p'p''})$$

$$- \sum_p \text{Tr}(\delta^{(1)}_p H^\text{MF}_p) - \sum_p \text{Tr}(d_p^\text{MF} h_p). \tag{16}$$

Substituting Eqs. (12) and (13), we observe immediately that the first term cancels the last term. Putting $A^{(1)}_0 = 0$ for arbitrary variations of $H^\text{MF}_p$, which are related to the variations $h_p$ via Eq. (15), we obtain the MF result

$$H^\text{MF}_p = L_p + \sum_p \text{Tr}(d_p^\text{MF} \Phi_{p'p''})$$

$$= L_p + \Phi_p^\text{MF}. \tag{17}$$

In order to investigate whether the MF solution corresponds to a local minimum of $A_{\text{var}}$, we must look at the second order variation $A^{(2)}_{\text{var}}$. All quantities occurring in $A_{\text{var}}$ can be expanded via Eq. (10), now taken up to the second order terms inclusive. Expanding the logarithm in Eq. (4) again, we get

$$A^{(2)} = -\beta^{-1} \sum_p \left[ \left( \int_0^\beta d\beta_1 \int_0^{\beta_1} d\beta_2 \tilde{h}_p(\beta_1) \tilde{h}_p(\beta_2) \right)_p \right.$$}

$$- \frac{1}{2} \left( \int_0^\beta d\beta_1 \tilde{h}_p(\beta_1) \right)_p^2$$

$$= -\beta^{-1} \sum_p \int_0^\beta d\beta_1 \int_0^{\beta_1} d\beta_2 \tilde{h}_p(\beta_1) \tilde{h}_p(\beta_2) - \frac{1}{2} \beta \sum_p \langle h_p \rangle_p^2. \tag{18}$$

The total second order variations in $A_{\text{var}}$ can then be written as

$$A^{(2)}_{\text{var}} = A^{(2)}_0 + \frac{1}{2} \sum_{p,p'} \text{Tr}(d_p^\text{MF} \delta^{(1)}_p \Phi_{p'p'})$$

$$+ \frac{1}{2} \sum_p \text{Tr}(\delta^{(1)}_p L_p + \frac{1}{2} \sum_{p',p''} \text{Tr}(d_p^\text{MF} \delta^{(1)}_p d_{p''}^\text{MF} \Phi_{p'p''})$$

$$- \sum_p \text{Tr}(\delta^{(1)}_p H^\text{MF}_p) - \sum_p \text{Tr}(d_p^\text{MF} h_p). \tag{19}$$

The terms with $\delta^{(2)}_p$ cancel after substituting the MF Hamiltonian (17) and the remaining terms.
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\[ A^{(2)}_{\text{var}} = A^{(2)}_0 + \frac{1}{2} \sum_{PP'} \text{Tr} \left( \delta^{(1)}_P \delta^{(1)}_{P'} \Phi_{PP'} \right) \]
\[ - \sum_P \text{Tr} \left( \delta^{(1)}_P h_P \right) \]  

(20)
can be worked out by substituting Eqs. (15) and (18). Taking the traces with respect to the eigenstates \( |\alpha_P\rangle = |\psi_P^{(a)}\rangle \) of the MF Hamiltonian

\[ H^{MF}_P(\alpha_P) = \epsilon^{(a)} |\alpha_P\rangle, \]

(21)
it is not difficult to obtain the result

\[ A^{(2)}_{\text{var}} = \frac{1}{2} \sum_{PP'} \sum_{|\alpha_P| \neq |\beta_P|} \langle \alpha_P | \Phi_{PP'} | \beta_P \rangle \langle \beta_P | \delta^{(1)}_P | \alpha_P \rangle \]
\[ - \frac{1}{2} \sum_P \sum_{|\alpha_P| \neq |\beta_P|} \frac{P^{(a)} - P^{(b)}}{\epsilon^{(a)} - \epsilon^{(b)}} \langle \alpha_P | h_P | \beta_P \rangle \langle \beta_P | h_P | \alpha_P \rangle + \frac{1}{2} \sum_P \sum_{|\alpha_P| \neq |\beta_P|} \beta P^{(a)} \langle \alpha_P | h_P | \alpha_P \rangle^2 - \frac{1}{2} \sum_P \beta \langle h_P \rangle^2. \]

(22)
The second term has been simplified via interchanging \( \alpha_P \) and \( \beta_P \).

The occupation numbers \( P^{(a)} \) are given by

\[ \langle \alpha_P | \delta^{(1)}_P | \beta_P \rangle = \frac{P^{(a)} - P^{(b)}}{\epsilon^{(a)} - \epsilon^{(b)}} \langle \alpha_P | h_P | \beta_P \rangle \quad \text{for} \quad \epsilon^{(a)} \neq \epsilon^{(b)} \]
\[ = - \beta P^{(a)} [ \langle \alpha_P | h_P | \alpha_P \rangle - \langle h_P \rangle_P ] \quad \text{for} \quad \epsilon^{(a)} = \epsilon^{(b)} \]

(24)
and to use this relation backwards, in order to express Eq. (22) completely in terms of the matrix elements of \( \delta^{(1)}_P \):

\[ A^{(2)}_{\text{var}} = \frac{1}{2} \sum_{PP'} \sum_{|\alpha_P| \neq |\beta_P|} \langle \alpha_P | \Phi_{PP'} | \beta_P \rangle \langle \beta_P | \delta^{(1)}_P | \alpha_P \rangle \]
\[ - \frac{1}{2} \sum_P \sum_{|\alpha_P| \neq |\beta_P|} \frac{P^{(a)} - P^{(b)}}{\epsilon^{(a)} - \epsilon^{(b)}} \langle \alpha_P | h_P | \beta_P \rangle \langle \beta_P | h_P | \alpha_P \rangle \]

(25)

The last two sums over diagonal terms in Eq. (22) correspond with the diagonal \( (|\alpha_P| = |\beta_P|) \) terms in the last summation of Eq. (25). These terms have been formally included in this summation via the relation

\[ \lim_{\beta P^{(a)} \to \beta P^{(b)}} \frac{P^{(a)} - P^{(b)}}{\epsilon^{(a)} - \epsilon^{(b)}} = - \frac{1}{\beta P^{(a)}}. \]

(26)
Equation (25) is identical to the expression obtained by Fredkin and Werthamer,\(^{16}\) who did not explicitly consider the diagonal terms.

It is easy to adapt this expression to the translational symmetry of the crystal. Defining the first order variations in the symmetry adapted density matrix as variational coefficients:

\[ C(q)_{\alpha,\beta,i} = N^{-1/2} \sum_n e^{i q R_n} \langle \alpha_P | \delta^{(1)}_P | \beta_P \rangle \]

(27)
with \( P = |n_i\rangle \) and the Fourier transformed pair interaction matrix:

\[ \Phi(q)_{\alpha,\beta,i,i'} = \sum \epsilon_n e^{i q R_n} \langle \alpha_P | \Phi_{PP'} | \beta_P \rangle \]

(28)
with \( P = |0_i\rangle \) and \( P' = |n_i'\rangle \), and \( \Phi_{PP'} = 0 \), just as in paper I, we find that \( A^{(2)}_{\text{var}} \) becomes additive in the wave vector \( q \):

\[ A^{(2)}_{\text{var}} = \sum_q A^{(2)}_{\text{var}}(q) \]

(29)

It can be assumed, without imposing any restriction, that the MF states \( |\alpha_P\rangle \) are real. Then the matrix \( \Phi(q) \) satisfies the following symmetry relations:

\[ \Phi(q)_{\alpha,\beta,i,i'} = \Phi(q)_{\alpha,\beta,i',i} = \Phi(q)_{\beta,\alpha,i,i'} \]

(30)
in addition to the usual properties

\[ \Phi(q) = (\Phi(q))^\dagger = (\Phi(q))^* \]

(31)
For Hermitean variations \( h_P \), Eq. (24) yields the following relation for the variation coefficients (27):

\[ C(q)_{\alpha,\beta,i} = C(-q)_{\beta,\alpha,i} \]

(32)
If we now order the MF states such that \( \alpha > \beta \) implies \( \epsilon^{(a)} > \epsilon^{(b)} \) and \( P^{(a)} > P^{(b)} \), relabel the coefficients

\[ C(q)_{\alpha,\beta,i} = u(q)_{\alpha,\beta,i} \quad \text{for} \quad \alpha > \beta, \]
\[ C(q)_{\alpha,\beta,i} = v(q)_{\alpha,\beta,i} \quad \text{for} \quad \alpha = \beta, \]
\[ C(q)_{\alpha,\beta,i} = w(q)_{\alpha,\beta,i} \quad \text{for} \quad \alpha < \beta, \]

(33)

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and use the relations (30) to (32), we can rewrite Eq. (29) in matrix form:

$$A_{\text{var}}^{(2)}(q) = \frac{1}{2} \begin{pmatrix} u(q) \end{pmatrix}^\dagger \begin{pmatrix} \Phi(q) - \chi & \Phi(q) \\ \Phi(q)^\dagger & f(q) - g & \Phi(q)^\dagger \end{pmatrix} \begin{pmatrix} u(q) \\ v(q) \\ w(q) \end{pmatrix} \begin{pmatrix} \Phi(q) & \Phi(q)^\dagger & \Phi(q) - \chi \end{pmatrix}$$

(34)

with the matrices $\Phi(q)$, $\phi(q)$, and $f(q)$ all being subblocks of the matrix $\Phi(q)$ in Eq. (28) with $\alpha' > \alpha$, $\alpha' > \beta'$, $\alpha > \beta$, and $\{\alpha = \beta, \alpha = \beta'\}$, respectively. The diagonal matrices $\chi$ and $g$ are defined as

$$\chi_{\alpha, \beta, \alpha', \beta'} = \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} \frac{e^{(\alpha)} - e^{(\beta')}}{P^{(\alpha)} - P^{(\beta')}}$$

for $\alpha > \beta$,

(35)

$$g_{\alpha, \alpha', \beta', \beta} = - \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} (\alpha P^{(\alpha)} - \beta P^{(\beta)})$$

(36)

The matrix occurring in Eq. (34) is related to the matrix $M(q)$ occurring in the TDH equations (cf. paper I) by

$$M(q) = \begin{pmatrix} -P & 0 \\ 0 & P \end{pmatrix} \begin{pmatrix} \Phi(q) - \chi & \Phi(q) \\ \Phi(q)^\dagger & f(q) - g & \Phi(q)^\dagger \end{pmatrix} \begin{pmatrix} -P \\ 0 \end{pmatrix} N(q),$$

(37)

where $P$ is a diagonal population difference matrix

$$P_{\alpha, \beta, \alpha', \beta'} = \delta_{\alpha, \alpha'} \delta_{\beta, \beta'} (P^{(\alpha)} - P^{(\beta)})$$

for $\{\alpha > \beta, \alpha' > \beta'\}$.

(38)

The second variation $A_{\text{var}}^{(2)}(q)$ is positive for any set of variation coefficients (33) if and only if the matrix in Eq. (34) is positive definite. Via the separation theorem for the eigenvalues of Hermitian matrices and their principal minors it follows then, that its submatrix $N(q)$ must be positive definite, too. The latter matrix can be blocked by means of a simple similarity transformation $T$: adding and subtracting its rows and columns, which corresponds with taking the real and imaginary parts of the variation coefficients $u$ and $w$ as new variables. This yields:

$$N(q) = T^{-1} N(q) T = \begin{pmatrix} 2\Phi(q) - \chi & 0 \\ 0 & -\chi \end{pmatrix}.$$  

(38)

The diagonal submatrix $-\chi$ is clearly positive definite, see Eq. (35). As a result, the matrices $N'(q)$ and $N(q)$, and therefore $A_{\text{var}}^{(2)}(q)$ as given by Eq. (34), can only be positive definite if the submatrix $2\Phi(q) - \chi$ is positive definite. The latter matrix occurs in the generalized eigenvalue problem, Eq. (20) of paper I, which yields the squares of the TDH frequencies. Multiplying this eigenvalue equation by $-1$ and using the fact that the metric matrix $-P^{-1} \chi P^{-1}$ is diagonal and positive definite, one easily shows that the squares of the TDH frequencies are all positive if and only if $2\Phi(q) - \chi$ is positive definite.

In summary, we have proved that the squares of the TDH eigenfrequencies are positive, provided that the mean-field solution corresponds with a local minimum in $A_{\text{var}}$. So, if one or more of these squares are negative, i.e., if one or more of the TDH frequencies $A^{(k)}(q)$ are imaginary, then the matrices $N'(q)$ and $N(q)$ have negative eigenvalues. Choosing the variation coefficients $u(q)$ and $w(q)$ in Eq. (33) as one of the eigenvectors of $N(q)$ associated with these negative eigenvalues and $v(q) = 0$ yields a negative value of $A_{\text{var}}(q)$ and thus a free energy which is lower than the MF value. Inspecting these eigenvectors can help us in finding a more stable MF solution.

### III. MEAN FIELD AND LIBRON CALCULATIONS

The methods applied for the lattice dynamics calculations on $\beta$-nitrogen are the same as those used in paper I. Also, we have employed the same $ab$ initio potential with the anisotropy expressed in the form of a spherical expansion, including spherical harmonics up to $l = 6$ on each molecule. We have used the experimental unit cell parameters $a$ and $c$ [see Fig. 1(b) of paper I], at zero pressure and temperature 46 K. The mean-field states of the molecules on each lattice site have been expanded in tesseral harmonics with even or odd $l$ for pure ortho or para nitrogen, respectively. Lattice summations over the potential have been extended over eight shells, $R < 9.87 \text{ Å}$. We have not assumed the mean-field potential to have axial symmetry around the $c$ axis, as Dunmore has done. For the existence of localized solutions with broken symmetry, see below, the nonaxial components are crucial.

Just as in Paper I we have started by assuming the experimentally observed crystal symmetry. Thus, the two molecules in the hexagonal unit cell have been given identical van der Avoird, Briels, and Jansen: Large amplitude motions in solid $N_2$. II

![FIG. 1. Calculated mean-field levels for $\beta$-nitrogen corresponding with the delocalized (unstable) mean-field states and the (stable) localized states. The arrows, which are the free rotor levels, indicate that the delocalized mean-field spectrum resembles a perturbed rotor spectrum.](image-url)
mean-field solutions. That is, the Euler angles in the matrices $D^j_k(\alpha,\beta,\gamma)$ which rotate mean-field expectation values from the original site in the unit cell to the equivalent sites, see Eq. (9) of paper I, have all been put to zero. The mean-field spectrum and the ground state wave function which result from these calculations are shown in Figs. 1 and 2, respectively. It is obvious from the contour plot in Fig. 2 that the orientations of the molecular axes in the mean-field states are delocalized. The motions can be described as precessions around the $c$ axis which are just slightly hindered by small sixfold barriers. In accordance with the picture of Press and Hüller, the angle $\theta$ between the molecular axes and the $c$ axis is not fixed, but it shows a rather broad distribution. The maximum of this distribution lies at the "experimental" precession angle, about 56°. We can easily calculate the coefficients $C_{lm}$ in the orientational form factors:

$$F_{\text{rot}}(q) = \sum_{l,m} (i)^l C_{lm} S_{lm}(\theta,\phi) j_l(qd/2), \quad (39)$$

where $S_{lm}(\theta,\phi)$ are tesseral harmonics, $j_l$ are spherical Bessel functions, $d$ is the molecular bond length, and $q$ is the wave vector. Our results are given in Table I. The experimental results are rather uncertain, but the general feature that $C_{20}$ is relatively very small, which is confirmed by the NMR and NQR data, agrees with our calculations. Also the mean-field spectrum at the left-hand side of Fig. 1, is characteristic for delocalized reorientational motions. It has the appearance of a perturbed free rotor spectrum, with significant differences between ortho and para nitrogen. Apart from the small sixfold modulation in Fig. 2, our results are similar to Dunmore's, although the intermolecular potentials used are different (see also paper I).

From the mean-field states thus obtained we wanted to calculate the libron frequencies by means of the TDH method. Using a basis of two or five excited mean-field states per molecule and 2 molecules in the unit cell, while conserving the full translational symmetry of the problem, one has to solve a four or ten dimensional complex generalized eigenvalue problem, respectively, in order to calculate the squares of the libron frequencies [cf. paper I, Eq. (20)]. Some of these frequencies (for $q = 0$) came out imaginary, however, i.e., their squares were negative, in both cases. According to the theory of Sec. II, this implies that the delocalized mean-field states do not correspond to a local minimum of the free energy. It should be possible to find a more stable mean-field solution which still has the correct translational symmetry. Inspecting the eigenvectors of the TDH problem belonging to the imaginary frequencies has taught us that the free energy could be lowered by out-of-phase motions of the two neighboring molecules in the unit cell.

Thus, we have modified our MF program in such a way that the two molecules in the unit cell are treated independently, within each others mean field. This leads to two steps in each cycle of the iterative MF procedure, which were previously reduced to one step by rotating the mean-field solution from the first molecule to the second one in the unit cell (over angles zero, in this case). Indeed, we have found a MF solution which is lower in free energy than the delocalized solution, by 0.87 kJ/mol at zero temperature. In this new solution, the orientations of the molecular axes are clearly localized, see Fig. 3. The MF states for the two neighboring molecules in the unit cell appear to be equivalent, but rotated over 180° around the $c$ axis, just as expected from the TDH eigenvectors for the previous, unstable, solution. This 180° rotation avoids the hindrance which would occur between

![Diagram](image_url)

**FIG. 2.** Orientational probability distribution of the molecular axes for the delocalized mean-field states in $\beta$-nitrogen, for both molecules in the unit cell. This picture is almost independent of the temperature up to (at least) 70 K. Reading of the contour plot as in paper I, Fig. 3.

**TABLE I.** Orientational form factors in $\beta$-nitrogen from mean field calculations, see Eq. (39).

<table>
<thead>
<tr>
<th></th>
<th>Delocalized</th>
<th>Calculated</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T = 30$ K</td>
<td>$45$ K</td>
<td>$30$ K</td>
</tr>
<tr>
<td>$C_{2,0}$</td>
<td>$-0.027$</td>
<td>$-0.020$</td>
<td>$0.048$</td>
</tr>
<tr>
<td>$C_{4,0}$</td>
<td>$-0.082$</td>
<td>$-0.060$</td>
<td>$-0.233$</td>
</tr>
<tr>
<td>$C_{6,0}$</td>
<td>$0.029$</td>
<td>$0.020$</td>
<td>$0.042$</td>
</tr>
<tr>
<td>$C_{6,6}$</td>
<td>$-0.016$</td>
<td>$-0.013$</td>
<td>$-0.035$</td>
</tr>
</tbody>
</table>

*Converted to normalized tesseral harmonics.
neighboring molecules when they precess freely. The motions of the molecules in this new MF solution can be described as localized librations about equilibrium orientations of the molecular axes which point to one of the square faces of the hexagonal cage, see Fig. 1(b) of paper I. The angle \( \theta = 52^\circ \) between the molecular axes and the crystal \( c \) axis is slightly smaller than for the delocalized case. The coefficients in the form factor are similar, see Table I. In particular, the coefficient \( C_{20} \) is still relatively small, as expected from the experimental data. The much higher excitation energies in the MF spectrum, Fig. 1 right-hand side, and the similarity between the \( \text{ortho} \) and \( \text{para} \) nitrogen solutions are typical for localized librations (cf. the \( \alpha \) and \( \gamma \) nitrogen results in I).

The most remarkable feature of the localized MF states is that the experimentally observed hexagonal symmetry of the crystal is completely lost. This experimental symmetry will be restored if we assume that, for each molecule, six equivalent MF solutions are available, which are related to each other by rotations of 60° around the \( c \) axis, and that the molecules can jump from one localized solution to another within the time that is characteristic for the observation process (the inverse NMR frequency, for example). We shall digress on this hypothesis in Sec. IV, when discussing the \( \alpha - \beta \) phase transition. Our jump model thus assumes six localized orientations for each molecule in the unit cell, i.e., 12 molecular positions or 24 atomic positions in each primitive cell. These are not the 24-fold degenerate Wyckoff positions of the space group \( \text{P} \overline{6}_3/mmc \), however, but two sets of 12-fold degenerate positions. Actually, as observed in Ref. 2, with the molecules in alternate layers packed as they are in the (near) hcp lattice, it is not possible that the atoms occupy just one set of 24-fold degenerate positions. This can easily be seen by checking that the centers of inversion of the space group are not located on the lattice sites occupied by the molecular midpoints.

Next we calculated the libron frequencies by the TDH method with two excited, localized, MF states on each molecule. All these frequencies are real now, as they should be for a stable MF solution. As can be expected from the localized nature of the MF states, we find that the libron frequencies (see Table II) are of similar size as those for the ordered \( \alpha \) and \( \gamma \) phases, and comparable also with the translational phonon frequencies. The experimental spectra show two very broad peaks of which the higher one around 50 cm\(^{-1}\) (depending on the temperature and pressure) has been interpreted as a libron band and the lower one around 25 cm\(^{-1}\) as a translational phonon band (Table II). The higher libron frequency agrees reasonably well with our results, but according to our calculated frequencies, the libron modes might cause some absorption in the lower band as well (apart from symmetry and intensity considerations, which we have not looked at). Our results indicate that the broadening of the observed libron band is caused by coupling localized librational modes with more or less random jumps in the orientations of the molecules by multiples of 60°.

### IV. THE \( \alpha - \beta \) PHASE TRANSITION

In Fig. 4 we have plotted the free energy \( A_{\text{var}} \) calculated from the different MF solutions of \( \alpha \) and \( \beta \) nitrogen, accord-
The free energy per particle will thus be equal to the result of the localized model, minus $k_B T \ln 6$. 

In principle, one could suggest that the same type of jumps occur between four equivalent localized solutions in $\alpha$-$N_2$, with the molecules oriented along one of the body diagonals of the cubic lattice (see paper I). One can argue, however, that such jumps of the individual molecules are energetically much more unfavorable in $\alpha$-$N_2$ than they are in $\beta$-$N_2$. The strongest indication for this is the experimentally observed crystal symmetry which agrees with the symmetry of a specific localized MF solution for $\alpha$-$N_2$. Further arguments can be found from the MF calculations themselves. In the first place, the overlap between the sixfold localized MF states in $\beta$-$N_2$ is substantially larger than the overlap between the four states in $\alpha$-$N_2$ and, therefore, tunneling will be faster in $\beta$-$N_2$. Secondly, we have tried to generate delocalized solutions for $\alpha$-$N_2$ by forcing all four molecules in the unit cell to have identical MF states as in the delocalized $\beta$-$N_2$ model. The molecules in $\alpha$-$N_2$ remain still localized, however, with their axes oriented along one of the cube edges. So, even at the expense of a substantial amount of lattice energy, the molecules in $\alpha$-$N_2$ will not reorient themselves as in $\beta$-$N_2$. Apparently, the rotation barriers are substantially higher in $\alpha$-$N_2$ than they are in $\beta$-$N_2$. A definite theoretical confirmation of the jump model in $\beta$-$N_2$ must wait for a sound theoretical formulation of the dynamics of this model, though.

Our jump model seems related to the 12-fold jump model invoked by Raich et al., who have also used their model to study the $\alpha$-$\beta$ phase transition. However, our results show that it is essential that the jumps occur between localized librational states of the molecules which lie in deep wells that can only be obtained from the full anisotropic potential. Raich et al. have used an effective, orientationally averaged, isotropic potential, which in our case would produce a free energy curve close to the free rotor curve in Fig. 4 and, thus, too high to cross the $\alpha$-$N_2$ curve. A certain amount of localization seems to be required, even in the $\beta$ phase, in order to stabilize this phase and obtain the $\alpha$-$\beta$ phase transition at the observed temperature.

So the physical picture for $\beta$-nitrogen that emerges from our calculations is that of a sixfold jump model between orientationally localized librational states of the molecules.
There is a tendency for neighboring molecules to stay 180° out of phase, in order to achieve a favorable lattice energy. Thus, it is clear that an appropriate quantum dynamical model for the jump process, which is still to be developed, must include the intermolecular (pair) correlations from the outset.

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