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Librational excitations in phase II of solid CD_4

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An attempt has been made to study the librational excitations in the partially ordered phase II of solid CD_4. The only parameter of the theory is fully determined by static properties of the system. The time-dependent Hartree approximation has been used to calculate the frequencies of the excitations. It is shown that the ordinary harmonic theory is not a good approximation for the system under study.

I. INTRODUCTION

In many molecular crystals the energies of the internal modes (involving deformations of the individual molecules) are much higher than the energies of the external modes (involving displacements or rotations of practically undeformed molecules). If one is only interested in the external modes, it then is a good approximation to treat the individual molecules as rigid units.[1] For the translational modes the harmonic approximation is usually a sufficient tool; only for the very lightest molecules such as H_2, HD, and D_2 are more elaborate techniques necessary. For the rotational modes two extreme cases can be distinguished: (i) If the moment of inertia of the molecules is large and if the rotational potential is strong, the harmonic approach is also a good starting point for the rotational motion,[2,3] i.e., one expands the potential energy for small rotations out of equilibrium. (ii) If the moment of inertia of the molecules is very small and if the rotational potential is weak, one starts from free-rotator wave functions and treats the potential as a perturbation.[4]

Solid CD_4 fits in neither of the two categories. At 27.0 K it undergoes a phase transition from a rotationally disordered high-temperature phase into an orientationally ordered one. At 24.5 K the mean angular displacements are 16°.[5] If an angular localization of this order were to be accomplished by an expansion into free-rotator functions the series would have to contain many terms. On the other hand displacements of 16° are much too big to be handled in a harmonic approach. The time-dependent Hartree approximation[6] appears to be extremely well suited for rotational excitations and its application to solid CD_4 is the main aim of this paper.

In Sec. II the structure of CD_4 in phase II (between 27.0 and 22.1 K) will be outlined and the model to be used in the calculations is introduced. It contains only one adjustable parameter, the octupole moment of the CD_4 tetrahedron. A summary of the approximations made is also given. In Sec. III, for reasons of later comparison, the harmonic theory for the model is developed. The Hartree solution for the static properties of CD_4 is presented in Sec. IV. The time-dependent Hartree approximation finally is given in Sec. V and the results are compared with those from the harmonic approach.

II. MODEL

The structure of methane II is shown in Fig. 1. This structure has been predicted by James and Keenan[7] on the basis of molecular-field theory and it has been verified in a neutron scattering experiment by Press.[5] In CD_4 phase II is realized from the plastic to ordered phase transition at 27.0 to 22.1 K where CD_4 undergoes another phase change. CH_4 probably stays in phase II from 20.4 K down to zero temperature. The main features of phase II are summarized as follows: The structure is fcc with eight molecules in the unit cell. Six of them are ordered orientationally in a way analogous to the order of the spins in an antiferromagnet. The cage of "antiferromagnetically" ordered molecules does not produce a field that interacts with the octupole (the lowest-order electrical multipole of a tetrahedral molecule) of the CD_4 molecules on sublattices 1 or 2. Thus these molecules are still disordered with an equal probability distribution of the deuterons on a sphere around the C nucleus (apart from a slight modulation due to higher-order multipole interactions). Figure 1 shows only the equilibrium orientation of the ordered molecules. Owing to zero-point motion and thermal excitations, the molecules will make excursions around their equilibrium orientations. The proton distribution for the ordered molecules therefore will be smeared out on the sphere with pronounced peaks at the equilibrium proton positions.

Besides the assumption of rigid molecules, some additional approximations will be made, to simplify the calculations. (I) It will be assumed that the centers of mass of the molecules are bound to a

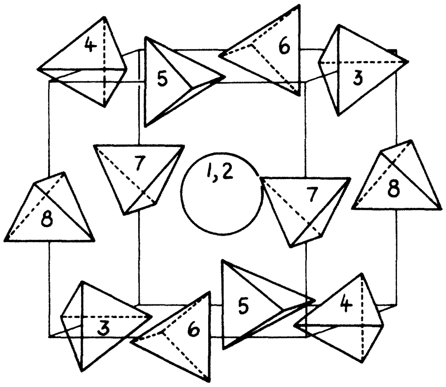

FIG. 1. Orientational arrangement of the molecules on the eight sublattices in phase II of solid CD_4. This structure corresponds to the minimum of the free energy (from 27.0 to 22.1 K) and to a local minimum of the potential energy of the octupoles. The octupolar field at sublattices 1 and 2 vanishes.

rigid lattice, i.e., all translational degrees of freedom are neglected. This amounts to a restriction to librational modes only. Translational phonons and the effect of phonon-libron interaction thus are neglected from the start. (II) A further approximation is the total neglect of excitations at the sites of the disordered molecules. In the harmonic approach there is no way to include these particles. In the time-dependent Hartree approximation they could be adequately described by free rotators. For simplicity it has been chosen, however, to replace them by inert units not showing any transitions to excited states. Thereby an important damping effect has been omitted, namely, that the energy of a libron may be transferred to a disordered molecule which is excited into one of its rotational levels. (III) The James and Keenan[7] Hamiltonian

$$\mathcal{H}_{\mathrm{JK}} = \frac{1}{2} \sum_{i,j=1}^{N} \sum_{a,b=1}^{8} V_{ab}^{ij} \tag{2.1}$$

is used for the angle-dependent interactions. Indices i and j run over all unit cells, indices a and b over the eight sublattices. V_{ab}^{ij} is restricted to nearest-neighbor octupole-octupole interactions:

$$V_{ab}^{ij} = \frac{I_3^2}{R^7} \sum_{\mu,\nu=1}^{7} U_{1\mu}^{(3)}(\omega_a^i)(C_{ab}^{ij})_{\mu\nu} U_{1\nu}^{(3)}(\omega_b^j) \tag{2.2}$$

if molecules (i,a) and (j,b) are nearest neighbors and $V_{ab}^{ij}=0$ otherwise. I_3 is the octupole moment of the CD_4 tetrahedron, R is the nearest-neighbor distance, and ω_a^i denotes the set of Euler angles that describe the orientation of molecule (i,a). $U_{\mu\nu}^{(l)}(\omega)$ is a cubic rotator function that is defined by the transformation properties of the cubic harmonics for a rotation of the coordinate system by Euler angles ω:

$$K_{l\sigma}(\theta', \phi') = \sum_{\mu=1}^{2l+1} K_{l\mu}(\theta, \phi) U_{\mu\sigma}^{(l)}(\omega). \tag{2.3}$$

For shorthand the notation $U_{\mu 1}^{(3)}(\omega) = u_\mu(\omega)$ will be used. $(C_{ab}^{ij})_{\mu\nu}$ is a dimensionless 7× 7 matrix for every pair of nearest neighbors. Approximation III is justified by the successful description of static critical phenomena at the 27-K phase transition of CD_4 with use of the James and Keenan Hamiltonian.[8]

In the harmonic approach two additional approximations are made: (IV) The potential energy is expanded about its minimum. Because of the large excursions out of their equilibrium orientations the deuterons are smeared out on a sphere around the molecular center. Therefore the effective angle-dependent interaction will be reduced. This effect is neglected in the harmonic theory. (V) Finally in the harmonic theory the expansion of the potential for small displacements is terminated after the second-order term. The approximations (IV) and (V) are avoided in the time-dependent Hartree approximation.

III. HARMONIC APPROXIMATION

In this section we follow a calculation by Stockmeyer[9] in which he obtained the librational frequencies for a hypothetical methane structure with all molecules parallel. A vector angular displacement $\vec{\lambda}_a^i$ is introduced ($a = 3, \ldots, 8$) with components $(\lambda_a^i)_\alpha$ ($\alpha = x, y, z$) that denote small rotations of the molecule (i,a) around the respective coordinate axes. In equilibrium $\vec{\lambda}_a^i = 0$. The Euler angles are functions of $\vec{\lambda}_a^i$

$$\omega_a^i = \omega_a^i(\vec{\lambda}_a^i) \tag{3.1}$$

and the equilibrium Euler angles are denoted by $\overline{\omega}_a^i = \omega_a^i(\vec{\lambda}_a^i = 0)$. The cubic rotator functions are expressed in terms of $\vec{\lambda}_a^i$:

$$u_\mu(\omega_a^i) = u_\mu(\omega_a^i(\vec{\lambda}_a^i)) \tag{3.2}$$

and expanded for small values of $\vec{\lambda}_a^i$:

$$u_\mu(\omega_a^i(\vec{\lambda}_a^i)) = u_\mu(\overline{\omega}_a^i) + \sum_{\alpha=1}^{3} \frac{\partial u_\mu}{\partial(\lambda_a^i)_\alpha} (\lambda_a^i)_\alpha + \frac{1}{2} \sum_{\alpha,\sigma=1}^{3} \frac{\partial^2 u_\mu}{\partial(\lambda_a^i)_\alpha \partial(\lambda_a^i)_\sigma} (\lambda_a^i)_\alpha (\lambda_a^i)_\sigma + \cdots . \tag{3.3}$$

The derivatives in Eq. (3.3) have to be taken at equilibrium, i.e., at $\vec{\lambda}_a^i = 0$ or $\omega_a^i = \overline{\omega}_a^i$. They do not depend on the cell index i and therefore the following abbreviations may be used:

$$A^a_\mu = u_\mu(\bar{\omega}^i_a), \tag{3.4a}$$

$$M^a_{\mu,\alpha} = \left[\frac{\partial u_\mu(\omega^i_a(\vec{\lambda}^i_a))}{\partial(\lambda^i_a)_\alpha}\right]_{\vec{\lambda}^i_a=0}, \tag{3.4b}$$

$$L^a_{\mu,\alpha\sigma} = \left[\frac{\partial^2 u_\mu(\omega^i_a(\vec{\lambda}^i_a))}{\partial(\lambda^i_a)_\alpha\,\partial(\lambda^i_a)_\sigma}\right]_{\vec{\lambda}^i_a=0}. \tag{3.4c}$$

Equation (3.3) now reads:

$$u_\mu(\omega^i_a(\vec{\lambda}^i_a)) = A^a_\mu + \sum_{\alpha=1}^{3} M^a_{\mu,\alpha}(\lambda^i_a)_\alpha + \frac{1}{2}\sum_{\alpha,\sigma=1}^{3} L^a_{\mu,\alpha\sigma}(\lambda^i_a)_\alpha(\lambda^i_a)_\sigma + \cdots . \tag{3.5}$$

Equation (3.5) is inserted into $\mathcal{H}_{\text{JK}}$ (2.1). The constant term is uninteresting. There is no term linear in $\vec{\lambda}^i_a$ as the expansion is about a minimum of $\mathcal{H}_{\text{JK}}$. The second-order term is denoted by ϕ_2:

$$\phi_2 = \frac{I_3^2}{R^7}\left[\frac{1}{2}\sum_{\alpha,\beta=1}^{3}\sum_{\mu,\nu=1}^{7}\sum_{ia,jb}(\lambda^i_a)_\alpha M^a_{\mu,\alpha}(C^{ij}_{ab})_{\mu\nu}M^b_{\nu,\beta}(\lambda^i_b)_\beta + \frac{1}{2}\sum_{\beta=1}^{3}\sum_{\mu,\nu=1}^{7}\sum_{ia,jb}A^a_\mu(C^{ij}_{ab})_{\mu\nu}L^b_{\nu,\beta\tau}(\lambda^j_b)_\beta(\lambda^j_b)_\tau\right]. \tag{3.6}$$

As an example the matrix M^a for $a=7$ is shown in Table I. Using the results of James and Keenan for C, the second term in (3.6) is simplified to

$$\frac{1}{2}\left(\frac{I_3^2}{R^7}\right)357\sum_{jb\beta}[(\lambda^j_b)_\beta]^2.$$

Going over to spatial Fourier transforms by

$$(\lambda^i_a)_\alpha = \sum_{\vec{q}}\lambda^a_\alpha(q)e^{i\vec{q}\cdot\vec{r}^i_a}, \tag{3.7}$$

it is observed that M does not depend on the cell index.

$$\phi_2 = \frac{N}{2}\frac{I_3^2}{R^7}\sum_{ab,\alpha\beta}\sum_{\vec{q}}\lambda^a_\alpha(\vec{q})\left(357\delta^{ab}_{\alpha\beta} + \sum_{\mu,\nu}M^a_{\mu,\alpha}C^{ab}_{\mu\nu}(\vec{q})M^b_{\nu,\beta}\right)\lambda^b_\beta(\vec{q}). \tag{3.8}$$

If the kinetic energy of the rotation

$$K = \frac{N}{2\Theta}\sum_{a=3}^{8}\sum_{\alpha=1}^{3}\sum_{\vec{q}}[p^a_\alpha(\vec{q})]^2 \tag{3.9}$$

(where Θ is the moment of inertia of the molecules and $\vec{p}^i_a = \Theta\dot{\vec{\lambda}}^i_a$) is added to ϕ_2, the Hamiltonian function of the system is obtained. The equation of motion

$$-\Theta\ddot{\lambda}^a_\alpha(\vec{q}) = \frac{I_3^2}{R^7}\sum_{b\beta}\left(357\delta^{ab}_{\alpha\beta} + \sum_{\mu,\nu}M^a_{\mu,\alpha}C^{ab}_{\mu\nu}(\vec{q})M^b_{\nu,\beta}\right)\lambda^b_\beta(\vec{q}) \tag{3.10}$$

is solved by the *Ansatz*

$$\lambda^a_\alpha(\vec{q},t) = e^a_\alpha(\vec{q},\xi)e^{i\omega(\vec{q},\xi)t}. \tag{3.11}$$

$e^a_\alpha(\vec{q},\xi)$ are the libron coordinates and $\omega(\vec{q},\xi)$ are the corresponding frequencies. ξ is the branch index. The libron frequencies are obtained from the solution of the secular equation

$$\omega^2(\vec{q},\xi)e^a_\alpha(\vec{q},\xi) = \frac{I_3^2}{R^7\Theta}\left(357\delta^{ab}_{\alpha\beta} + \sum_{\mu\nu}M^a_{\mu,\alpha}C^{ab}_{\mu\nu}(\vec{q})M^b_{\nu,\beta}\right)e^b_\beta(\vec{q},\xi). \tag{3.12}$$

The libron frequencies along the [100] and [111] directions in reciprocal space are plotted in Fig. 2. $I_3^2/R^7\Theta$ is the only adjustable parameter of our theory. If I_3^2/R^7 is estimated on the basis of the phase-transition temperature of CD$_4$ [7]: $I_3^2/R^7 = \frac{4}{51}k_BT_c = 2.12k_B$; and if $\hbar^2/\Theta$ is calculated from the known C-D distance: $\hbar^2/\Theta = 7.59k_B$, the energy scale in Fig. 2 is found from $\epsilon = (\hbar^2 I_3^2/R^7\Theta)^{1/2} = 4.0k_B$. A better estimate for I_3^2/R^7 is obtained when quantum effects are included into the calculation of T_c.[10] However, to stay consistently within classical theory, the improved value of I_3^2/R^7 should not be used in this section.

TABLE I. The matrix $M^7_{\mu,\alpha}$ denotes the linear change of the seven functions u_μ for small-angle rotations from the reference position.

$\mu\alpha$	x	y	z
1	0	0	-2
2	0	$-\frac{1}{2}\sqrt{15}$	0
3	$-\frac{1}{2}\sqrt{15}$	0	0
4	0	0	0
5	0	$-\frac{1}{2}$	0
6	$+\frac{1}{2}$	0	0
7	0	0	0

IV. HARTREE SOLUTION

For the description of the single-molecule rotation it is convenient to transform from Euler angles

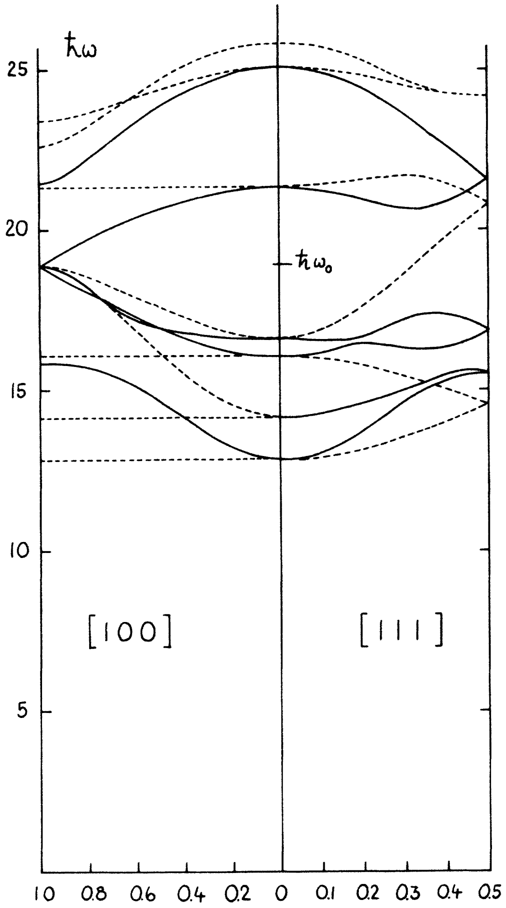

FIG. 2. Libron frequencies for the [100] and [111] directions in reciprocal space (full lines, twofold degenerate; dashed lines, single). The energy is given in units of $\epsilon = (\hbar^2 I_3^2/R^7\Theta)^{1/2}$. The band distance $h\omega_0 = (357)^{1/2}\epsilon$ is due to the Einstein term in Eq. (3.12). Frequencies along [110] are in the same energy range.

$\omega = (\alpha, \beta, \gamma)$[11] to quaternions.[3,12] The quaternion elements are defined by:

$$\begin{aligned} \tau_1 &= \sin\frac{\beta}{2}\,\sin\frac{\alpha-\gamma}{2}\,, \\ \tau_2 &= \sin\frac{\beta}{2}\,\cos\frac{\alpha-\gamma}{2}\,, \\ \tau_3 &= \cos\frac{\beta}{2}\,\sin\frac{\alpha+\gamma}{2}\,, \\ \tau_4 &= \cos\frac{\beta}{2}\,\cos\frac{\alpha+\gamma}{2}\,, \end{aligned} \tag{4.1}$$

and they fulfill the condition $\sum_{\alpha=1}^{4} \tau_i^2 = 1$. In terms of quaternions, the kinetic energy of a CD_4 molecule becomes[3]

$$K = -\frac{\hbar^2}{8\Theta} \sum_{\alpha=1}^{4} \left(\frac{\partial^2}{\partial \tau_\alpha^2} - 3\tau_\alpha \frac{\partial}{\partial \tau_\alpha} - \sum_{\beta=1}^{4} \tau_\alpha \tau_\beta \frac{\partial^2}{\partial \tau_\alpha \partial \tau_\beta} \right) . \tag{4.2}$$

The cubic rotator functions [Eq. (2.3)] are also expressed in terms of quaternions,

$$H_{\mu\nu}^{(l)}(\tau) \equiv U_{\mu\nu}^{(l)}(\omega), \tag{4.3}$$

if τ and ω are related to each other by Eq. (4.1). If the notation $h_\mu(\tau) = H_{\mu 1}^{(3)}(\tau)$ is introduced, the octupole-octupole interaction [Eq. (2.2)] becomes

$$V_{ab}^{ij}(\tau_a^i, \tau_b^j) = \frac{I_3^2}{R^7} \sum_{\mu,\nu=1}^{7} h_\mu(\tau_a^i)(C_{ab}^{ij})_{\mu\nu} h_\nu(\tau_b^j). \tag{4.4}$$

The seven functions $h_\mu(\tau)$ are listed in Appendix A.

Guided by the classical solution of the molecular-field equations for methane phase II[7] and its experimental verification[5] the orientational density matrix is approximated by the Hartree density matrix, a product of single-particle density matrices:

$$P_H(\tau_1, \ldots, \tau_M, \tau_1', \ldots, \tau_M') = \prod_{i=1}^{N} \prod_{a=1}^{8} \rho_a^i(\tau_a^i, \tau_a^{i\prime}), \tag{4.5}$$

a runs over the eight sublattices in phase II and i runs over the N unit cells. $M = 8N$ is the total number of molecules in the crystal. ρ_a^i is expected not to depend on i. The time-independent Hartree density matrix fulfills the equation

$$[P_H, \mathcal{H}] = 0, \tag{4.6}$$

with the Hamiltonian

$$\mathcal{H} = \sum_{ia} K_a^i + \frac{1}{2} \sum_{iajb} V_{ab}^{ij}, \tag{4.7}$$

where K_a^i is found on replacing τ by τ_a^i in (4.2). From (4.6) the single-particle equations

$$[\rho_a^i, \mathcal{H}_a^{i\,(\mathrm{H})}] \tag{4.8}$$

are obtained, where the Hartree Hamiltonian is given by:

$$\mathcal{H}_a^{i\,(\mathrm{H})} = K_a^i + V_a^{i\,(\mathrm{H})}\,, \tag{4.9}$$

$$V_a^{i\,(\mathrm{H})}(\tau_a^i) = \sum_{jb} \oint d\tau_b^j\, \rho_b^j(\tau_b^j, \tau_b^j) V_{ab}^{ij}. \tag{4.10}$$

The integration is performed over the surface of the four-dimensional unit sphere. For the solution of Eq. (4.8) that has been found experimentally, ρ_a^i and the Hartree potential $V_a^{i\,(\mathrm{H})}$ do not depend on i. $V_a^{i\,(\mathrm{H})}$ vanishes for $a=1$ and $a=2$ (disordered molecules) and is proportional to $-h_5$, h_5, $-h_6$, h_6, $-h_7$, and h_7 at sublattices 3, 4, 5, 6, 7, and 8, respectively. It is convenient to use an individual primed coordinate system (θ', ϕ') for each of the six sublattices 3–8. These coordinate systems are fixed in the crystal but rotated with respect to crystal axes by $+\frac{1}{4}\pi$ and $-\frac{1}{4}\pi$ around the x axis for molecules 3 and 4, around the y axis for molecules 5 and 6, and around the z axis for molecules

7 and 8. Rotations of a molecule with respect to its primed coordinate system are described by quaternions $\tilde{\tau}$. In these individual coordinate systems the Hartree potential has the same form at the six sublattices:

$$V^{(\mathrm{H})}(\tilde{\tau}) = A(T) h_1(\tilde{\tau}). \tag{4.11}$$

From Eq. (4.10) and the numerical values of the matrix C (Ref. 7, Table V and Erratum) a self-consistency equation for $A(T)$ is derived:

$$A(T) = -\frac{357}{4} \frac{I_3^2}{R^7} \oint d\tilde{\tau}\, \rho(\tilde{\tau}, \tilde{\tau}) h_1(\tilde{\tau}), \tag{4.12}$$

where the single-particle density matrix in (4.12) in turn depends on $A(T)$ via the relation

$$\rho(\tilde{\tau}, \tilde{\tau}) = \exp[-\beta \mathcal{H}^{(\mathrm{H})}(\tilde{\tau})] / \mathrm{Tr}\{\exp[-\beta \mathcal{H}^{(\mathrm{H})}(\tilde{\tau})]\}. \tag{4.13}$$

For the calculation of the trace we restrict ourselves to the ground state and the first excited states of the Hartree Hamiltonian. The wave functions (N_0 and N_1 are normalization constants)

$$|000\rangle = \exp(\tilde{\tau}_4^2/\alpha_0^2)/N_0, \tag{4.14}$$

$$\begin{aligned} |100\rangle &= \tilde{\tau}_1 \tilde{\tau}_4 \exp(\tilde{\tau}_4^2/\alpha_1^2)/N_1, \\ |010\rangle &= \tilde{\tau}_2 \tilde{\tau}_4 \exp(\tilde{\tau}_4^2/\alpha_1^2)/N_1, \\ |001\rangle &= \tilde{\tau}_3 \tilde{\tau}_4 \exp(\tilde{\tau}_4^2/\alpha_1^2)/N_1, \end{aligned} \tag{4.15}$$

are used in a variational approach with α_0 and α_1 as variational parameters, determined from $\partial E_0(\alpha_0)/\partial \alpha_0 = 0$ and $\partial E_1(\alpha_1)/\partial \alpha_1 = 0$. E_0 and E_1 are the expectation values of the Hartree Hamiltonian in the ground state and first excited state, respectively. The wave functions (4.14) and (4.15) have to be symmetric with respect to an inversion in $\tilde{\tau}$ space ($\tilde{\tau} \to -\tilde{\tau}$), as $\tilde{\tau}$ and $-\tilde{\tau}$ correspond to the same set of Euler angles. The limiting forms of the wave functions are free-rotator wave functions (α_0, $\alpha_1 \to \infty$) for a shallow potential and harmonic-oscillator wave functions (α_0, $\alpha_1 \to 0$) for a deep Hartree potential. Equations (4.14) and (4.15) represent so-called pocket states,[13] where the wave function is concentrated in one of the twelve equivalent minima of the Hartree potential. Level splittings due to overlap between different pocket states have been estimated and found to be negligible. Integrals over the surface of the four-dimensional unit sphere, appearing in E_0 and E_1, have been performed term by term after expansion of the exponentials. If I_3^2/R^7 were known, Eqs. (4.12) and (4.13) could be solved self-consistently, yet no direct measurements of I_3 exists. Therefore $\rho(\tilde{\tau}, \tilde{\tau})$ will be evaluated for different values of $A = A_{\mathrm{trial}}$. The value of A_{trial} that yields the experimentally observed width of 16° of the deuteron distribution at $T = 24.5$ K[5] will be chosen as $A(T = 24.5\ \mathrm{K})$. I_3^2/R^7 may then be extracted from Eq. (4.12). For $A_{\mathrm{tria'}} = -240\hbar^2/8\Theta$ the ground state has an energy $E_0 = -118.9\hbar^2/8\Theta$ and a width $\alpha_1 = 0.227$. The first excited state has an energy $E_1 = -44.0\hbar^2/8\Theta$ and a width $\alpha_1 = 0.240$. From these numbers at $T = 24.5$ K a rotational amplitude of 16.2° is obtained. The thermal expectation value of $h_1(\tilde{\tau})$ is found to be: $\oint d\tilde{\tau}\, \rho(\tilde{\tau}, \tilde{\tau}) h_1(\tilde{\tau}) = 0.696$. From Eq. (4.12) we find: $I_3^2/R^7 = 3.86\hbar^2/8\Theta = 3.67 k_B$ (±10% for an estimated experimental error of 1°) which differs by a factor 1.73 from the classical estimate in Sec. III. Our result is very close to the value of $3.40 k_B$ obtained by Kataoaka and Yamamoto[10] in their quantum-mechanical version of the James and Keenan paper. It should be stressed, however, that our value of I_3^2/R^7 does not suffer from the uncertainty in the determination of the critical temperature in molecular-field theory.

V. TIME-DEPENDENT HARTREE APPROXIMATION

In the application of the time-dependent Hartree (or random-phase) approximation[6] to the problem of rotational excitations in CD_4 phase II, we will follow very closely the formulations of Fredkin and Werthamer[14] and of Schmidt.[15] To the Hamiltonian of the system a small time-dependent external disturbance $\hat{H}_a^i(t)$ is added:

$$\mathcal{H} = \sum_{ia} K_a^i + \frac{1}{2} \sum_{ia, jb} V_{ab}^{ij} + \sum_{ia} \hat{H}_a^i(t). \tag{5.1}$$

The expected elementary excitations are librational motions of the molecules and therefore we shall calculate the response of the system to a torque applied to the individual molecules:

$$\hat{H}_a^i(t) = -\vec{\mathrm{M}}_a^{i\prime}(t) \cdot \vec{\lambda}_a^i. \tag{5.2}$$

$\vec{\mathrm{M}}_a^{i\prime}(t)$ is the applied torque and $\vec{\lambda}_a^i$ describes a rotation of the molecule with $\vec{\lambda}_a^i$ as rotation axis and a rotation angle $|\vec{\lambda}_a^i|$. In terms of quaternions

$$(\lambda_a^i)_\alpha = \arcsin[2(\tau_a^i)_\alpha (\tau_a^i)_4],$$

which for small rotation angles is approximated by:

$$(\lambda_a^i)_\alpha = 2(\tau_a^i)_\alpha (\tau_a^i)_4. \tag{5.3}$$

The perturbing term in the Hamiltonian will change the equilibrium density matrix by a small amount to:

$$\rho_a^i(t) = \rho_a + \hat{\rho}_a^i(t), \tag{5.4}$$

which in turn will give rise to an additional term $\hat{V}_a^i(t)$ in the Hartree potential:

$$\mathcal{H}_a^{i\,(\mathrm{H})}(t) = \mathcal{H}^{a\,(\mathrm{H})} + \hat{V}_a^i(t), \tag{5.5}$$

$$\hat{V}_a^i(t) = \sum_{jb} \mathrm{Tr}\{V_{ab}^{ij} \hat{\rho}_b^j(t)\}_{jb}. \tag{5.6}$$

$\mathrm{Tr}\{\cdots\}_{jb}$ denotes the trace over the states of molecule (j,b). The von Neumann equation for the single-particle density matrix ($\hbar = 1$)

$$i\frac{\partial}{\partial t}\hat{\rho}_a^i(t) = [\rho_a^i(t), \mathcal{H}_a^{i\,(\mathrm{H})}(t)] \tag{5.7}$$

is linearized with respect to the external disturbance:

$$i\frac{\partial}{\partial t}\hat{\rho}_a^i(t) = [\hat{\rho}_a^i(t), \mathcal{H}^{a\,(\mathrm{H})}] + [\rho_a, \hat{V}_a^i(t)] + [\rho_a, \hat{H}_a^i(t)]\,. \tag{5.8}$$

In the Hartree representation with wave functions $|i,a,s\rangle$ describing the sth energy state of the (i,a) molecule:

$$\langle i,a,s|\mathcal{H}^{a\,(\mathrm{H})}|i,a,s'\rangle = E_s\,\delta_{s,s'}\,; \tag{5.9}$$

also ρ^a is diagonal:

$$\langle i,a,s|\rho^a|i,a,s'\rangle = f_s\,\delta_{s,s'}\,, \tag{5.10}$$

and a matrix element of Eq. (5.8) reads

$$\omega\langle i,a,s|\hat{\rho}_a^i|i,a,s'\rangle = (E_s - E_{s'})\langle i,a,s|\hat{\rho}_a^i|i,a,s'\rangle + (f_{s'} - f_s)\langle i,a,s|\hat{V}_a^i|i,a,s'\rangle + (f_{s'} - f_s)\langle i,a,s|\hat{H}_a^i|i,a,s'\rangle\,. \tag{5.11}$$

In (5.11) Fourier transforms with respect to time have been used:

$$g(t) = \frac{1}{2\pi}\int d\omega\, e^{-i\omega t} g(\omega). \tag{5.12}$$

From (5.6) we find for the matrix element of $\hat{V}_a^i$

$$\langle i,a,s|\hat{V}_a^i|i,a,s'\rangle = \sum_{j,b}\sum_{r,r'}\langle i,a,s;j,b,r|V_{ab}^{ij}|j,b,r';i,a,s'\rangle\langle j,b,r'|\hat{\rho}_b^j|j,b,r\rangle. \tag{5.13}$$

With the explicit expression for V_{ab}^{ij} [Eq. (4.4)] one obtains

$$\langle i,a,s;j,b,r|V_{ab}^{ij}|j,b,r';i,a,s'\rangle = \frac{I_3^2}{R^7}\sum_{\mu,\nu}\langle i,a,s|h_\mu(\tau_a^i)|i,a,s'\rangle(C_{ab}^{ij})_{\mu\nu}\langle j,b,r|h_\nu(\tau_b^j)|j,b,r'\rangle\,. \tag{5.14}$$

The matrix elements of $h_\mu(\tau_a^i)$ do not depend on the cell index i and are denoted by

$$N_{\mu,ss'}^a = \langle i,a,s|h_\mu(\tau_a^i)|i,a,s'\rangle\,. \tag{5.15}$$

An explicit calculation of the matrix N is performed in Appendix B. Insertion of Eqs. (5.13)–(5.15) into (5.11) yields the result

$$\begin{aligned}(\omega - E_s + E_{s'})\langle i,a,s|\hat{\rho}_a^i|i,a,s'\rangle = {} & \frac{I_3^2}{R^7}(f_{s'} - f_s)\sum_{r,r'}\sum_{j,b}\sum_{\mu,\nu}N_{\mu,ss'}^a(C_{ab}^{ij})_{\mu\nu}N_{\nu,rr'}^b\langle j,b,r|\hat{\rho}_b^j|j,b,r'\rangle \\ & + (f_{s'} - f_s)\langle i,a,s|\hat{H}_a^i|i,a,s'\rangle\,.\end{aligned} \tag{5.16}$$

With use of the spatial Fourier transform

$$\langle i,a,s|\hat{\rho}_a^i|i,a,s'\rangle = \frac{1}{N}\sum_{\vec{q}} e^{i\vec{q}\cdot\vec{R}_a^i}\hat{\rho}_{ss'}^a(\vec{q}), \tag{5.17}$$

Eq. (5.16) may be written

$$(\omega - E_s + E_{s'})\hat{\rho}_{ss'}^a(\vec{q}) = \frac{I_3^2}{R^7}(f_{s'} - f_s)\sum_{r,r'}\sum_{b}\sum_{\mu,\nu}N_{\mu,ss'}^a C_{\mu\nu}^{ab}(\vec{q})N_{\nu,rr'}^b\,\hat{\rho}_{rr'}^b(\vec{q}) + (f_{r'} - f_r)\hat{H}_{rr'}^a(\vec{q}). \tag{5.18}$$

As in Sec. IV the actual calculation is restricted to the ground state $|0\rangle$ and the triply degenerate first excited state of the Hartree Hamiltonian. A state $|s = \alpha\rangle$, with $\alpha = x$, y, or z corresponds to an excited state with one of the crystal axes as the rotation axis. (See also Appendix B.) The only nonvanishing matrix elements of N then are $N_{\mu,0\alpha}^a$ and $N_{\mu,\alpha 0}^a$. The elementary excitations of the system are found from the homogeneous version of Eq. (5.18). With use of $\omega_0 = E_\alpha - E_0$ it reads

$$(\omega - \omega_0)\hat{\rho}_{\alpha 0}^a(\vec{q}) = \frac{I_3^2}{R^7}(f_0 - f_\alpha)\sum_{\beta}\sum_{b}\sum_{\mu,\nu}N_{\mu,\alpha 0}^a C_{\mu\nu}^{ab}(\vec{q})[N_{\nu,\beta 0}^b\hat{\rho}_{\beta 0}^b(\vec{q}) + N_{\nu,0\beta}^b\,\hat{\rho}_{0\beta}^b(\vec{q})]\,, \tag{5.19}$$

$$(\omega + \omega_0)\hat{\rho}_{0\alpha}^a(\vec{q}) = \frac{I_3^2}{R^7}(f_\alpha - f_0)\sum_{\beta}\sum_{b}\sum_{\mu,\nu}N_{\mu,0\alpha}^a C_{\mu\nu}^{ab}(\vec{q})[N_{\nu,\beta 0}^b\hat{\rho}_{\beta 0}^b(\vec{q}) + N_{\nu,0\beta}^b\,\hat{\rho}_{0\beta}^b(\vec{q})]\,. \tag{5.20}$$

The angle of rotation by which the molecules respond to the applied torque is:

$$\begin{aligned}\langle(\lambda_a^i)_\alpha\rangle &= 2\langle(\tau_a^i)_\alpha(\tau_a^i)_4\rangle = 2\sum_{\gamma\gamma'}\langle i,a,\gamma|\hat\rho_a^i|i,a,\gamma'\rangle\langle i,a,\gamma'|(\tau_a^i)_\alpha(\tau_a^i)_4|i,a,\gamma\rangle \\ &= 2c[\langle i,a,\alpha|\hat\rho_a^i|i,a,0\rangle + \langle i,a,0|\hat\rho_a^i|i,a,\alpha\rangle]\,, \end{aligned} \tag{5.21}$$

where c is shorthand for a matrix element:

$$\langle i,a,\gamma'|(\tau_a^i)_\alpha(\tau_a^i)_4|i,a,\gamma\rangle = c(\delta_{\gamma',0}\delta_{\gamma,\alpha}+\delta_{\gamma',\alpha}\delta_{\gamma,0}). \tag{5.22}$$

With use of (5.21) and $N^a_{\mu,\alpha 0}=N^a_{\mu,0\alpha}$, Eqs. (5.19) and (5.20) can be combined to one single equation:

$$(\omega^2-\omega_0^2)\lambda^a_\alpha(\vec{q}) = 2\frac{I_3^2}{R^7}\,\omega_0(f_0-f_\alpha)\sum_{b,\beta}\sum_{\mu,\nu}N^a_{\mu,\alpha 0}C^{ab}_{\mu\nu}(\vec{q})N^b_{\nu,\beta 0}\lambda^b_\beta(\vec{q}). \tag{5.23}$$

Equation (5.23) is the random-phase-approximation (RPA) analog of the classical equation (3.12). In the classical limit $\Theta\to\infty$ and for $T=0$, Eq. (5.23) must become identical with (3.12). In this limit $\rho(\bar\tau,\bar\tau)$ is a δ function at $\tau=(0,0,0,1)$ and Eq. (4.12) yields: $A(T=0)=\frac{357}{4}I_3^2/R^7$. The classical frequency ω_0 is obtained from an expansion of (4.11) for small values of x,[3] if $\tau=(x,0,0,[1-x^2]^{1/2})$ or $\lambda_1=2x$.

$$\begin{aligned} V_{\text{class}} &= -\frac{357}{4}\frac{I_3^2}{R^7}(1-2\lambda_1^2) \\ &= -\frac{357}{4}\frac{I_3^2}{R^7}+\tfrac{1}{2}k\lambda_1^2. \end{aligned} \tag{5.24}$$

$\omega_0^2=k/\Theta=357I_3^2/R^7\Theta$ then coincides with the classical value in Eq. (3.12). For the comparison of the right-hand side of Eq. (5.23) with the corresponding term in (3.12), use is made of the fact, that the matrices M and N differ only by a factor $\frac{1}{2}b$ (see Appendix B). Inserting the classical value for ω_0 and putting $f_0=1$ and $f_\alpha=0$, the right-hand side of (5.23) becomes

$$\left[\frac{1}{2}\left(357\frac{I_3^2}{R^7}\frac{\Theta}{\hbar^2}\right)^{1/2}b^2\right]\frac{I_3^2}{R^7}\Theta\tilde{M}CM, \tag{5.25}$$

where $\tilde{M}$ is the transpose of M. The matrix element b is defined in Eq. (B1). In the classical limit $h_\nu(\tau)$ again has to be expanded around equilibrium ($h_5\approx-4\tau_1\approx-2\lambda_1$). If the wave functions are replaced by harmonic-oscillator wave functions $b=(2\hbar/\omega_0\Theta)^{1/2}$ and the large square bracket in (5.25) becomes 1. If we compare the RPA result from Eq. (5.23) with the classical result, the following improvements are noted: (1) From the solution of the Hartree equations an improved value for the parameter I_3^2/R^7 has been found. This value differs by a factor 1.73 from the classical estimate. (2) The frequency ω_0 is given by $\hbar\omega_0=E_1-E_0$. Contrary to the classical case, it is temperature dependent, as the Hartree potential itself depends on temperature. (3) $\hbar\omega_0$ has been obtained by a variational approach from the full Hartree Hamiltonian whereas the result of Sec. III depends on the harmonic approximation which is unreliable for a shallow rotational potential. At $T=24.5$ K, the combined effect of temperature and anharmonicities overcompensate the factor 1.73. The value $\hbar\omega_0=71k_B$ is slightly below the value $(357)^{1/2}\epsilon$ ($75.6k_B$) obtained in Sec. III. (4) The right-hand side of Eq. (5.23) responsible for the width of the libron band and for libron dispersion, differs from its classical analog by a factor $1.73b^2\omega_0(f_0-f_\alpha)\Theta/2\hbar$, where b, ω_0, and f_0-f_α depend on temperature. For $T=24.5$ K, the whole factor is 0.74. Thus the main effect of the RPA approach, relative to a consistent classical approach, is a reduction of the band distance $\hbar\omega_0$ in Fig. 2 by a factor 0.94 and a reduction of bandwidth by a factor 0.74. It should be noted however, that the reduction factors are 0.54 and 0.43 if our best estimate of the interaction strength $I_3^2/R^7=3.67k_B$ were used also in the harmonic approach.

VI. CONCLUSIONS

Libron frequencies in the partially ordered phase II of solid CD_4 have been calculated. In this calculation the translational modes have been discarded from the start by assuming a rigid center-of-mass lattice. Furthermore, possible excitations at the sites of the disordered molecules were not taken into account. For the orientation dependent interaction of the molecules, use was made of the James and Keenan[7] Hamiltonian, which has the obvious advantage that it contains only one adjustable parameter, the octupole moment I_3 of a CD_4 molecule. The octupole-octupole interaction provides the mechanism for the 27.0-K phase transition and I_3 therefore may be estimated from the phase-transition temperature. An alternative approach, that is free from the uncertainties of the molecular-field approximation to the calculation of the critical temperature, has been adopted in this paper. I_3 is related to the known width of the deuteron distribution at 24.5 K.

Contrary to the case of translational modes, the use of the time-dependent Hartree approximation

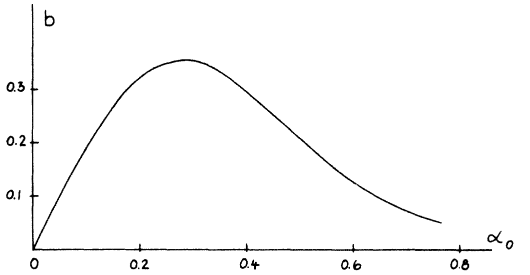

FIG. 3. Matrix element b [see Eq. (B1)] as a function of α_0 when $\alpha_1 = \alpha_0$.

TABLE II. N^7_{μ,α_0} is the transition matrix of u_μ between the rotational ground state and the first excited states.

$\mu\alpha$	x	y	z
1	0	0	$-b$
2	0	$-\frac{1}{4}\sqrt{15}b$	0
3	$-\frac{1}{4}\sqrt{15}b$	0	0
4	0	0	0
5	0	$-\frac{1}{4}b$	0
6	$+\frac{1}{4}b$	0	0
7	0	0	0

is essential for the calculation of libron frequencies in CD_4. If the same interaction constant I_3 is used in a harmonic approach, these frequencies are overestimated by roughly a factor 2. (For translational modes both theories agree within a few percent.[14])

The total neglect of the disordered molecules is a crude approximation. If these molecules are treated as free rotators, their inclusion into the RPA seems to be straightforward. The main difficulty however is not the problem of an additional molecule with a free-rotator spectrum. The main difficulty is that these molecules belong to three different spin-symmetry species (A, E, and T[16]) which differ in their excitation spectrum. As these symmetry types are randomly distributed over the lattice, an inclusion of the disordered molecules destroys the translational symmetry of the lattice. For the same reason the method of this paper cannot be transferred to CH_4 without precautions. Larger zero-point motions and consequentially a shallower Hartree potential lead to a substantial overlap between different pocket states. Thus spin symmetry might be essential for the excitation spectrum of the ordered molecules and therefore also the system of the ordered molecules lacks the translational symmetry of the lattice.

A first attempt to observe librational excitations in CD_4 by thermal neutron scattering[17] was unsuccessful. This may be due to two reasons: (1) The inelastic structure factors may be too small to allow the detection of these excitations. (2) The combined effect of anharmonicities, the coupling to translational modes, and the coupling to the disordered molecules may result in heavy damping of the excitations. The modes might be too broad to be resolved from the background.

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APPENDIX A

The symbol $H^{(l)}_{\mu\nu}(\tau)$ is used for the cubic rotator functions $U^{(l)}_{\mu\nu}(\omega)$ when given in terms of quaternions τ [see Eq. (4.3)]. The seven functions $U^{(3)}_{\mu 1}(\omega) = u_\mu(\omega)$ have been listed by James and Keenan.[7] (Termed tetrahedral rotator functions in Ref. 7.) Here the same functions $H^{(3)}_{\mu 1}(\tau) = h_\mu(\tau)$ are given in terms of quaternions:

$$h_1(\tau) = 16(\tau_1^6 + \tau_2^6 + \tau_3^6 + \tau_4^6) - 20(\tau_1^4 + \tau_2^4 + \tau_3^4 + \tau_4^4) + 5,$$

$$h_2(\tau) = \tfrac{1}{4}\sqrt{15}\,\{\tau_4\tau_1[(\tau_2^2 - \tau_3^2) - 2(\tau_2^4 - \tau_3^4)] + \tau_2\tau_3[(\tau_4^2 - \tau_1^2) - 2(\tau_4^4 - \tau_1^4)]\},$$

$$h_3(\tau) = \tfrac{1}{4}\sqrt{15}\,\{\tau_4\tau_2[(\tau_3^2 - \tau_1^2) - 2(\tau_3^4 - \tau_1^4)] + \tau_3\tau_1[(\tau_4^2 - \tau_2^2) - 2(\tau_4^4 - \tau_2^4)]\},$$

$$h_4(\tau) = \tfrac{1}{4}\sqrt{15}\,\{\tau_4\tau_3[(\tau_1^2 - \tau_2^2) - 2(\tau_1^4 - \tau_2^4)] + \tau_1\tau_2[(\tau_4^2 - \tau_3^2) - 2(\tau_4^4 - \tau_3^4)]\},$$

$$h_5(\tau) = 4\{\tau_4\tau_1[5(\tau_4^2 - \tau_1^2) - 6(\tau_4^4 - \tau_1^4)] + \tau_2\tau_3[5(\tau_2^2 - \tau_3^2) - 6(\tau_2^4 - \tau_3^4)]\},$$

$$h_6(\tau) = 4\{\tau_4\tau_2[5(\tau_4^2 - \tau_2^2) - 6(\tau_4^4 - \tau_2^4)] + \tau_3\tau_1[5(\tau_3^2 - \tau_1^2) - 6(\tau_3^4 - \tau_1^4)]\},$$

$$h_7(\tau) = 4\{\tau_4\tau_3[5(\tau_4^2 - \tau_3^2) - 6(\tau_4^4 - \tau_3^4)] + \tau_1\tau_2[5(\tau_1^2 - \tau_2^2) - 6(\tau_1^4 - \tau_2^4)]\}.$$

APPENDIX B

To calculate the matrix elements $N^a_{\mu,ss'}$ defined by Eq. (5.15) one starts from the primed coordinate system of sublattice a, which is fixed in the crystal but rotated around one of the cubic crystal axes by an angle $\pm\frac{1}{4}\pi$. Rotations of the molecule relative to this coordinate system are described by quaternions $\tilde{\tau}$, the librational ground state by $|000\rangle$ and the p states for librations around the x', y', and z' axes by $|100\rangle$, $|010\rangle$, and $|001\rangle$. [See Eq. (4.14) and (4.15).] To calculate the matrix elements

$$\begin{aligned} \langle 100|h_\nu(\tilde{\tau})|000\rangle &= -b\delta_{\nu,5} \\ \langle 010|h_\nu(\tilde{\tau})|000\rangle &= -b\delta_{\nu,6}, \\ \langle 001|h_\nu(\tilde{\tau})|000\rangle &= -b\delta_{\nu,7}, \end{aligned} \tag{B1}$$

the exponentials in the wave functions are expanded and the resulting polynomial is integrated term by term (on the surface of the four-dimensional unit sphere). In Fig. 3 the value of b is plotted against α_0 for the special case $\alpha_1 = \alpha_0$.

Out of the p-state wave functions linear combinations are formed that describe rotations around the cubic crystal axes. For sublattice $a = 7$ these combinations are written down explicitly:

$$\begin{aligned} |7,x\rangle &= \frac{1}{\sqrt{2}}(|100\rangle - |010\rangle), \\ |7,y\rangle &= \frac{1}{\sqrt{2}}(|100\rangle + |010\rangle), \\ |7,z\rangle &= |001\rangle. \end{aligned} \tag{B2}$$

The matrix elements between these states and the ground state are

$$\begin{aligned} \langle 7,x|h_\nu(\tilde{\tau})|000\rangle &= -(b/\sqrt{2})(\delta_{\nu,5} - \delta_{\nu,6}), \\ \langle 7,y|h_\nu(\tilde{\tau})|000\rangle &= -(b/\sqrt{2})(\delta_{\nu,5} + \delta_{\nu,6}), \\ \langle 7,z|h_\nu(\tilde{\tau})|000\rangle &= -b. \end{aligned} \tag{B3}$$

Cubic rotator functions depending on τ, i.e., on rotations with respect to the unprimed coordinate system can be expressed as linear combinations of cubic rotator functions depending on $\tilde{\tau}$. Denoting the polar angles in a coordinate system that is rotating with the molecule by θ'' and ϕ'', $K_{31}(\theta'',\phi'')$ may be expressed in terms of $K_{3\sigma}(\theta, \phi)$ directly:

$$K_{31}(\theta'', \phi'') = \sum_{\sigma=1}^{7} K_{3\sigma}(\theta, \phi) H^{(3)}_{\sigma 1}(\tau), \tag{B4}$$

or with a detour via the primed coordinate system rotated by $\frac{1}{4}\pi$ relative to the unprimed system:

$$\begin{aligned} K_{31}(\theta'', \phi'') &= \sum_{\rho=1}^{7} K_{3\rho}(\theta', \phi') H^{(3)}_{\rho 1}(\tilde{\tau}) \\ &= \sum_{\rho,\sigma=1}^{7} K_{3\sigma}(\theta, \phi) H^{(3)}_{\sigma\rho}(\tau_0) H^{(3)}_{\rho 1}(\tilde{\tau}). \end{aligned} \tag{B5}$$

τ_0 describes the $\frac{1}{4}\pi$ rotation that relates the primed and unprimed coordinate systems. Equations (B4) and (B5) are combined to:

$$h_\sigma(\tau) = \sum_{\sigma=1}^{7} H^{(3)}_{\sigma\rho}(\tau_0) h_\rho(\tilde{\tau}). \tag{B6}$$

$H^{(3)}_{\sigma\rho}$ is obtained from an expansion of $K_{3\rho}(\theta', \phi')$ in terms of $K_{3\sigma}(\theta, \phi)$

$$K_{3\rho}(\theta', \phi') = \sum_{\sigma=1}^{7} K_{3\sigma}(\theta, \phi) H^{(3)}_{\sigma\rho}(\tau_0), \tag{B7}$$

$$H^{(3)}(\tau_0) = \frac{1}{\sqrt{32}} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & +\sqrt{32} \\ 0 & -1 & +1 & 0 & +\sqrt{15} & +\sqrt{15} & 0 \\ 0 & -1 & -1 & 0 & +\sqrt{15} & -\sqrt{15} & 0 \\ 0 & 0 & 0 & +\sqrt{32} & 0 & 0 & 0 \\ 0 & +\sqrt{15} & -\sqrt{15} & 0 & +1 & +1 & 0 \\ 0 & -\sqrt{15} & -\sqrt{15} & 0 & -1 & +1 & 0 \\ -\sqrt{32} & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} . \tag{B8}$$

From (B3) and (B6) the matrix $N^7_{\mu,\alpha 0}$ is obtained. It is listed in Table II. It differs from $M^7_{\mu,\alpha}$ which was obtained in Sec. III only by a factor $\frac{1}{2}b$.

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