Theory of crystal-field interactions in solid hydrogen. I. Single ortho impurities in solid parahydrogen[1]

S. Luryi and J. Van Kranendonk

Department of Physics, University of Toronto, Toronto, Ont., Canada M5S 1A7

The theory of the crystal-field splitting, V_c, of the $J = 1$ level of an ortho impurity in a parahydrogen matrix, due to the coupling of the rotational motion of the ortho molecule to the lattice vibrations, is developed taking due account of the quantum-crystal nature of the solid. Two contributions to V_c are identified, both arising from the anisotropy in the lattice vibrations. One contribution is due to the difference in the relative zero-point motion of the molecules in in-plane and out-of-plane pairs in the hcp lattice, and is parametrized in terms of the second moments of the pair distribution function. The other contribution is due to the local, quasi-state distortion of the lattice around the impurity induced by the terms in the coupling linear in the phonon variables. This self-energy effect is calculated using a generalized Debye model for the self-consistent harmonic phonons, in which the anisotropy of the velocity and of the polarization of the sound waves is parametrized in terms of the elastic constants of the crystal. The theory is compared with that of Raich and Kanney, which is shown to be based on unrealistic assumptions. The remaining uncertainties in the anisotropic pair potential and the phonon renormalization factors are discussed in connection with the available experimental data.

La théorie de la séparation V_c, par le champ cristallin, du niveau $J = 1$ d'une impureté ortho dans une matrice de parahydrogène, sous l'effet du couplage du mouvement de rotation de la molécule ortho avec les vibrations du réseau, est développée en tenant compte du fait que le solide est un cristal quantique. On identifie deux contributions à V_c, provenant toute les deux de l'anisotropie des vibrations du réseau. L'une de ces contributions est due à la différence dans le mouvement relatif du point zéro des paires de molécules dans le plan et hors du plan dans le réseau hc; elle est paramétrisée en termes des seconds moments de la fonction de distribution des paires. L'autre contribution est due à la distorsion quasi-statique locale du réseau autour de l'impureté, distorsion qui est induite par les termes de couplage linéaires par rapport aux variables de phonons. Cet effet de self-énergie est calculé en utilisant un modèle de Debye généralisé pour les phonons harmoniques self-consistants, dans lequel l'anisotropie de la vitesse et de la polarisation des ondes acoustiques est paramétrisée en termes des constantes élastiques du cristal. On compare la théorie avec celle de Raich et Kanney, et on montre que cette dernière s'appuie sur des hypothèses non réalistes. Les incertitudes qui subsistent dans le potentiel anisotropique de paires et les facteurs de renormalisation des phonons sont discutées en relation avec les données expérimentales disponibles.

[Traduit par le journal]

1. Introduction

The part of the interaction energy between the molecules in a crystal described by terms depending on the orientation of only a single molecule is usually called the crystal-field interaction, cf. ref. 1, eq. [25]. In solid hydrogen this interaction is of particular importance for single ortho impurities in pure parahydrogen, in connection with the nmr (2–6) and caloric properties of the solid at very low ortho concentrations, and for pairs of neighbouring ortho impurities in connection with the infrared and Raman spectra, cf. ref. 1, and the high-resolution microwave spectra observed by Hardy *et al.* (7). In the present paper the theory of the crystal-field interaction for single ortho impurities is developed, and expressions for the energy eigenvalues and eigen-

states of the system are obtained in terms of the anisotropic intermolecular potential. A similar treatment for pairs of ortho impurities will be presented in a separate paper.

For a single substitutional ortho impurity in the $J = 1$ rotational state in a rigid, undistorted, hexagonal close-packed (hcp) lattice, no appreciable crystal-field interaction exists (8) resulting in an accidental degeneracy of the $J = 1$ level. This property is common to a number of anisotropic properties described by second-rank tensors in an hcp lattice (9), when the c/a ratio has the value $(8/3)^{1/2}$ characteristic of close packing. As pointed out in ref. 9, this property also explains the isotropy of the compressibility of hcp solid hydrogen, as well as the hcp structure of the solid which is blown up considerably by the zero-point lattice vibrations. A finite crystal-field interaction can arise only (10) because of an overall deviation, Δc, of the c/a ratio

of the crystal from the value $(8/3)^{1/2}$, and as a result of the coupling between the rotational motion of the ortho molecule and the lattice vibrations arising from the anisotropic intermolecular interactions. In this paper we assume that $\Delta c = 0$, and we consider only the effect of the 'spin–lattice' coupling, where spin refers to the rotational angular momentum, J, of constant magnitude, $J^2 = J(J + 1)$.

The main effect of the spin–lattice coupling is a lowering of the rotational energy level J with unperturbed energy

$$[1] \qquad\qquad E_J = J(J + 1)Bhc$$

without a removal of the $(2J + 1)$-fold degeneracy, by an amount which, according to second-order perturbation theory (10), is given by

$$[2] \quad \Delta E_J = -[4J(J + 1)/(2J - 1)(2J + 3)]A$$

where A is a constant depending on the properties of the spin–lattice coupling and the phonon field, cf. ref. 10, where A is devoted by $\tilde{E}_\infty$. The energy [2] can be regarded as the self-energy of the spin in the phonon field. Its value is insensitive to the anisotropy of the spin–lattice coupling and of the phonon field, and in first approximation may be evaluated by neglecting both of these anisotropies. In a classical picture (10), the frequency of the rotating ortho molecule is large compared with the Debye frequency for all $J \geq 1$. The rotating ortho molecule therefore drives the lattice oscillators above their resonance frequencies and produces a local, non-propagating distortion of the lattice in which the molecules vibrate around distorted equilibrium positions. Two aspects of this self-energy effect are worth pointing out since they are liable to cause confusion. The first one is that in the presence of the spin–lattice coupling the energy levels are no longer properties of the ortho molecule alone but of the crystal as a whole. The energy shifts [2] are in fact equal to the sum of the anisotropic interaction energy of the ortho molecule with the neighbouring molecules, which can be interpreted as the energy of the ortho molecule in the 'crystal field,' and the elastic deformation energy of the lattice. These two contributions are of the same order of magnitude, but opposite sign, and both must always be taken into account. The second point is that even in a completely isotropic model in which the anisotropies of the coupling and of the field are neglected, the components of J are not constants of the motion and m_J is in general not a good quantum number. Nonetheless, the resulting levels of the system in the isotropic model have the same degeneracy as the unperturbed levels, but the new stationary states are linear combinations of products of rotational and phonon states, cf. Sect. 4. This

argument is familiar from the discussion of the dynamic Jahn–Teller effect in ref. 11, where the electronic coordinates play the role analogous to the spin in the present case.

The secondary effect of the spin–lattice coupling is to partially lift the $(2J + 1)$-fold degeneracy of the levels because of the anisotropy in the coupling and in the field. This splitting is usually called the crystal-field splitting, and although the energy involved in the splitting is of the same nature as the lowering [2] of the centre-of-gravity of the levels, we will follow this nomenclature, keeping in mind that the splitting is also made up of anisotropic interaction energy and elastic deformation energy of the lattice. The fact that the $(2J + 1)$-fold degeneracy can be lifted by the spin–lattice coupling is not in contradiction with the statement (11) that in the dynamic Jahn–Teller effect the electron–phonon coupling cannot remove the degeneracy of a vibronic state. The latter property follows because the degeneracy and the coupling have the same symmetry, viz., the point symmetry of the lattice site, whereas the degeneracy of the ortho states is an accidental degeneracy not due to the symmetry.

It turns out (10) that the anisotropy of the spin–lattice coupling itself gives only a small contribution to the crystal-field splitting which is therefore mainly due to the anisotropy of the phonon field. In the previous paper (10) this anisotropy was taken into account only in a crude way, and the main purpose of the present paper is to give a more realistic treatment of the phonon anisotropy as well as using a more realistic anisotropic potential. Our treatment is based on the generalized Debye model introduced recently in connection with the elastic properties of the solid (9). In this model, the dependence of the frequencies and polarization vectors of the phonon modes on the direction of propagation relative to the crystal axes is parametrized in terms of the elastic constants of the solid, and this dependence is taken into account exactly in our calculations.

An attempt to calculate the crystal-field splitting for single ortho impurities was recently made by Raich and Kanney (12). Unfortunately this work is based on unrealistic assumptions which deprive their results of any definite significance, as will be discussed more fully in Sect. 4. Our main criticism is that in ref. 12 only the coupling of the spin to the phonon modes belonging to the symmetric representation of the group of rotations around the c axis is taken into account, viz., the term v_0 in [53] in Sect. 4. This coupling leads to a lowering of the $m = 0$ level by an amount which is always four times larger than the lowering of the $m = \pm 1$ level, thus predicting a positive definite value of the splitting

$V_c = E(\pm 1) - E(0)$, quite irrespective of the phonon anisotropy. We remark incidentally that the elastic deformation energy mentioned earlier is not taken into account in ref. 12 and the energy shifts given in ref. 12 are therefore a factor of two too large. Applying the approach of ref. 12 to the completely isotropic model, one obtains a splitting of the same order of magnitude, although the symmetry, of course, forbids any splitting in this case. As will be shown in Sect. 4, the various phonon modes compete in determining the sign of V_c, and in an isotropic model their contributions cancel exactly. The quantity V_c calculated in ref. 12 therefore bears no relation to the actual crystal-field splitting, but is a quantity proportional to the overall lowering [2] of the $J = 1$ level.

Another point of our disagreement with ref. 12 concerns the use of the *unrenormalized* anisotropic interaction in conjunction with an effective harmonic Hamiltonian for the lattice dynamics. Solid hydrogen is a true quantum crystal, and although its phonon dispersion curves as observed by inelastic neutron scattering experiments (13) can be fitted quite well by the Born – von Karman dispersion curves calculated on the basis of a model harmonic Hamiltonian, this Hamiltonian cannot be regarded as governing the actual molecular motions in the solid. If this Hamiltonian is nonetheless used for the lattice dynamics, then consistency requires that the anisotropic interaction be averaged over the actual zero-point motion in the crystal. This has been the usual approach for a long time (14, 15), and this "phonon-renormalization" procedure in its finer details (16, 17) leads to results which are in good agreement with the high-resolution microwave data (7). In ref. 12 this renormalization, which leads to changes of up to 75% in the spin–lattice coupling constants and an order of magnitude in the splitting, is not performed and representative values of the unrenormalized potential and its derivatives are used. This approach may find a justification in our poor knowledge of the anisotropic potential function, but it hardly allows one to compare the merits of different potentials, as is done in ref. 12.

A rigorous derivation of the Hamiltonian for the spin–lattice coupling resulting from a given aniso-tropic intermolecular potential in a quantum crystal represents an interesting and not yet completely solved problem. In Sect. 2 we derive the form of this coupling on the basis of the coherent-state inter-pretation of the phonons in a quantum crystal proposed in a previous paper (18). Two different contributions to the crystal-field splitting arising from the spin–lattice coupling can be distinguished. One contribution, discussed in Sect. 3, is due to the

difference in the relative zero-point motion of the molecules in in-plane (ip) and out-of-plane (op) nearest neighbouring pairs in the hcp lattice, which spoils the accidental vanishing of the crystal field in a rigid hcp lattice. The other contribution arises from the self-energy effects due to the terms in the spin–lattice coupling linear in the phonon variables, and is discussed in Sect. 4. Finally, in Sect. 5 we calculate the resulting crystal-field splitting in terms of the available anisotropic intermolecular potential, and we compare our results with the existing experimental data.

2. Spin–Lattice Interaction in a Quantum Crystal

Solid hydrogen belongs to the class of quantum crystals for which the standard harmonic approx-imation for the lattice dynamics breaks down. The crystal is blown up by the zero-point motion to the extent that the equilibrium separation between the molecules is close to or beyond the inflexion point in the isotropic intermolecular pair potential. Expand-ing this potential in powers of the displacements, u_i, of the molecules from the lattice sites, R_i^0,

$$[3] \qquad V = V^0 + \tfrac{1}{2}\sum_{ij}\Phi_{ij}^0 : u_i u_j + \dots$$

and constructing the harmonic Hamiltonian

$$[4] \qquad H_h^0 = \sum_i p_i^2/2m + \tfrac{1}{2}\sum_{ij}\Phi_{ij}^0 : u_i u_j$$

one finds, upon transforming to the normal co-ordinates, that the normal mode frequencies are imaginary in at least part of the Brillouin zone (19). The standard harmonic Hamiltonian, H_h^0, therefore does not provide a meaningful starting point for the lattice dynamics. Nevertheless, inelastic neutron scattering experiments (13) show that phonon-like excitations exist in quantum crystals and that the interaction between these phonons (anharmonic effects) is not more important than in ordinary crystals, except perhaps in solid helium. One is then naturally led to the idea of modeling these excitations by a harmonic Hamiltonian of the form [4],

$$[5] \qquad H_h = \sum_i p_i^2/2m + \tfrac{1}{2}\sum_{ij}\Phi_{ij} : u_i u_j - \tilde{E}_0$$

where the force constants Φ_{ij} are treated as varia-tional parameters, and the zero-point energy,

$$[6] \qquad \tilde{E}_0 = \sum_\lambda \tfrac{1}{2}\hbar\omega_\lambda$$

has been subtracted corresponding to the fact that the Hamiltonian [5] describes the excitations and not the ground state of the quantum crystal. Various developments along these lines have been reviewed by Koehler (20). Our derivation of the model spin-

lattice Hamiltonian is based on the coherent-state interpretation of the harmonic Hamiltonian [5].

As shown in ref. 18, the Hamiltonian [5] can be interpreted as the classical Hamiltonian governing the motion of the centres of the single-particle probability distributions in the coherent states of the phonon field. Briefly, this interpretation can be obtained as follows. In the self-consistent phonon theory, cf. ref. 20, the ground state, $|\phi_0\rangle$, of the actual lattice Hamiltonian,

$$[7] \qquad H_1 = \sum_i p_i^2/2m + \tfrac{1}{2}\sum_{ij} v_{ij}(R_{ij})$$

is assumed to be a product of a correlated Gaussian and a Jastrow factor,

$$[8] \qquad \langle u^N|\phi_0\rangle = \langle u^N|CG\rangle F(R^N)$$

where $R^N = (R_1, ..., R_N)$ and $u^N = (u_1, ..., u_N)$. The function F describes the short-range correlations at distances corresponding to the hard-core region of the intermolecular potential, and $|CG\rangle$ defines the phonon modes. The posing of a particular $|CG\rangle$ is equivalent to assuming a set of frequencies, ω_λ^0, and polarization vectors, e_λ^0, for all the phonon modes λ, or to stipulating a model Hamiltonian [5] of which $|CG\rangle$ is the ground state. As pointed out by Horner (21), the internal consistency of the product assumption [8] requires that the Jastrow factor should affect explicitly only the higher than second moments of the multidimensional distribution function for the molecular displacements in the ground state, i.e.,

$$\langle \phi_0|\phi_0\rangle = \langle CG|CG\rangle$$
$$[9] \qquad \langle \phi_0|u_i|\phi_0\rangle = \langle CG|u_i|CG\rangle$$
$$\langle \phi_0|u_i u_j|\phi_0\rangle = \langle CG|u_i u_j|CG\rangle$$

Moreover, as shown by Werthamer (22), Horner's conditions [9] are automatically satisfied if [8] is optimized variationally.

Following ref. 18, we define a time-dependent state, $|\phi(t)\rangle$, by acting with the Glauber displacement operator

$$[10] \quad D_\lambda(t) = \prod_{i=1}^{N} \exp\left[-(i/\hbar)(s_{i\lambda}\cdot p_i - \pi_{i\lambda}\cdot u_i)\right]$$

where

$$[11] \quad s_{i\lambda} = s_\lambda e_\lambda \cos\left(q\cdot R_i^0 - \omega_\lambda t\right), \qquad \pi_{i\lambda} = m\dot{s}_{i\lambda}$$

on the phonon part of [8],

$$[12] \qquad |\phi_\lambda(t)\rangle = FD_\lambda(t)|CG\rangle$$

The requirement that the state [12] satisfies, to second order in the amplitudes s_λ, the 'average' Schrödinger equation

$$[13] \qquad i\hbar\langle\phi(t)|\dot{\phi}(t)\rangle = \langle\phi(t)|H_1|\phi(t)\rangle$$

where H_1 is given by [7], leads to equations of motion for the variables $s_{i\lambda}$ from which the parameters ω_λ and e_λ appearing in [11] can be determined. Furthermore, if Horner's conditions [9] constraining the form of F are assumed from the outset, which was not done in ref. 18 but which simplifies the analysis considerably, then the equations satisfied by the functions [11] correspond to the classical Hamiltonian

$$[14] \qquad \tilde{H}_1 = \sum_i \pi_i^2/2m + \tfrac{1}{2}\sum_{ij} \Phi_{ij}:s_i s_j$$

where the Φ_{ij} are identical to those appearing in [5] for the optimized $|CG\rangle$, i.e., $\omega_\lambda = \omega_\lambda^0$ and $e_\lambda = e_\lambda^0$.

In the present context it is important to note that the Hamiltonian [14] describes the low-lying coherent excitations of the crystal above the ground state but not the ground state itself. If [14] is quantized, the resultant zero-point energy which is equal to [6],

$$[15] \qquad \tilde{E}_0 = \langle CG|\tilde{H}_1|CG\rangle = \tfrac{1}{2}\sum_\lambda \hbar\omega_\lambda$$

is not to be added to the ground state energy of the crystal, which is given by

$$[16] \qquad E_0 = \langle\phi_0|H_1|\phi_0\rangle$$

where H_1 contains the full intermolecular potential, cf. [7].

We now consider a single ortho impurity at the lattice site R_1^0 in a pure parahydrogen host crystal. The spin–lattice coupling arises from the anisotropic interaction between the ortho and the neighbouring para molecules,

$$[17] \qquad V = \sum_{p=2}^{\infty} V_{1p}(\omega_1, R_{1p})$$

where ω_1 specifies the orientation of molecule 1, and $R_{1p} = R_1 - R_p$ is the instantaneous separation of molecules 1 and p. For the $J = 1$ state, to which we restrict ourselves, one can write

$$[18] \quad V_{1p} = 2B(R_{1p}) \sum_{m=-2}^{+2} C_{2m}(\hat{R}_{1p})^* C_{2m}(\omega_1)$$

where $\hat{R}_{1p} = R_{1p}/R_{1p}$ and $C_{lm} = (4\pi/2l + 1)^{1/2} Y_{lm}$. Generalizing the analysis of ref. 18 to the present case, we find that the motion of the centres, s_i, of the single-particle distributions is now governed by the modified Hamiltonian

$$[19] \qquad \tilde{H} = \tilde{H}_1 + \tilde{V}$$

where the effective spin–lattice coupling $\tilde{V}$ is equal to the expectation value of [17] over the coherent state [12]. Introducing the notation

$$[20] \qquad S_{ij} = R_{ij}^0 + s_i - s_j = R_{ij}^0 + s_{ij}$$

[35] $\tilde{V}^{(0)}(\Omega) = \sum_{pm} \lambda^{(p)}(R_{1p}{}^0)C_{2m}(\theta_p, \phi_p)^*C_{2m}(\Omega)$

By symmetry, only the $m = 0$ term survives, whence

[36] $\tilde{V}^{(0)}(\Omega) = \varepsilon_{2c}C_{20}(\Omega)$

with

[37] $\varepsilon_{2c} = \sum_{p=1}^{12} \lambda^{(p)}(R_0)C_{20}(\theta_p, \phi_p)$

where R_0 is the nearest-neighbour equilibrium separation. The result, [36] and [37], is the general result for the static renormalization of the crystal-field interaction.

If the displacement correlation function were the same for ip and op pairs, $\lambda^{(p)}(R) = \lambda(R)$, [37] would imply $\varepsilon_{2c} = 0$. Therefore we can write [37] in the form

[38] $\varepsilon_{2c} = \sum_{p=ip} \Delta[\lambda]C_{20}(\theta_p, \phi_p) = -3\Delta[\lambda]$

where $\Delta[Q]$ denotes the difference in any pair quantity $Q(p)$ between ip and op pairs,

[39] $\Delta[Q] = Q(ip) - Q(op)$

Using [33], [38] and the relations

[40] $\begin{aligned} \Lambda_0 - 2\Lambda_1 &= \langle u \cdot u \rangle \\ 2(\Lambda_0 + \Lambda_1) &= \langle 2u_z{}^2 - u_x{}^2 - u_y{}^2 \rangle \equiv -\zeta R_0{}^2 \end{aligned}$

we obtain

[41] $\varepsilon_{2c} = -\Delta[R_0{}^{-2}\langle u^2 \rangle]g_1 + \Delta[\zeta]g_2$

where

[42] $\begin{aligned} g_1 &= R_0{}^2 B''(R_0) - 2R_0 B'(R_0) + 6B(R_0) \\ g_2 &= R_0{}^2 B''(R_0) + R_0 B'(R_0) - 3B(R_0) \end{aligned}$

The result [41] shows that a nonvanishing contribution to the crystal field is produced by a possible difference in the relative zero-point motion of the molecules in ip and op pairs. Unfortunately, the lattice dynamical parameters entering [41] are quite uncertain at present. Our calculations (9) based on the anisotropic Debye model give

[43] $\Delta[\zeta] \simeq -10^{-3}$, $|\Delta[R_0{}^{-2}\langle u^2 \rangle]| \ll |\Delta[\zeta]|$

On the other hand, from our analysis (17) of the microwave spectrum of ortho pairs (7) it was inferred that $|\Delta[\zeta]| \lesssim 10^{-4}$. This discrepancy is not surprising, since an important contribution to the oblateness parameter ζ comes from the short wavelength modes for which the Debye model cannot be expected to be accurate. From a numerical integration using a self-consistent ground-state wave function, the authors of ref. 16 also inferred that $\Delta[\zeta] \simeq 0$ to about 1 part in 10^4. Until a more accurate determination of the

pair correlation matrix in solid hydrogen becomes available, the contribution [36] which gives a crystal-field splitting $V_c{}^{(0)} = -(3/5)\varepsilon_{2c}$, therefore remains uncertain, though its value is most likely small.

4. The Linear Spin–Phonon Coupling

On the basis of the discussion in Sect. 2, we assume that the effects of the linear spin–phonon coupling are described by a Hamiltonian of the form

[44] $\tilde{H} = \tilde{H}_1 + \tilde{V}^{(1)}$

which we now regard as a quantum-mechanical operator, assuming the standard commutation relations between s_i and π_i. The operator $\tilde{V}^{(1)}$ is given by [26] and $\tilde{H}_1$ by [14] minus the zero-point energy [15]; i.e.,

[45] $\tilde{H}_1 = \sum_{\lambda} \hbar\omega_{\lambda} b_{\lambda}{}^{\dagger} b_{\lambda}$

where the b_{λ} are the usual amplitude operators. The frequencies ω_{λ} are assumed to coincide with those observed in the neutron scattering experiments (13).

Expressing $\tilde{V}^{(1)}$ in terms of the normal mode variables, we obtain, cf. ref. 10,

[46] $\tilde{V}^{(1)} = \sum_{\lambda v} A_v(\lambda)^* C_{2v}(\Omega)c_{\lambda}$

where $c_{\lambda} = b_{\lambda} + b_{-\lambda}{}^{\dagger}$, and

[47] $A_v(\lambda) = \left(\dfrac{2\hbar}{MN\omega_{\lambda}}\right)^{1/2} \sum_l \left(\dfrac{2l + 1}{5}\right)^{1/2} \tilde{f}_l$

$\times \displaystyle\sum_{p=1}^{12} T_{2v}{}^{(1l)}(\hat{R}_{1p}, e_{\lambda})[1 - \exp(-iq \cdot R_{1p})]$

The coefficients $\tilde{f}_l$ are given by

[48] $\begin{aligned} \tilde{f}_1 &= -(2/5)^{1/2}(\tilde{B}' + 3R_0{}^{-1}\tilde{B}) \\ \tilde{f}_2 &= 0 \\ \tilde{f}_3 &= (3/5)^{1/2}(\tilde{B}' - 2R_0{}^{-1}\tilde{B}) \end{aligned}$

and the functions

[49] $T_{lm}^{(l_1 l_2)}(\hat{R}, e) =$

$\displaystyle\sum_{m_1 m_2} C(l_1 l_2 l; m_1 m_2 m)C_{l_1 m_1}(\hat{R})C_{l_2 m_2}(e)$

are the so-called bipolar harmonics (23). We note that the function $B(R)$ used here is related to the function $g(R)$ of ref. 10 by $B(R) = (5/16\pi)^{1/2}g(R)$.

As discussed in Sect. 1, the coupling [46] gives rise to self-energy effects which result in a lowering [2] of the centre-of-gravity of the $J = 1$ level and in a splitting of the level due to the anisotropy of the coupling and of the phonon field. As shown in ref. 10, both of these effects are adequately described, because of the weakness of the spin–phonon

coupling, by second-order perturbation theory in which the self-energy effect is described in terms of virtual phonon emission and re-absorption processes. However, it is useful for gaining more insight into the dynamics of the coupled system to proceed somewhat differently and to diagonalize part of the spin–lattice Hamiltonian exactly by using the point symmetry of the lattice, which is D_{3h}. Since the Hamiltonian $\tilde{H}$, [45], is invariant under the operations of D_{3h}, it is possible to express $\tilde{H}$ as a sum of products of linear combinations of the spherical harmonics on the one hand and of the Bloch phonon modes (definite q) on the other, which both transform according to irreducible representations of D_{3h}. We will not carry out this transformation explicitly but consider only the behaviour under the Abelian subgroup, G, of D_{3h} consisting of the identity and the reflections σ_h and σ_v in the horizontal symmetry plane (the xy plane) and one of the three vertical symmetry planes (the xz plane), respectively. We separate $\tilde{V}^{(1)}$ into a part, $\tilde{V}_s^{(1)}$, containing the functions belonging to the completely symmetric representation $(++)$ of G, and a remaining part, $\tilde{V}_a^{(1)}$, containing the functions belonging to the other representations, $+-$, $-+$, and $--$

[50] $\tilde{V}^{(1)} = \tilde{V}_s^{(1)} + \tilde{V}_a^{(1)}$

[51] $\tilde{V}_s^{(1)} = v_0 + v_2^+$

[52] $\tilde{V}_a^{(1)} = v_1 + v_2^-$

where

$$v_0 = \sum_\lambda A_0(\lambda)^* C_{20}(\Omega) c_\lambda$$

$$v_1 = \sum_\lambda [A_1(\lambda) + A_{\bar{1}}(\lambda)]^* C_{21}^+(\Omega) c_\lambda$$

[53]
$$+ \sum_\lambda [A_1(\lambda) - A_{\bar{1}}(\lambda)]^* C_{21}^-(\Omega) c_\lambda$$

$$= v_1^+ + v_1^-$$

$$v_2^\pm = \sum_\lambda [A_2(\lambda) \pm A_{\bar{2}}(\lambda)]^* C_{22}^\pm(\Omega) c_\lambda$$

and

[54] $C_{2m}^\pm = \tfrac{1}{2}(C_{2m} \pm C_{2\bar{m}}),$ $(m = 1, 2)$

If the Bloch modes λ in the term v_0 are expressed in terms of the linear combinations transforming irreducibly under G, it is clear that only the terms corresponding to the $++$ modes survive, and the same is true of the term v_2^+. Hence the terms v_0 and v_2^+ describe the coupling of the spin to the $++$ modes and the remaining terms v_1 and v_2^- the coupling to all the other modes.

The part of the Hamiltonian [44] containing the coupling to the $++$ modes,

[55] $\tilde{H}_0 = \tilde{H}_1 + \tilde{V}_s^{(1)}$

can be diagonalized exactly as follows. We first remark that the eigenstates, $|\psi\rangle$, of $\tilde{H}_0$ can be chosen to be products of spin (i.e., rotational) and phonon states,

[56] $|\psi\rangle = |\text{spin}\rangle|\text{phonon}\rangle$

This can be seen as follows. The spin-dependent factors, C_{20} and C_{22}^+, in H_0 are invariant under the operations of G. Let G' be the group of operators in Hilbert space corresponding to the symmetry operations of G, but acting only on the spin and not on the phonon variables. Then $\tilde{H}_0$ commutes with the operators of G'. Note that this is not true of $\tilde{V}_a^{(1)}$ nor of $\tilde{H}$, although these operators are, of course, invariant under the symmetry operations of G. The eigenstates of $\tilde{H}_0$ can hence be chosen to be simultaneous eigenstates of the operators of G'. Furthermore, the linear combinations of the rotational states, $|Jm\rangle$, for $J = 1$, where m refers to the crystal frame, transforming irreducibly under G', to be denoted by $|\sigma\rangle$, $\sigma = 0, 1, -1$, are given by

[57] $\begin{aligned}|0\rangle &= |10\rangle \\ |\pm 1\rangle &= 2^{-1/2}(|11\rangle \pm |1\bar{1}\rangle)\end{aligned}$

and belong to the $-+$, $+-$, and $++$ representations of G', or G. The key point is that no representation occurs more than once here, and from this it follows that the eigenstates of $\tilde{H}_0$ can indeed be chosen to be of the form [56], viz.,

[58] $|\psi_\sigma\rangle = |\sigma\rangle|\text{phonon}\rangle_\sigma$

By symmetry the two states $|\psi_{\pm 1}\rangle$ of lowest energy (there is a continuum of excited states of the form [58] corresponding to the presence of one or more real phonons) have the same energy, and since the phonon parts of [58] are different for $\sigma = \pm 1$, one cannot say that the lowest eigenstates of $\tilde{H}_0$ are all of the form [56].

For each of the spin states $|\sigma\rangle$, the remaining phonon part of $\tilde{H}_0$, $\langle\sigma|\tilde{H}_0|\sigma\rangle$, can be diagonalized by means of the transformation

[59] $b_\lambda = a_{\lambda\sigma} + \beta_\lambda(\sigma)$

to new phonon operators $a_{\lambda\sigma}$, where the c-number parameters $\beta_\lambda(\sigma)$ are given by

[60] $5\hbar\omega_\lambda\beta_\lambda(\sigma) = (3|\sigma| - 2) A_0(\lambda)^*$
$$+ (3/2)^{1/2}\sigma[A_2(\lambda) + A_{\bar{2}}(\lambda)]^*$$

For each value of σ, the lowest eigenstate of [55], $|\psi_\sigma\rangle$, satisfies the equations

[61] $a_{\lambda\sigma}|\psi_\sigma\rangle = 0$ (all λ)

and the excited states are obtained by acting on

$|\psi_\sigma\rangle$ with products of $a_{\lambda\sigma}{}^\dagger$ operators. From [59] and [61] we see that the three eigenstates of $\tilde{H}_0$ containing no real phonons are given by

[62] $$|\psi_\sigma\rangle = |\sigma\rangle \prod_\lambda |\beta_\lambda(\sigma)\rangle_\lambda$$

where $|\beta_\lambda(\sigma)\rangle_\lambda$ is a coherent state of mode λ with amplitude $\beta_\lambda(\sigma)$,

[63] $$b_\lambda |\beta_\lambda(\sigma)\rangle_\lambda = \beta_\lambda(\sigma)|\beta_\lambda(\sigma)\rangle_\lambda$$

The phonon part of [62] describes the local distortion of the lattice induced by the impurity in the state σ, assuming $\tilde{V}_a{}^{(1)} = 0$. The energy shifts of the states [62] are easily found to be given by

[64] $$E_s(0) = -4\varepsilon^{(0)}$$
$$E_s(\pm 1) = -\varepsilon^{(0)} - 3\varepsilon^{(2)}$$

where

[65] $$\varepsilon^{(v)} = \frac{1}{25}\sum_\lambda |A_v(\lambda)|^2/\hbar\omega_\lambda$$

The same energy shifts [64] are obtained when $\tilde{V}_s{}^{(1)}$ is treated in second-order perturbation theory.

We now add to [64] the second-order energy shifts due to the term $\tilde{V}_a{}^{(1)}$ in [50], which are given by

[66] $$E_a(0) = -6\varepsilon^{(1)}$$
$$E_a(\pm 1) = -3(\varepsilon^{(1)} + \varepsilon^{(2)})$$

so that the total energy shifts due to the linear spin-lattice coupling are given by

[67] $$E(0) = -4\varepsilon^{(0)} - 6\varepsilon^{(1)}$$
$$E(\pm 1) = -\varepsilon^{(0)} - 3\varepsilon^{(1)} - 6\varepsilon^{(2)}$$

In the presence of the term $\tilde{V}_a{}^{(1)}$ the eigenstates are, of course, no longer of the form [58] but are linear combinations of such states. In first order in the wave functions, these linear combinations may be written in terms of the states [58] or in terms of the states of the uncoupled system. The main point to remember is that the labels 0, ± 1 in [66] and [67] refer to the unperturbed states and do not imply that the corresponding states are of the product form [58]. The remaining two-fold degeneracy, $E(1) = E(-1)$, is due to the D_{3h} symmetry and remains valid to all orders.

In an isotropic model in which the environment of the impurity and the phonon dispersion relations are assumed to be rotationally invariant, the quantities [65] are all equal, $\varepsilon^{(\mu)} = \bar{\varepsilon}$, as can easily be shown from [47]. From [67] we then see that $E(0) = E(\pm 1)$, so that no crystal-field splitting results in this case, as expected. We remark that in ref. 12 only the term v_0 in [53] was taken into account giving $\varepsilon^{(1)} = \varepsilon^{(2)} = 0$ and hence

[68] $$V_c \equiv E(\pm 1) - E(0) = 3\varepsilon^{(0)}$$

which leads to the erroneous prediction of a positive definite splitting. As remarked in Sect. 1, the energies quoted in ref. 12 correspond to $V_c = 6\varepsilon^{(0)}$ rather than [68], because the elastic deformation energy was not taken into account in ref. 12, which in this case is equal to minus one half times the anisotropic interaction energy. In reality, the crystal-field splitting due to the linear spin-lattice coupling is given by

[69] $$V_c{}^{(1)} = E(\pm 1) - E(0)$$
$$= 3[\varepsilon^{(0)} + \varepsilon^{(1)} - 2\varepsilon^{(2)}]$$

and the sign of $V_c{}^{(1)}$ hence clearly depends on the relative magnitudes of the quantities [65]. The evaluation of these quantities is discussed in the next section.

5. Calculation of the Crystal-field Splitting Due to the Phonon Anisotropy

As shown previously (10), the contribution of the anisotropy of the spin-lattice coupling to the splitting [69] is small and we may therefore replace the coupling [46] by the isotropic coupling obtained by averaging the coefficients [47] over the directions of the vectors $\hat{R}_{1p}$, giving

[70] $$A_v(\lambda) = -12i^l(\hbar/2MN\omega_\lambda)^{1/2}\sum_l \bar{f}_l j_l(qR_0)$$
$$\times T_{2v}{}^{(ll)}(\hat{q}, e_\lambda)$$

Substituting this expression into [65], we evaluate the resulting sums over the phonon modes by using the anisotropic Debye model introduced previously (9), which is characterized by the dispersion relations

[71] $$\omega_j(q) = v_j(\hat{q})q$$

where $v_j(\hat{q})$ is the velocity of sound of polarization j and propagation direction $\hat{q}$. The directional dependence of $v_j(\hat{q})$ and of the polarization vectors $e_\lambda = e_j(q)$ are parameterized in terms of the elastic constants of the solid for which we take the values determined by neutron scattering (13). Replacing the summation over the Brillouin zone by an integral over the Debye sphere, we obtain

[72] $$\varepsilon^{(v)} = \kappa \sum_{ll'} \tilde{\phi}_l \tilde{\phi}_{l'} \alpha_v(ll')k_{ll'}$$

where

[73] $$\tilde{\phi}_l = R_0 \bar{f}_l/\hbar\omega_D$$

are dimensionless, renormalized interaction constants, and

[74] $$k_{ll'} = \int_0^{q_D R_0} j_l(x)j_{l'}(x)\,dx$$

In a close-packed lattice we have $q_D R_0 = (6\pi^2 \sqrt{2})^{1/3}$, giving

[75] $$k_{11} = 0.413, \qquad k_{33} = 0.072, \qquad k_{13} = k_{31} = 0.106$$

The coefficient κ in [72] is equal to

[76] $$\kappa = \frac{864}{625} \frac{\hbar}{M R_0^2 q_D R_0} = 1.846 \text{ cm}^{-1}$$

and

[77] $$\alpha_v(ll') = i^{l-l'}(\bar{v}^2/4\pi)(2l + 1)^{1/2}(2l' + 1)^{1/2}\int d\hat{q} \sum_j T_{2v}^{(l1)}(\hat{q}, e_\lambda)^* T_{2v}^{(l'1)}(\hat{q}, e_\lambda)v_j(\hat{q})^{-2}$$

where $\bar{v}$ is the average sound velocity defined by

[78] $$\bar{v} = \left[\frac{1}{12\pi}\sum_j \int d\hat{q}\, v_j(\hat{q})^{-3}\right]^{-1/3}$$

and $\omega_D = \bar{v}q_D$. The value of $\bar{v}$ obtained in this way using the values of the density and of the elastic constants given in ref. 13 is $\bar{v} = 1348.3$ m/s, corresponding to a Debye temperature

[79] $$\Theta_D = \hbar\omega_D/k = 119.5 \text{ K}$$

The values of the coefficients [77] obtained in our model are given in Table 1. We note that for isotropic dispersion relations, i.e., assuming the frequencies [71] to be independent of $\hat{q}$, we have

[80] $$\alpha_v(ll') = \delta_{ll'}$$

The splitting [69] then vanishes, and the energy shifts [67] are all equal to the self-energy shift of the $J = 1$ level,

[81] $$E_1 = -10\varepsilon = -10\kappa(\tilde{\phi}_1^2 k_{11} + \tilde{\phi}_3^2 k_{33})$$

which agrees with eq. [97] of ref. 10.

With the help of [72]–[77] and Table 1, one can calculate the crystal-field splitting [69] once the interaction parameters [48] are known. Unfortunately there is still considerable uncertainty in the values of these parameters because of our poor knowledge of the anisotropic intermolecular potential and the additional uncertainty brought about by the renormalization.

We point out that the contribution [69] of the linear spin–lattice coupling to the crystal-field splitting is predicted to be negative in our model for any anisotropic potential. An examination of the coefficients $\alpha_v(ll')$ in Table 1 shows that the quantities $\varepsilon^{(1)} - \varepsilon^{(0)}$ and $\varepsilon^{(2)} - \varepsilon^{(0)}$, where $\varepsilon^{(v)}$ is given by [72], are positive definite quadratic forms in the parameters $\tilde{\phi}_1$ and $\tilde{\phi}_3$, defined by [73], and $\varepsilon^{(1)} \approx \varepsilon^{(2)}$ implying that $V_c^{(1)} < 0$ for all values of the coupling constants $\tilde{f}_l$. This result is a consequence of the nature of the elastic anisotropy of solid hydrogen

and can be traced back to the property that the velocity of propagation of the L mode is a maximum, and that of the T_2 mode a minimum, in the direction of the c acis, cf. ref. 24. The T_1 mode is nearly isotropic and does not contribute to the splitting.

To our knowledge, the most recent *ab initio* calculation of the anisotropic pair potential for H_2 is that of Gallup (25). In ref. 25 the radial part of the potential is presented in the form of a series of spline functions. Taking derivatives of the spline in Table 3 of ref. 25 corresponding to the range $6.6 \le R \le 7.2$ bohr, we obtain at the nearest-neighbour separation $R_0 = 3.784$ Å the values (in cm^{-1})

$$B(R_0) = 0.73$$
[82] $$R_0 B'(R_0) = -11.45$$
$$R_0^2 B''(R_0) = 93.70$$

where $B(R)$ is defined in [18]. The values of the parameters [42] corresponding to [82] are

[83] $$g_1 = 121 \text{ cm}^{-1}, \qquad g_2 = 80 \text{ cm}^{-1}$$

The spline form of the potential is not very convenient for the purpose of renormalization, and to estimate the parameters $\tilde{f}_l$ defined by [48], we therefore use instead an exp-6 model,

[84] $$B(R) = \beta_1 \exp[-\eta(R - R_0)/R_0]$$
$$- \beta_2 (R_0/R)^6$$

which was also used in refs. 10, 14, and 12. Choosing the potential used in ref. 12 and $R_0 = 3.784$ Å, we obtain the values

[85] $$\beta_1 = 0.858 \text{ cm}^{-1}$$
$$\beta_2 = 1.024 \text{ cm}^{-1}$$
$$\eta = 12.96$$

The values of the parameters [42] following from [84] and [85],

[86] $$g_1 = 112 \text{ cm}^{-1}, \qquad g_2 = 98 \text{ cm}^{-1}$$

are not very different from [83], and the difference

TABLE 1. Coefficients $\alpha_v(ll')$ defined by [77]

v	$\alpha_v(11)$	$\alpha_v(33)$	$\alpha_v(13) = \alpha_v(31)$
0	0.633	0.663	-0.266
1	0.999	0.739	-0.425
2	0.925	0.762	-0.429

indicates the magnitude of the uncertainty remaining in the values of these parameters.

The phonon renormalization of a potential of the form [18], [84] was calculated in ref. 10 where the distribution function of the relative displacements of neighbouring molecules was assumed to be Gaussian. This calculation was improved in ref. 14 by including the effect of the short-range correlations via a Jastrow function. The resulting renormalization factors depend on the value of η in [84]. The potential used in ref. 14 corresponds to $\eta = 13.29$ which is sufficiently close to the value in [85] so that we may use the results of ref. 14 which in the present notation are

$$[87] \quad \begin{aligned} \tilde{f}_1 &= (2/5)^{1/2}(12.2\beta_1 - 2.13\beta_2)R_0^{-1} \\ \tilde{f}_3 &= -(3/5)^{1/2}(25.9\beta_1 - 8.03\beta_2)R_0^{-1} \end{aligned}$$

The values of the dimensionless parameters [73] obtained from [85] and [87] are

$$[88] \quad \tilde{\phi}_1 = 6.33 \times 10^{-2}, \qquad \tilde{\phi}_3 = -13.10 \times 10^{-2}$$

From [67] and [72] we then obtain the following values for the energy shifts,

$$[89] \quad \begin{aligned} \varepsilon^{(0)} &= 0.13 \text{ GHz}, \quad \varepsilon^{(1)} \simeq \varepsilon^{(2)} = 0.18 \text{ GHz} \\ E(0) &= -1.62 \text{ GHz}, \quad E(\pm 1) = -1.75 \text{ GHz} \end{aligned}$$

and hence from [69],

$$[90] \quad V_c^{(1)} = -0.13 \text{ GHz}$$

We emphasize that this result is only an order-of-magnitude estimate of $V_c^{(1)}$. For example, if instead of [87] we use the renormalization results of ref. 10, correcting a sign error in the expression for $\tilde{f}_3$,

$$[91] \quad \begin{aligned} \tilde{f}_1 &= (2/5)^{1/2}(31\beta_1 - 5\beta_2)R_0^{-1} \\ \tilde{f}_3 &= -(3/5)^{1/2}(46\beta_1 - 11\beta_2)R_0^{-1} \end{aligned}$$

which differ from [87] in the neglect of the short-range correlations, then with the values [85] for the potential parameters, we get $V_c^{(1)} = -0.77$ GHz, almost an order-of-magnitude change from [90]. And using the unrenormalized values,

$$[92] \quad \begin{aligned} \tilde{f}_1 &= (2/5)^{1/2}(10\beta_1 - 3\beta_2)R_0^{-1} \\ \tilde{f}_3 &= -(3/5)^{1/2}(15\beta_1 - 8\beta_2)R_0^{-1} \end{aligned}$$

the result is $V_c^{(1)} = -0.045$ GHz. The calculated values of $V_c^{(1)}$ therefore depend very strongly on the renormalization, and of particular importance is the shape of the pair correlation function in the hard-core region of the anisotropic potential. With our present limited knowledge of the anisotropic potential and of the pair correlation function, all we can conclude is that the contribution of the linear spin–lattice coupling to the crystal-field splitting lies in the range between 0 and -0.5 GHz.

To obtain the full crystal-field splitting, we must add to $V_c^{(1)}$ the contribution

$$[93] \quad V_c^{(0)} = -\tfrac{3}{5}\varepsilon_{2c}$$

due to the static renormalization, where ε_{2c} is given by [41]. Using the values [83] or [86] for g_1 and g_2, and the estimate [43] for the lattice dynamical parameters based on the anisotropic Debye model, we get

$$[94] \quad V_c^{(0)} = 1.5 \text{ GHz}$$

As discussed below [43], the true value of $V_c^{(0)}$ may be considerably smaller, but most likely it is positive and lies in the range between 0 and 1 GHz.

The experimental values of V_c inferred from nmr measurements (2–6) also show a rather wide variation. Schweizer et al. (6) reported the value $|V_c| = (0.29 \pm 0.06)$ GHz in agreement with earlier results of the same group (4), which placed an upper limit, $|V_c| < 0.6$ GHz on the magnitude of V_c, but left the sign undetermined. These results are seen to be consistent with our estimates for reasonable values of the parameters involved. On the other hand, Gaines et al. (5) have recently reported a positive value, $V_c = 0.92$ GHz, from nmr spectra in single crystals. If V_c is indeed positive, this implies a nonvanishing contribution from $V_c^{(0)}$, since $V_c^{(1)}$ is always negative according to our theory, and the magnitude of the required $V_c^{(0)}$ is of the order of [94]. If this result is confirmed, the Debye model prediction [43] for $\Delta[\zeta]$ should be taken seriously. In particular, this result would have important consequences for the interpretation of the microwave pair spectra (7). As discussed in ref. 17, the adoption of the theoretical estimate [43] contradicts the tentative assignment of one of the observed lines, B_2, in the microwave spectrum, and would lead to a modified set of values for the parameters of the effective anisotropic pair potential in the solid, cf. eqs. [126] and [127] of ref. 17.

6. Conclusions

We have investigated the rotational energy level structure of a single orthohydrogen molecule in a parahydrogen matrix. To describe the interaction

between the rotational motion of the ortho molecule and the quantum-crystal lattice vibrations we constructed a Hamiltonian which combines the orientation dependent potential with an effective harmonic model for the lattice dynamics. On the assumption that the host lattice has the hcp structure with $c/a = (8/3)^{1/2}$, we identified and calculated two distinct contributions to the crystal-field splitting, V_c, of the $J = 1$ level, both originating from the anisotropy in the lattice vibrations associated with the uniaxial crystal structure. One contribution which we call 'static', arises when the anisotropic interaction between the ortho molecule and the surrounding molecules is averaged over the zero-point lattice vibrations, and results from the difference in the relative motion of the molecules in ip and op pairs. The second, 'dynamical,' contribution arises from the self-energy, or lattice-polarization, effects, and corresponds in second-order perturbation theory to the emission and re-absorption of virtual self-consistent phonons by the rotating molecule. In the presence of the dynamical coupling, the ortho molecule is no longer in a definite quantum state, and the splitting V_c refers to the states of the combined rotational-phonon system. The dynamical contribution to V_c is mainly due to the anisotropy of the phonon field which we described by a generalized Debye model in which the anisotropy of the long-wavelength modes is expressed in terms of the elastic constants of the crystal.

Our results for V_c are expressed in terms of the parameters characterizing the lattice dynamical model and the effective anisotropic pair potential in the solid. The static and dynamical contributions to V_c are of opposite sign, and although our results in order-of-magnitude are consistent with the experimental data, the accuracy of our knowledge of the relevant parameters is not sufficient to calculate the two contributions with certainty. The main limitation in calculating the dynamical contribution arises from the uncertainty in the parameters of the renormalized anisotropic pair potential. For the static effect, one needs a more accurate calculation of the displacement correlation matrix for ip and op pairs. Further theoretical work is also needed to predict the behaviour of V_c at higher pressures.

1. J. VAN KRANENDONK and G. KARL. Rev. Mod. Phys. **40**, 531 (1968).
2. W. N. HARDY and J. R. GAINES. Phys. Rev. Lett. **19**, 1417 (1967).
3. J. H. CONSTABLE and J. R. GAINES. Solid State Commun. **9**, 155 (1971).
4. R. F. BUZERAK, M. CHAN, and H. MEYER. J. Low Temp. Phys. **28**, 415 (1977); P. PEDRONI, M. CHAN, R. SCHWEIZER, and H. MEYER. J. Low Temp. Phys. **19**, 537 (1975).
5. J. R. GAINES, A. MUKHERJEE, and YAN-CHI SHI. Phys. Rev. B, **17**, 4188 (1978).
6. R. SCHWEIZER, S. WASHBURN, and H. MEYER. Phys. Rev. Lett. **40**, 1035 (1978).
7. W. N. HARDY, A. J. BERLINSKY, and A. B. HARRIS. Can. J. Phys. **55**, 1150 (1977).
8. T. NAKAMURA. Prog. Theor. Phys. **14**, 135 (1955).
9. S. LURYI and J. VAN KRANENDONK. Can. J. Phys. **57**, 136 (1979).
10. J. VAN KRANENDONK and V. F. SEARS. Can. J. Phys. **44**, 313 (1966).
11. F. S. HAM. In Electron paramagnetic resonance. Edited by S. Geschwind. Plenum Press, New York, NY. 1972.
12. J. C. RAICH and L. B. KANNEY. J. Low Temp. Phys. **28**, 95 (1977).
13. M. NIELSEN. Phys. Rev. B, **7**, 1626 (1973).
14. A. B. HARRIS. Phys. Rev. B, **1**, 1881 (1970).
15. J. NOOLANDI. Can. J. Phys. **48**, 2032 (1970).
16. A. B. HARRIS, A. J. BERLINSKY, and W. N. HARDY. Can. J. Phys. **55**, 1180 (1977).
17. S. LURYI and J. VAN KRANENDONK. Can. J. Phys. **57**, 307 (1979).
18. J. NOOLANDI and J. VAN KRANENDONK. Can. J. Phys. **50**, 1815 (1972).
19. F. W. DeWETTE and B. R. A. NIJBOER. Phys. Lett. **18**, 19 (1965).
20. T. R. KOEHLER. In Dynamical properties of solids. Edited by G. K. Horton and A. A. Maradudin. North-Holland Publishing Co., Amsterdam, The Netherlands. 1975.
21. H. HORNER. Z. Phys. **242**, 432 (1971).
22. N. R. WERTHAMER. Phys. Rev. A, **7**, 254 (1973).
23. D. M. BRINK and G. R. SATCHLER. Angular momentum. 2nd ed. (reprinted 1971 with corrections). Clarendon Press, Oxford, England. 1968.
24. V. V. GOLDMAN. J. Low Temp. Phys. **26**, 203 (1977).
25. C. A. GALLUP. Mol. Phys. **33**, 943 (1977).