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¹⁰This corresponds to a representative pressure of about 1.7 Mbars.

¹¹For a static lattice, the energy (to second order) is conventionally written as $E = E_0 + E_M + E_b^{(2)} + \dots$, where E_0 is the energy of the homogeneous interacting elec-

tron gas, E_M the Madelung energy, and $E_b^{(2)}$ the second-order band-structure energy. To obtain Eq. (1), we must not only include dynamics but also combine E_M and $E_b^{(2)}$ so that they each contribute to the potential Φ .

¹²The ratio of $\{\langle u^2 \rangle\}^{1/2}$ to nearest-neighbor distance is readily calculated (from the self-consistent frequencies and polarizations) to be 0.1687 for the fcc structure at $r_s = 1.36$ [see D. Straus, thesis, Cornell University Materials Science Laboratory Report No. 2739 (unpublished)]. This should be compared to the value for Na which for melting ($p = 0$) is 0.123 [D. Stroud and N. W. Ashcroft, *Phys. Rev. B* **5**, 371 (1972)].

¹³A plot of the static ground-state Gibbs energy G (at a pressure corresponding to the fcc crystal of Fig. 1) looks almost identical to the static-energy plot of Fig. 1; and minimization of G at constant p is, in this case, essentially equivalent to E at constant r_s .

¹⁴We have used for $\epsilon(k)$ the Hubbard-Geldart-Vosko form, and in the structure-independent terms of Eq. (1) we have used the Nozières-Pines approximation to the correlation-energy contribution.

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¹⁶Full details of the calculational methods are found in Straus, Ref. 12. The important point is that the correlation functions $\lambda_{\alpha\beta}(\vec{X})$ were computed using the techniques of D. M. Straus and N. W. Ashcroft [*Phys. Rev. B* **14**, 448 (1976)], except that the full directional dependence rather than the angular average of the $\vec{q} \rightarrow 0$ portion of the integrand in Eq. (3) has been completely included.

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Renormalized Pair Interactions and Three-Body Polarization Forces in Solid Hydrogen*

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We find that the inclusion of the pseudo-three-body forces between all neighbors does not remove the difficulty of obtaining a consistent analysis of the microwave spectrum of solid hydrogen observed by Hardy and Berlinsky. We propose a novel anisotropic interaction, due to the deviation from axial symmetry of the pair distribution function of neighboring molecules, leading to a satisfactory interpretation, and yielding new information about lattice dynamics.

The intermolecular interactions and the rotational and lattice-vibrational motions of the molecules in solid hydrogen have been studied extensively in recent years; and attempts at comprehensive theoretical treatments have also been published.¹⁻³ An important advance in our knowl-

edge in this field is the recent observation by Hardy and Berlinsky⁴ of the microwave spectrum of bound pairs of ortho molecules in a parahydrogen crystal. These authors interpreted this spectrum on the basis of previous theoretical work of Harris,³ but they came to the conclusion that the

TABLE I. Numerical values of the coefficients in the expression for the axial energy levels [cf. Eq. (1)].

State	a_0	b_0	b_2	c_0	a	b	c	d	e	f
(20)	6	1	1	1	-6.03	0.15	-0.23	-4.73	-0.10	-0.07
(22) $_{\pm}$	1	1	-1	-1	1.08	0.30	-0.02	0.19	0.44	0.02
(00)	0	10	0	0	8.75	-1.17	-0.82	7.49	1.40	-0.06
(10)	0	-5	-7	-1	3.75	2.82	0.93	-1.65	1.35	0.26
(11) $_{\pm}$	0	-5	$\frac{7}{2}$	$\frac{1}{2}$	-8.43	-0.54	0.15	-4.79	-1.72	-0.08
(21) $_{\pm}$	-4	1	$\frac{1}{2}$	$\frac{1}{2}$	4.12	-0.67	-0.08	4.05	-0.04	-0.00

theory was incomplete: Agreement with the observed frequencies could be obtained only by assigning a negative value to the static polarizability of the molecules. We have re-examined the theory and have succeeded in resolving the difficulty by the introduction of a new type of anisotropic interaction arising from the renormalization of the electric quadrupole-quadrupole (EQQ) interaction by the zero-point lattice vibrations.

The most general anisotropic interaction between a pair of isolated ortho molecules results in six rotational levels—three doublets and three singlets (cf. the first column of Table I). In the solid there are two types of nearest-neighbor (nn) pairs depending on whether the two molecules are in the same hexagonal plane ($t = \alpha$, $\sigma = 1$) or in neighboring planes ($t = \beta$, $\sigma = -1$). The energies of the six levels under the most general axially symmetric interaction are given by

$$E_t(J, M)_{\pm} = a_0 \Gamma_0 \xi_{54} + \frac{1}{5} (b_0 \epsilon_0 + b_2 \epsilon_2) + c_0 \left(\frac{4}{5} \Delta B + \frac{1}{3} \sigma V_{ct} \right) + (a \xi_{43}^2 + b \xi_{43} + c) \Gamma_0 \rho + (d \xi_{54}^2 + e \xi_{54} + f) \Gamma_0'^2 / B. \quad (1)$$

The quantities ϵ_0 , ϵ_2 , and $\epsilon_4 \equiv \Gamma_0 \xi_{54}$ are the direct anisotropic interaction constants which may be assumed to be the same for α and β pairs. V_{ct} is the strength of the crystalline field symmetric about the hexagonal axis. One can expect that $V_{c\alpha} \neq V_{c\beta}$ since the crystalline field is very sensitive to local distortions of the lattice. Strictly speaking, the parameter ΔB should also receive a contribution from lattice distortions and thus be different for α and β pairs. In this work, however, we treat ΔB assuming an undistorted hcp lattice. The terms proportional to $\Gamma_0 \rho$ and $\Gamma_0'^2 / B$ in Eq. (1) represent the axial parts of the "three-body" forces, where the terms containing the second, first, and zeroth powers of the ξ factors correspond to the contributions from the four nn's common to both ortho molecules, the remaining fourteen of the nn's of the pair, and the more distant neighbors, the ξ factors being appreciably different from unity only for nn pairs.²

The three doublets are split by the nonaxial interactions, and the resulting splittings, $\Delta_t(J, M) \equiv E_t^+(J, M) - E_t^-(J, M)$, are given by

$$\Delta_t(J, M) = a_0' + \frac{1}{5} c_0' V_{ct} + 2(a' \xi_{43}^2 + b' \xi_{43} + c') \Gamma_0 \rho + 2(d' \xi_{54}^2 + e' \xi_{54} + f') \Gamma_0'^2 / B. \quad (2)$$

The coefficients appearing in Eqs. (1) and (2) are given in Tables I and II, and the coefficients a, \dots, f' have been determined by evaluating numerically the lattice sums ($g_{\nu\nu'}$ and $h_{\nu\nu'}$ of Ref. 3) involved in the expressions for the three-body forces.⁵ The inclusion of all the para molecules, instead of only the four nn's taken into account in Ref. 3, alters these sums appreciably, in some cases by an order of magnitude or a change of sign. However, we find that inclusion of all the three-body forces by itself does not lead to an acceptable interpretation of the observed spectrum, and we are left with the same conclusion that the theory is incomplete. This difficulty is successfully removed by the introduction of the interaction term a_0' in Eq. (2), which represents an effect which has not been considered before. This new anisotropic interaction finds its origin in the fact that the zero-point motion of the intermolecular axis of a nn pair cannot be expected to show complete axial symmetry. The EQQ interaction is of the form

$$V_{\text{EQQ}}(\vec{R}_{12}) = \sum_M \gamma_{4M}(\vec{R}_{12}) T_{4M}(\hat{\omega}_1, \hat{\omega}_2), \quad (3)$$

where $\gamma_{4M} = \Gamma_0 (R_0 / R_{12})^5 C_{4M}^*(\hat{R}_{12})$, and $\vec{R}_{12} \equiv R_{12} \hat{R}_{12} = \vec{R}_0 + \vec{u}$, \vec{u} being the relative displacement of molecules

TABLE II. Numerical values of the coefficients in the expression for the splitting of the doublets due to nonaxial interactions [cf. Eq. (2)].

Splitting	a'_0	c'_0	a'	b'	c'	d'	e'	f'
$\Delta_\alpha(22)$	0	0	3.83	-0.46	-0.01	3.04	-0.53	-0.02
$\Delta_\beta(22)$	0	0	-4.92	0.69	0.01	-3.91	0.88	0.00
$\Delta_\alpha(11)$	0	3	-1.19	0.55	-0.02	-0.83	0.60	-0.03
$\Delta_\beta(11)$	0	-1	-3.56	1.47	-0.03	-2.49	1.61	-0.04
$\Delta_\alpha(21)$	δ_α	-3	0.12	0.01	-0.01	0.42	-0.10	0.00
$\Delta_\beta(21)$	δ_β	1	0.38	-0.04	-0.00	1.26	-1.31	0.00

1 and 2. Expanding in powers of \tilde{u} , we find that to second order the average value of γ_{4M} is given by

$$\langle \gamma_{4M} \rangle = \gamma_{4M}(\vec{R}_0) - \frac{1}{4} [\langle u_x^2 + u_y^2 - 2u_z^2 \rangle \nabla_z^2 \gamma_{4M}(\vec{R}_0)] - \frac{1}{4} (\langle u_y^2 - u_x^2 \rangle) (\nabla_1^2 + \nabla_{-1}^2) \gamma_{4M}(\vec{R}_0). \quad (4)$$

In the intermolecular coordinate frame⁶ the first two terms are proportional to δ_{M0} , and when substituted in Eq. (3) give rise to the renormalized EQQ interaction $\xi_{54} V_{\text{EQQ}}(\vec{R}_0)$. This effect is due to an axially symmetric deviation of the distribution function of \vec{R}_{12} from spherical symmetry brought about by the long- and short-range phonon correlations.² The third term in Eq. (4) is nonvanishing for $M = \pm 2$ and therefore contributes to the splitting of the ground doublet by an amount $\delta_i = 30 \Gamma_0 (\langle u_y^2 - u_x^2 \rangle) / R_0^2$. The environment of the two ortho molecules is strongly asymmetric and quite different for α and β pairs, and one can therefore expect $\delta_\alpha \neq \delta_\beta$.

To reduce the number of adjustable parameters as much as possible, we use the relation $2(1 - \xi_{54}) = 3(1 - \xi_{43})$ which follows from the tensorial properties when one assumes that the axial flattening of the distribution of \vec{R}_{12} is independent of the angular momenta of the two molecules. The rigid-lattice parameters are known accurately, and we use the values $\Gamma_0 = 20.67$, $\Gamma_0 \rho = 0.31$, and $\Gamma_0'^2 / B = 0.24$ (in GHz). The main contribution to ΔB comes from the difference between the rotational "polarization" energies of para and ortho molecules ($J=0-2$ versus $J=1-3$). We have estimated this effect to be $\Delta B = 0.6$ GHz, and this is the value of ΔB we use. The remaining parameters are uniquely determined by a fit to the observed frequencies of the microwave absorption lines,⁷ yielding $\xi_{54} = 0.85$, $\epsilon_0 = -0.14$, $\epsilon_2 = -0.50$, $V_{c\alpha} = 1.82$, $V_{c\beta} = -1.13$, $\delta_\alpha = 1.66$, and $\delta_\beta = 1.21$ (in GHz). It is encouraging to observe that the combination $6\epsilon_2 + 12\epsilon_0$ falls well within the empirical range -0.1 to -0.2 cm^{-1} derived earlier.²

The magnitude obtained here for the deviation

from axial symmetry of the distribution function of \vec{R}_{12} is small, $\langle u_y^2 \rangle - \langle u_x^2 \rangle \simeq 2 \times 10^{-3} R_0^2$, and appears quite realistic. It would be interesting to make a first-principles calculation of this effect from the lattice dynamics, and to investigate the roles played by the crystal structure, the anharmonicity, and the quantum-crystal nature.

It is clear that the microwave spectra observed by Hardy and Berlinsky⁴ contain a wealth of information on the finer details of the anisotropic interactions and, through the renormalization effect, of the lattice dynamics. Observation of the remaining lines in the ortho pair spectrum would clearly be of great value.

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⁶We use the notation of Harris (Ref. 3) for the interaction parameters; the pair states are labeled by their total angular momentum with respect to the intermolecular frame defined as in Ref. 3, p. 1885.

⁷Our assignment of the lines agrees with that given in Ref. 1, Table I. The transition rates were calculated with the following expression for the induced dipole moment: $\mu_0 = 0$, $\mu_{\pm 1} \propto Y_{2,\pm 2}(\Omega_1) + \sigma Y_{2,\pm 2}(\Omega_2)$, where Ω_1 and Ω_2 refer to the crystal frame.