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Orientational Order in Solid Ortho-Hydrogen. I. Cubic Close-Packed Molecular Lattice*

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Previous theories of the orientational ordering of the molecules in solid ortho-hydrogen have been based on the assumption that the lattice is hcp, and on a quantum-mechanical treatment that is not self-consistent. It now seems clear that a change from a fcc lattice to a hcp lattice is associated in some way with the thermal and NMR phenomena that indicate the occurrence of orientational reordering. This paper develops a self-consistent theory of orientational ordering of molecules on a rigid fcc lattice, assuming orientational coupling of the quadrupole-quadrupole form between nearest neighbors only, or throughout the lattice. It is shown how the special properties of hydrogen and its isotopes facilitate application of the self-consistent theory to solid hydrogen. It is found that at all temperatures, up to the transition temperature, the symmetry axes of the molecular orientation distributions are arranged like the equilibrium directions in the corresponding classical system. If one includes quadrupole-quadrupole couplings between all pairs of molecules, one finds that there would be a first-order transition to orientational disorder at 5.07°K in hydrogen, and at 6.37°K in deuterium, if the molecular lattice were fcc throughout. These values exceed the observed transition temperatures by more than a factor of 2—a discrepancy that is not surprising if the actual transition is one from a fcc lattice to a hcp lattice at a temperature determined by the properties of the two phases. Molecular energy levels and thermodynamic properties are given for the fcc phase up to the transition temperature.

I. INTRODUCTION

A LAMBDA anomaly in the specific heat of solid hydrogen occurs, at normal pressures, at temperatures that fall from about 2.8°K for 95% ortho-hydrogen to 1.4°K for 70% ortho-hydrogen.[1,2] With decreasing ortho-concentration the anomaly becomes less marked, and it has not been observed below 62%. Smaller peaks have also been observed[3] on the high temperature side of the λ anomaly, for ortho-concentrations in the range near 70%; comparable observations are lacking for higher ortho-concentrations. In the case of solid deuterium,[4] there is a λ anomaly at a temperature that falls from 3.22° for 87% para-deuterium ($J=1$) to 1.82°K for 65% para-deuterium; no additional structure in the specific heat curve has been reported. Associated with the thermal anomaly in both substances there is a nuclear magnetic resonance anomaly.[5-8]

There has been an accumulation of evidence that solid hydrogen has a cubic close-packed lattice if the ortho-hydrogen concentration is sufficient and the temperature is not too high; otherwise, it is hexagonal close-packed. Mills, Schuch and Depatie[9] have shown, for a considerable range of conditions, that the λ anomaly is associated with the change in the molecular lattice from cubic to hexagonal close-packed as the temperature rises; there may, however, be some question as to the nature of the association, in view of the considerable hysteresis and the existence of structure other than the λ peak in the specific-heat curve. Observations of Schuch and Mills[10] and of Mucker *et al.*[11] suggest that there exists a similar relation between the thermal anomaly and the change in molecular lattice in the case of deuterium.

Of all crystals, solid hydrogen is the one in which there is the closest approach to free molecular rotation. At normal pressures the energy of coupling between neighboring molecules varies by some 20 cm^{-1} as the orientations of the molecules vary, whereas the separation of the lowest rotational levels of free para-hydrogen ($J=0$ and $J=2$) is 356 cm^{-1}, and of free ortho-hydrogen ($J=1$ and $J=3$) is 593 cm^{-1}. The perturbations due to orientational coupling in the crystal thus produce little mixing of molecular states with different J. The resulting possibility of treating J as a good molecular quantum number, for all J, seems to exist only in solid hydrogen and its isotopes. In both solid hydrogen and solid deuterium the separation of the rotational levels is so much higher than kT that one can treat all molecules as being in their lowest rotational states, $J=0$ or $J=1$, depending on the nuclear species.

Originally, the specific heat anomaly in H_2 was explained as arising from a hindrance by the crystalline field to the rotation of the ortho-molecules[12,13] More

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recently, several treatments[14–16] of the λ anomaly have been based on the idea that the degeneracy of the $J=1$ states of each ortho-molecule is partially removed by an axially symmetric crystal field that represents the interaction of the molecule with its nearest neighbors, and that the λ transition is due to the onset of a cooperative ordering of the ortho-molecules under the influence of their quadrupole-quadrupole interactions. These treatments have in common the assumptions that the crystal structure is hcp, that there is a unique axis of quantization for all molecules with $J=1$, parallel to the threefold axis of symmetry of the hcp lattice, and that each molecule is of one of two species: it has $M=0$, or $M=\pm 1$. Examination of the results shows that these theories are not self-consistent; the derived orientational distributions would not produce a charge distribution that would give rise to molecular potentials with the axial symmetry required if M, as well as J, is to be a good quantum member. These theories can not, therefore, be considered to be satisfactory even as treatments of hcp hydrogen.

The work reported in this paper is directed toward a self-consistent treatment of the orientational order in both hcp and fcc hydrogen and deuterium, with the aim of explaining all features in their thermal behavior, including (perhaps ultimately) those associated with a change in the molecular lattice. To avoid, at the beginning, involvement in the problem of mixtures, attention is focused on pure ortho-hydrogen and para-deuterium, in which all molecules have $J=1$. It is also assumed that lattice vibrations are negligible—that the molecules can be treated as distributed over a rigid lattice—and that the molecules are subject to orientational couplings having at least the form (if not the origin) of electrostatic quadrupole-quadrupole couplings. Section II and Appendix A develop the basic formalism of the internal field as it applies to an assembly of molecular rotators. Section III discusses the special features of the hydrogen problem that make it relatively easy to develop a self-consistent treatment. Finally, these ideas are illustrated in Sec. IV by application to cubic-close-packed hydrogen.[17] Treatment of the orientational ordering in hcp hydrogen, a much more complex problem, is deferred to a companion paper.

II. THE INTERNAL FIELD APPROXIMATION

We consider a system of rigid rotators, representing hydrogen molecules, with centers of gravity fixed at the points of a rigid lattice. Ignoring the electrons, we describe the orientation of the molecule on site i by the polar angles $(\theta_i,\varphi_i)=\mathbf{\Omega}_i$ of the internuclear axis. The Hamiltonian for the system will be

$$H=\sum_i H_i(\mathbf{\Omega}_i)+\tfrac{1}{2}\sum_i\sum_j V_{ij}(\mathbf{\Omega}_i,\mathbf{\Omega}_j)\,, \tag{2.1}$$

where H_i is the rotational kinetic energy operator and V_{ij} is the potential energy of interaction of molecules i and j, which will depend on the direction of the intermolecular axis, and will be zero if $i=j$.

In the internal field approximation, one assumes that each molecule i can occur in states described by a set of orthonormal functions $\psi_\mu{}^i(\mathbf{\Omega}_i)$, $\mu=1, 2, \cdots$, determined by an effective field or effective potential energy $U^i(\Omega_i)$ that represents its interactions with the other molecules. Wave functions for the crystal can then be written in product form:

$$\Psi_{\{\mu\}}=\prod_i \psi_{\mu_i}{}^i\,, \tag{2.2}$$

where $\{\mu\}$ denotes the set of quantum numbers μ_1, μ_2, $\cdots$ that specify the ψ's for the individual molecules. (Since the molecules are distinguishable by their sites, no symmetrization of the product is required.) Further, one treats the probability $P_\mu{}^i$ that molecule i is in state μ as independent of the states of the other molecules in the crystal; one thus assumes that $\Psi_{\{\mu\}}$ will describe the state of the crystal with probability

$$P_{\{\mu\}}=\prod_i P_{\mu_i}{}^i. \tag{2.3}$$

Since this approximation completely neglects the details of the orientational correlations of neighboring molecules, it is comparable to the Bragg-Williams approximation for order-disorder phenomena.

The (wave-mechanical) average energy associated with $\Psi_{\{\mu\}}$ is

$$\langle H\rangle=\sum_i w_{\mu_i}{}^i+\tfrac{1}{2}\sum_i\sum_j w_{\mu_i}{}^i{}_{\mu_j}{}^j\,, \tag{2.4}$$

where

$$w_\mu{}^i=\langle\psi_\mu{}^i|H_i|\psi_\mu{}^i\rangle \tag{2.5}$$

is the rotational energy of molecule μ in state i, and

$$w_{\mu\nu}{}^{ij}=\langle\psi_\mu{}^i\psi_\nu{}^j|V_{ij}|\psi_\mu{}^i\psi_\nu{}^j\rangle \tag{2.6}$$

is the average interaction energy of molecules i and j in states μ and ν, respectively. The internal energy of the crystal implied by the assumptions in Eqs. (2.2) and (2.3) is

$$\begin{aligned}U_a&=\sum_{\{\mu\}}\langle H\rangle_{\{\mu\}}P_{\{\mu\}}\\&=\sum_{i\mu}w_\mu{}^iP_\mu{}^i+\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu}w_{\mu\nu}{}^{ij}P_\mu{}^iP_\nu{}^j\,,\end{aligned} \tag{2.7}$$

and the entropy is

$$S_a=-k\sum_{i\mu}P_\mu{}^i\ln P_\mu{}^i. \tag{2.8}$$

Finally, the corresponding free energy

$$F_a=U_a-TS_a\,, \tag{2.9}$$

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which is a functional of the $\psi_\mu{}^i$ and $P_\mu{}^i$ appearing in those equations, can be shown to be an upper limit for the free energy F of the system described by Eq. (2.1), for all choices of the ψ's and P's. (This is the quantum analog of a well-known classical result,[18] and is similar to known results for interacting particles;[19,20] a proof appropriate to the present context is given in Appendix A). The P's and ψ's that minimize $F_a(T)$ give the best value of F and are, in this sense, the best choices for these quantities.

The condition that F_a shall be stationary to all variations of the P's consistent with the identity $\Sigma_\mu P_\mu{}^i=1$ yields

$$P_\mu{}^i=\frac{\exp(-\beta[w_\mu{}^i+\sum_{j\nu} w_{\mu\nu}{}^{ij}P_\nu{}^j])}{\sum_\mu \exp(-\beta[w_\mu{}^i+\sum_{j\nu} w_{\mu\nu}{}^{ij}P_\nu{}^j])}, \quad \text{all } i,\, \mu. \tag{2.10}$$

To write this in more compact form, we define

$$\epsilon_\mu{}^i=w_\mu{}^i+\sum_{j\nu} w_{\mu\nu}{}^{ij}P_\nu{}^j, \tag{2.11}$$

which is the average energy of molecule i in state μ in the average potential field

$$U^i=\sum_{j\nu} \langle\psi_\nu{}^j|\, V_{ij}\,|\psi_\nu{}^j\rangle P_\nu{}^j \tag{2.12}$$

of the other molecules in the crystal. Then

$$P_\mu{}^i=\exp(-\beta\epsilon_\mu{}^i)/\sum_\nu \exp(-\beta\epsilon_\nu{}^i), \quad (\text{all } i,\, \mu). \tag{2.13}$$

It is not evident how many sets of $P_\mu{}^i$ will satisfy Eq. (2.10); in any case, one must choose the set that minimizes F_a. Using Eq. (2.13) to rewrite Eq. (2.8), one finds

$$(F_a)_P=-\frac{1}{\beta}\sum_i \ln\sum_\mu \exp(-\beta\epsilon_\mu{}^i) -\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}P_\mu{}^iP_\nu{}^j. \tag{2.14}$$

The first term on the right is a sum of contributions from each molecule, each contribution being expressed in terms of a sum-over-states in which the energy associated with each state is the average energy of molecule i with the prescribed $\psi_\mu{}^i$ in the average field of the other molecules. The second term corrects for the fact that this method of computing F_a would otherwise include twice the average energy of the mutual interaction of the molecules.

The condition that F_a be stationary to variations of $\psi_\mu{}^i$, with the $P_\mu{}^i$ and T constant, is, in an obvious notation,

$$\begin{aligned}\delta_\mu{}^iF_a=\delta_\mu{}^iU_a&=[\delta_\mu{}^iw_\mu{}^i+\sum_{j\nu}(\delta_\mu{}^iw_{\mu\nu}{}^{ij})P_\nu{}^j]P_\mu{}^i\\ &=(\delta_\mu{}^i\epsilon_\mu{}^i)P_\mu{}^i=0, \quad \text{all } i,\, \mu.\end{aligned} \tag{2.15}$$

The condition that $\delta_\mu{}^i\epsilon_\mu{}^i=0$ for all variations of $\psi_\mu{}^i$ that maintain normalization is (by the most familiar variation principle of wave mechanics) in the present notation:

$$\{H_i+U^i\}\psi_\mu{}^i=\epsilon_\mu{}^i\psi_\mu{}^i. \tag{2.16}$$

If F_a is minimized with respect to all permitted variations of $\psi_\mu{}^i$ and $P_\mu{}^i$, Eqs. (2.12), (2.16), and (2.13) must be satisfied for all (i,μ) for which $P_\mu{}^i\neq 0$. This optimum choice of the P's and ψ's assures the self-consistency of the internal field picture: the average internal potential energies U^i will, through Eqs. (2.16) and (2.13), determine ψ's and P's which imply, through Eq. (2.12), that U^i is indeed the average potential energy of molecule i. This will be true even though one does not consider a complete set of one-molecule states $\psi_\mu{}^i$ (that is, takes some $P_\mu{}^i=0$), but it is to be expected (and is provable by means indicated in Appendix A) that F_a will become a better approximation to the correct F as one enlarges the set of states considered. The accuracy of the calculation is, of course, ultimately limited by the approximations characteristic of the internal field method.

The probabilities $P_\mu{}^i$, and hence the U^i and the $\psi_\mu{}^i$, depend on the temperature T under consideration. The parametric dependence of the ψ's on T is important, having the result that the states of the crystal that occur with high probability at the chosen T are given the best representation consistent with the simple product form; the associated energies are correspondingly well-adapted for the calculation of the free energy at that particular T.

In practical calculations one will usually need to express the $\psi_\mu{}^i$ as expansions in terms of an appropriately chosen fixed set of orthonormal functions ϕ_α:

$$\psi_\mu{}^i=\sum_\alpha \gamma_{\mu\alpha}{}^i\phi_\alpha{}^i. \tag{2.17}$$

Equation (2.16) then becomes a condition on the expansion coefficients γ:

$$\sum_\beta [\mathfrak{U}_{\alpha\beta}{}^i-\epsilon_\mu{}^i\delta_{\alpha\beta}]\gamma_{\mu\beta}{}^i=0, \quad \text{all } \alpha, \tag{2.18}$$

where

$$\mathfrak{U}_{\alpha\beta}{}^i=\langle\phi_\alpha{}^i|\, U^i\,|\phi_\beta{}^i\rangle. \tag{2.19}$$

By Eq. (2.12),

$$\mathfrak{U}_{\alpha\beta}{}^i=\sum_{j\nu}\sum_{\alpha'\beta'} P_\nu{}^j\gamma_{\nu\alpha'}{}^j\gamma_{\nu\beta'}{}^j\langle\alpha\alpha'|\, V_{ij}\,|\beta\beta'\rangle, \tag{2.20}$$

where the quantities

$$\langle\alpha\alpha'|\, V_{ij}\,|\beta\beta'\rangle=\langle\phi_\alpha{}^i\phi_{\alpha'}{}^i|\, V_{ij}\,|\phi_\beta{}^i\phi_{\beta'}{}^j\rangle \tag{2.21}$$

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can be computed once for all. The self-consistency condition then involves only constants: the values of the P's and γ's must yield, through Eq. (2.20), values of the matrix elements $\mathfrak{U}_{\alpha\beta}{}^i$ which in turn, through Eqs. (2.18) and (2.13), lead one back to these values of the P's and γ's.

In general, it is unnecessary, as well as impracticable, to start from the assumption that all functions $\psi_\mu{}^i$ may be different. In an ordered phase, the lattice will certainly be made up of a limited number of sublattices, such that all molecules on the same sublattice are translationally and orientationally equivalent. Given a sublattice structure, it is sufficient to consider an independent set of functions $\psi_\mu{}^i$ for each sublattice, and to minimize F_a or to satisfy the consistency relations by proper choice of these ψ's and the associated P's. Direct observation may indicate what sublattice structure needs to be considered. This paper deals with a case (fcc ortho-H_2) in which direct observation is lacking, but analogy to a comparable system (fcc N_2) suggests an appropriate sublattice structure; symmetry considerations then verify the self-consistency of the assumed $\psi_\mu{}^i$ and reduce the problem to the finding of self-consistent $P_\mu{}^i$. A later paper will deal with a case (hcp ortho-H_2) in which both observation and satisfying analogy are lacking, and one must make calculations for various choices of the sublattices, seeking that which permits calculation of the lowest F_a. Since such a calculation will reveal any equivalence of sublattices originally assumed to be distinct, an excessively fine division of the lattice into sublattices will do no harm, except as it increases the labor involved.

III. CONSIDERATIONS PRELIMINARY TO THE SELF-CONSISTENT TREATMENT OF ORTHO-H_2

We now develop some ideas needed in the treatment of solid ortho-H_2.

In a self-consistent procedure, one would like to represent the molecular states by exact solutions of Eq. (2.16). Since the orientational coupling of the molecules is weak, U^i constitutes a small perturbation on the free-rotator problem. If one neglects the higher-order terms of perturbation theory, one will neglect intermixture of free-rotator states with different J: one will treat J as a good quantum number, as is customary and as will be done here. On the other hand, it is important to use the correct zero-order solutions of the problem, and these, because of the degeneracy of the free-rotator states with the same J, are sensitive to (in fact, are completely determined by) the form of U^i. It is thus not possible to prescribe the form of the functions $\psi_\mu{}^i$ independently of consideration of the form of U^i; one can not say in advance that the states shall be described by the familiar functions $Y_{JM}(\mathbf{\Omega}_i)$, but only that each ψ is (approximately) some appropriate linear combination of Y's with the same J. Thus, for $J=1$,

$$\psi_\mu{}^i=\sum_{M=-1}^{+1} c_{\mu M}{}^i Y_{1M}\,,\quad (\mu=1,2,3)\,, \tag{3.1}$$

with c's to be determined by the condition of self-consistency. It is in this respect that the present theory differs from those of Bell and Fairbairn and of Danielian, who do not consider, and indeed do not satisfy, the conditions of self-consistency. Consideration of these conditions here leads to a different picture of the orientational ordering of the molecules, with a lower free energy and higher temperature of transition to the orientationally disordered phase.

The terms in the Hamiltonian that involve nuclear spin are negligibly small, and it is consequently possible to ignore nuclear spin throughout, except as it limits ortho-states to odd J. Further, at the low temperatures under consideration, kT is so small that one can ignore the possible excitation of molecules to states with $J=3$, $5, \cdots$. In consequence, for each i there will be considered just three functions of the form given by Eq. (3.1). Use of this limited manifold of functions will certainly be less serious as an approximation than is use of the internal field idea itself.

Since $w_\mu{}^i$ is the same for all functions considered here, the rotational energy plays no significant role in determining the forms of the ψ's and P's, and makes only an uninteresting constant contribution to U_a and F_a. It will henceforth be omitted from consideration; in consequence, $\epsilon_\mu{}^i$, U_a, and F_a will denote energies of orientational coupling only, to which the rotational energy may be added if desired. In particular,

$$\epsilon_\mu{}^i=\langle\psi_\mu{}^i|\,U^i|\psi_\mu{}^i\rangle\,. \tag{3.2}$$

Form of the Wave Functions

In this problem, it is useful to employ the real orthonormal basis functions

$$\begin{aligned}\Phi_1&=2^{-1/2}(-Y_{11}+Y_{1,-1})\,,\\ \Phi_2&=i2^{-1/2}(Y_{11}+Y_{1,-1})\,,\\ \Phi_3&=Y_{10}\,,\end{aligned} \tag{3.3}$$

where the Y's include the phase factors $(-1)^{(M+|M|)/2}$ introduced by Condon and Shortley. These functions have the same form, but different orientations in space: they are proportional to the x, y, and z components of a unit vector $u(\mathbf{\Omega})$ having the direction $\mathbf{\Omega}$. One can write

$$\Phi_\alpha(\mathbf{\Omega})=[3/4\pi]^{1/2}x_\alpha(\mathbf{\Omega})\,,\quad (\alpha=1,2,3)\,, \tag{3.4}$$

where $(x_1,x_2,x_3)=(x,y,z)$. Since H_i+U^i is real, one can without loss of generality restrict attention to real functions $\psi_\mu{}^i$ expanded in terms of the real Φ_α with real coefficients $\gamma_{\mu\alpha}{}^i$:

$$\psi_\mu{}^i=\sum_\alpha \gamma_{\mu\alpha}{}^i\Phi_\alpha\,. \tag{3.5}$$

Orthonormality of the $\psi_\mu{}^i$ implies

$$\sum_\alpha \gamma_{\mu\alpha}{}^i \gamma_{\nu\alpha}{}^i = \delta_{\mu\nu}. \tag{3.6}$$

The γ's thus have the character of direction cosines of three mutually orthogonal directions, the $X_\mu{}^i$ axes in directions $\mathbf{\Omega}_\mu{}^i$ fixed in the crystal. The components of $u(\mathbf{\Omega})$ along these axes are

$$X_\mu{}^i(\mathbf{\Omega}) = \sum_\alpha \gamma_{\mu\alpha}{}^i x_\alpha(\mathbf{\Omega}). \tag{3.7}$$

Thus

$$\psi_\mu{}^i(\mathbf{\Omega}) = [3/4\pi]^{3/2} X_\mu{}^i(\mathbf{\Omega}) = Y_{10}(\Theta_\mu{}^i), \tag{3.8}$$

where $\Theta_\mu{}^i$ is the polar angle between the $X_\mu{}^i$ axis and the symmetry axis of molecule i. All this is in consequence of the possibility of restricting attention to ψ's that are real surface harmonics of the first order. Orthogonality of the symmetry axes for given i follows from the orthogonality of the ψ's, but the orientation of these axes in space and the associated values of the $\epsilon_\mu{}^i$ are determined by U^i.

Intermolecular Coupling

The molecular interactions to be considered in the present paper are the electrostatic quadrupole-quadrupole interactions. These can be written[21] as

$$V_{ij} = \frac{20\pi}{9}(70\pi)^{1/2}\Gamma_{ij} \sum_{MN} C(224; MN) \times Y_{2M}(\mathbf{\Omega}_i) Y_{2N}(\mathbf{\Omega}_j) Y_{4,M+N}{}^*(\mathbf{\Omega}_{ij}). \tag{3.9}$$

Here $C(224;MN)$ is a Clebsch-Gordan coefficient (notation of Rose[22]) given in Table I; $\mathbf{\Omega}_{ij}$ specifies the orientation of the ij-intermolecular axis with respect to the fixed reference axes, and

$$\Gamma_{ij} = 6Q^2/25R_{ij}{}^5, \tag{3.10}$$

R_{ij} being the distance between molecules i and j and Q the average quadrupole moment of each molecule, defined by

$$Q = \tfrac{1}{2}\langle \sum_k e_k(2z_k'^2 - x_k'^2 - y_k'^2)\rangle. \tag{3.11}$$

Here the sum is over-all charged particles in the molecule, and the (x',y',z') coordinate system has its origin midway between the nuclei, with the z' axis along the internuclear axis.

Using the definitions of the Y's, one can rewrite the orientational distribution of molecule i in state k as

$$|\psi_\mu{}^i|^2 = |Y_{10}(\Theta_\mu{}^i)|^2 = \frac{1}{\sqrt{(5\pi)}} Y_{20}(\Theta_\mu{}^i) + \frac{1}{4\pi}. \tag{3.12}$$

TABLE I. $C(224; MN)$.

$N=$	-2	-1	0	1	2
$M=-2$	1	$(1/2)^{1/2}$	$(3/14)^{1/2}$	$(1/14)^{1/2}$	$(1/70)^{1/2}$
-1	$(1/2)^{1/2}$	$(4/7)^{1/2}$	$(3/7)^{1/2}$	$(8/35)^{1/2}$	$(1/14)^{1/2}$
0	$(3/14)^{1/2}$	$(3/7)^{1/2}$	$(18/35)^{1/2}$	$(3/7)^{1/2}$	$(3/14)^{1/2}$
1	$(1/14)^{1/2}$	$(8/35)^{1/2}$	$(3/7)^{1/2}$	$(4/7)^{1/2}$	$(1/2)^{1/2}$
2	$(1/70)^{1/2}$	$(1/14)^{1/2}$	$(3/14)^{1/2}$	$(1/2)^{1/2}$	1

By the spherical-harmonic addition theorem, one can write

$$Y_{20}(\Theta_\mu{}^i) = (4\pi/5)^{1/2} \sum_{M=-2}^{+2} Y_{2M}{}^*(\mathbf{\Omega}_i) Y_{2M}(\mathbf{\Omega}_\mu{}^i). \tag{3.13}$$

On use of Eqs. (3.9), (3.12), (3.13), and the orthonormality of the Y's, Eq. (2.6) yields

$$w_{\mu\nu}{}^{ij} = \frac{16\pi}{45}(70\pi)^{1/2}\Gamma_{ij} \sum_{MN} C(224; MN) \times Y_{2M}(\mathbf{\Omega}_\mu{}^i) Y_{2N}(\mathbf{\Omega}_\nu{}^j) Y_{4,M+N}{}^*(\mathbf{\Omega}_{ij}), \tag{3.14}$$

or

$$w_{\mu\nu}{}^{ij} = (4/25) V_{ij}(\mathbf{\Omega}_\mu{}^i, \mathbf{\Omega}_\nu{}^j). \tag{3.15}$$

Thus, for molecules having orientational distributions of optimal form, the average energy of quadrupole-quadrupole interaction differs only by a factor of 4/25 from what it would be if the quadrupoles had fixed orientations along the symmetry axes of the distributions.

It is an immediate consequence of Eq. (3.15) that the problems of minimizing $F_a(T=0)$ in classical and quantum-mechanical treatments *of the present model* are equivalent— provided only that $\epsilon_1{}^i < \epsilon_2{}^i$ for all i, and thus $P_1{}^i = 1$, $P_2{}^i = P_3{}^i = 0$. In either treatment, the entropy makes no contribution to $F_a(T=0)$: the problem is that of finding orientations $\mathbf{\Omega}_i$ or $\mathbf{\Omega}_1{}^i$ that minimize

$$U_{\text{class}}{}^a = \tfrac{1}{2}\sum_{ij} V_{ij}(\mathbf{\Omega}_i, \mathbf{\Omega}_j) \tag{3.16}$$

or

$$U_{\text{q.m.}}{}^a = \tfrac{1}{2}\sum_{ij} w_{11}{}^{ij}(\mathbf{\Omega}_1{}^j, \mathbf{\Omega}_1{}^j), \tag{3.17}$$

and the results differ only by the factor 4/25. In consequence, despite the great importance of quantum effects in solid hydrogen, one can get a useful indication of the sublattice structure in hydrogen at $T \cong 0$ from classical considerations, or from observations on more massive molecules. An application of this idea will be made in the next section.

The contribution to U^i of molecule j in state ν can be computed by the method used in deriving Eq. (3.14). One finds

$$\langle\psi_\nu{}^j|V_{ij}|\psi_\nu{}^j\rangle = \frac{8\pi}{9}(70\pi)^{1/2}\Gamma_{ij} \sum_{MN} C(224; MN) \times Y_{2M}(\mathbf{\Omega}_i) Y_{2N}(\mathbf{\Omega}_\nu{}^j) Y_{4,M+N}{}^*(\mathbf{\Omega}_{ij}). \tag{3.18}$$

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[21] H. P. Gush and J. Van Kranendonk, Can. J. Phys. **40**, 1461 (1962).

[22] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York), 1957.

The potential U^i, calculated by summing over j and ν with appropriate weights $P_\nu{}^j$ [Eq. (2.12)], is

$$U^i(\mathbf{\Omega}_i)=\sum_M \kappa_M{}^i Y_{2M}(\mathbf{\Omega}_i)\,, \tag{3.19}$$

where

$$\kappa_M{}^i=\frac{8\pi}{9}(70\pi)^{1/2}\sum_j\sum_\nu\sum_N P_\nu{}^j\Gamma_{ij}C(224;MN) \times Y_{2N}(\mathbf{\Omega}_\nu{}^j)Y_{4,M+N}{}^*(\mathbf{\Omega}_{ij})\,. \tag{3.20}$$

Equation (3.19) makes it evident that U^i will vanish when it is averaged over all $\mathbf{\Omega}_i$. Since it follows from Eqs. (3.4)–(3.6) that

$$\sum_\mu |\psi_\mu{}^i|^2=\sum_\alpha |\Phi_\alpha(\Omega)|^2=(3/4\pi)\,, \tag{3.21}$$

one sees that

$$\sum_\mu \langle\psi_\mu{}^i|U^i|\psi_\mu{}^i\rangle=\sum_\mu \epsilon_\mu{}^i=0\,. \tag{3.22}$$

From this it follows that one can satisfy the consistency conditions by taking $P_\mu{}^i=\frac{1}{3}$ for all (i,μ): Equations (2.12) and (3.21) show that this makes $U^i=0$ for all i; Eq. (3.2) then shows that all $\epsilon_\mu{}^i$ are the same; and Eq. (2.13), finally, shows that this leads to the values of $P_\mu{}^i$ originally assumed. This solution of the problem of self-consistency, for which $F_a(T)\equiv -NkT\ln 3$, represents the state of complete orientational disorder in the crystal, which is stable only at temperatures for which no solution with lower F exists.

Another useful conclusion can be drawn from the fact, evident from Eq. (3.19), that U^i is a quadratic form in the direction cosines γ_1, γ_2, γ_3 of the internuclear axis with respect to the (x_1,x_2,x_3) directions. By an appropriate rotation of coordinate axes one can introduce direction cosines γ_1', γ_2', γ_3' in terms of which U^9 is a sum of squares:

$$U^i=\sum_{\alpha=1}^{3}\lambda_\alpha(\gamma_\alpha')^2. \tag{3.23}$$

Because of the axial symmetry of the distributions $|\psi_\mu{}^i|^2$, $\langle\psi_\mu{}^i|U^i|\psi_\mu{}^i\rangle$ is stationary to the possible variations of $\psi_\mu{}^i$, which are simply reorientations of the axis of symmetry, if and only if the axis of symmetry coincides with one of the x' axes; thus, the $X_\alpha{}^i$ axis is identical with the x_α' axis. The corresponding stationary value of the molecular energy is, by Eqs. (3.8) and (3.23),

$$\begin{aligned}\epsilon_\alpha{}^i&=\frac{3}{4\pi}\int d\Omega(\gamma_\alpha')^2\sum_\beta\lambda_\beta(\gamma_\beta')^2\\&=\tfrac{3}{5}\lambda_\alpha+\tfrac{1}{5}\sum_{\beta\neq\alpha}\lambda_\beta\,.\end{aligned} \tag{3.24}$$

Since

$$\sum_\alpha \epsilon_\alpha{}^i=\sum_\alpha\lambda_\alpha=0\,, \tag{3.25}$$

one has

$$\epsilon_\alpha{}^i=\tfrac{2}{5}\lambda_\alpha\,. \tag{3.26}$$

The problem of determining the functions $\psi_\mu{}^i$ and energies $\epsilon_\mu{}^i$ is thus equivalent to the problem of reducing U^i to a sum of squares.

To examine the self-consistency of a set of direction cosines $\gamma_\alpha{}^i$, one must calculate the matrix elements $\mathfrak{U}_{\alpha\beta}{}^i$ [Eq. (2.19)]. This is conveniently done by introduction of the constants

$$\mathfrak{Y}_{\alpha\beta}{}^M=\langle\Phi_\alpha|Y_{2M}|\Phi_\beta\rangle\,, \tag{3.27}$$

which are easily computed. Then

$$\mathfrak{U}_{\alpha\beta}{}^i=\sum_M \kappa_M{}^i\mathfrak{Y}_{\alpha\beta}{}^M\,. \tag{3.28}$$

Using Eqs. (3.13), (3.12), and (3.5), one finds

$$Y_{2N}(\mathbf{\Omega}_\nu{}^j)=\tfrac{5}{2}\sum_{\alpha'\beta'}\gamma_{\nu\alpha'}{}^j\gamma_{\nu\beta'}{}^j\mathfrak{Y}_{\alpha'\beta'}{}^N\,. \tag{3.29}$$

One can thus express κ_M and $\mathfrak{U}_{\alpha\beta}{}^i$ in terms of the γ's, rather than the angles $\mathbf{\Omega}_\mu{}^i$. The resulting multiple sum looks cumbersome, but can sometimes be drastically simplified. The quantities

$$L_{Nl\nu}=P_\nu{}^jY_{2N}(\mathbf{\Omega}_\nu{}^j) \tag{3.30}$$

will be the same for all molecules j on a given sublattice l. One can write

$$\mathfrak{U}_{\alpha\beta}{}^i=\sum_M\mathfrak{Y}_{\alpha\beta}{}^M\frac{8\pi}{9}(70\pi)^{1/2}\sum_N C(224;MN)\sum_{l\nu}L_{Nl\nu} \times\sum_{j(l)}\Gamma_{ij}Y_{4,M+N}{}^*(\mathbf{\Omega}_{ij})\,. \tag{3.31}$$

It is advantageous to start the calculation by summing over $j(l)$, the molecules j on sublattice l. If the reference axes are well chosen with respect to the sublattice structure, the result may vanish except for a limited set of $M+N$. If U^i is symmetric about the chosen z axis, only $\kappa_0{}^i\neq 0$; only $M=0$ will contribute to the sum. In any case, interest centers on two summations, over sublattices l and over states ν characteristic of molecules on those sublattices.

We now turn to a case in which self-consistency of a set of γ's can be proved with relative ease.

IV. ORTHO-H_2 WITH FCC MOLECULAR LATTICE

If solid ortho-H_2 has an fcc molecular lattice at very low T, it is comparable to the low temperature α phase of N_2, in which the molecular lattice is fcc and the orientational couplings of the molecules have the char-

Table II. Orientations of Molecules in α-N_2.

Sublattice	Coordinates with respect to cube corner	Direction cosines γ of molecules on sublattice	Direction cosines γ' of molecules on sublattice	Directions from molecule on sublattice 4 to neighbors on other sublattices (signs coherent)
1	$a/2,a/2,0$	$3^{-1/2}(-1,1,1)$	$-\sqrt{(\frac{2}{3})},-\sqrt{(2/9)},\frac{1}{3}$	$\theta'=\pi/2,\varphi'=0,\pi$ $\theta'=\cos^{-1}(\pm\sqrt{\frac{2}{3}}),\varphi'=\pm\pi/2$
2	$0,a/2,a/2$	$3^{-1/2}(1,-1,1)$	$\sqrt{(\frac{2}{3})},-\sqrt{(2/9)},\frac{1}{3}$	$\theta'=\pi/2,\varphi'=2\pi/3,5\pi/3$ $\theta'=\cos^{-1}(\pm\sqrt{\frac{2}{3}}),\varphi'=2\pi/3\pm\pi/2$
3	$a/2,0,a/2$	$3^{-1/2}(1,1,-1)$	$0,\ \sqrt{(8/9)},\frac{1}{3}$	$\theta'=\pi/2,\varphi'=\pi/3,4\pi/3$ $\theta'=\cos^{-1}(\pm\sqrt{\frac{2}{3}}),\varphi'=4\pi/3\pm\pi/2$
4	$0,0,0$	$3^{-1/2}(1,1,1)$	$0,\ 0,\ 1$	

acter of a quadrupole-quadrupole coupling.[23,24] It is observed[25] that the α-N_2 molecular lattice can be divided into four sublattices, such that all molecules on a sublattice are orientationally and translationally equivalent. The lattice can be considered to be made up of cubes with edge $a/2$, each cube having one corner occupied by one molecule from each sublattice. The equilibrium orientations of the molecules, shown in Fig. 1, tend to maximize the separations of nuclei in adjacent molecules, each molecular axis being directed toward unoccupied corners of two adjacent cubes. In the equilibrium configuration of the crystal, each molecular axis is directed along a threefold axis of symmetry of the system, with direction cosines γ given in Table II. (Because of the molecular symmetry, the signs of any set of γ's can be reversed.) The sublattices of oriented molecules are physically equivalent, and can be interchanged by translations and rotations of the crystal.

Ortho-H_2 and N_2 differ markedly in the importance of quantum effects, which are so much greater in the case of ortho-H_2 that a quantum-mechanical calculation can follow lines quite different from and much simpler than those followed by Kohin in the latter case. However, in accordance with the argument from Eq. (3.15), one can expect the axial directions $\Omega_1{}^j$ of the orientational distributions of ortho-H_2 molecules at $T=0$ to be the same as the equilibrium directions of the molecules in α-N_2. The same conclusion is supported by the classical calculations of Nagai and Nakamura[24] and of Felsteiner[26] on the equilibrium orientation of electrostatic quadrupoles on an fcc lattice. As an extension of this, one can test the idea that, *at all T*, each molecular potential $U^{(i)}$ and each molecular charge distribution has axial symmetry about an axis in the direction indicated in Fig. 1. This assumption establishes an internal-field description of ortho-H_2 that can be tested for self-consistency, and from which one can derive molecular energy levels and the free energy of the crystal in this particular state of orientational order.

Figure 2 presents the same array in a way that brings out the existence of hexagonal close packed planes of molecules perpendicular to the [1,1,1] direction. A central molecule on sublattice 4 is shown, with its six neighbors in the same plane and its three neighbors in the hexagonal planes above and below. This figure also shows another set of axes of which use will be made: the z' axis lies in the [1,1,1] direction, perpendicular to the hexagonal planes, while the x' axis, in the [1,−1,0] direction, passes through a neighbor molecule on sublattice 1. Polar and azimuthal angles $\Omega'=(\theta',\varphi')$ are defined with respect to these primed axes in the usual way. Table II gives the direction cosines γ' for the molecular axes with respect to the primed axes, and also the angles θ_{ij}', φ_{ij}' for the directions from the central molecule to each of its neighbors.

It will first be shown that the assumption concerning the axial symmetries of the molecular potentials U^i is self-consistent: existence of such U's will imply the existence in the crystal of a total charge distribution that will, in turn, produce such U's. The assumption that U^4 has axial symmetry about the z' direction

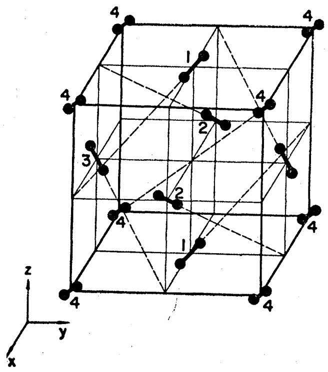

Fig. 1. Self-consistent orientations of H_2 molecules on an fcc lattice. The numbers show the sublattice to which each molecule belongs. Space group *Pa*3.

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[23] B. C. Kohin, J. Chem. Phys. **33**, 882 (1960), finds that R^{-6} and R^{-16} dispersion and overlap interactions of neighboring molecules would produce orientational couplings of the same order of magnitude as the electrostatic quadrupole coupling, and would make contributions of similar form to the effective internal field.

[24] O. Nagai and T. Nakamura, Progr. Theoret. Phys. (Kyoto) **24**, 432 (1960).

[25] The statements in this paragraph are based on the description of the α-phase structure given by R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, New York, 1963), 2nd ed., Vol. 1, p. 29. and used by Kohin. It has been found by T. H. Jordan, H. W. Smith, W. E. Streib and W. N. Lipscomb, J. Chem. Phys. **41**, 756 (1964) that the N_2 molecules are displaced from the centrosymmetric positions, parallel to their axes, with the result that the group is changed from *Pa*3 to $P2_13$, but the molecular orientations described here remain unchanged.

[26] J. Felsteiner, Phys. Rev. Letters **15**, 1025 (1965).

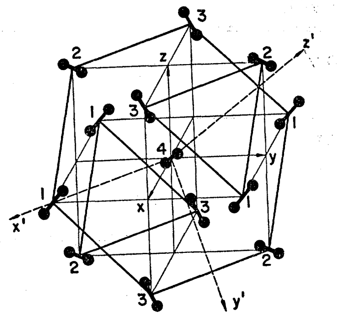

FIG. 2. Self-consistent orientations of H_2 molecules on an fcc. lattice. Molecular centers connected by solid lines lie in the same hexagonal plane.

requires

$$U^4=\kappa_0 Y_{20}(\mathbf{\Omega}'). \tag{4.1}$$

It follows from the discussion of Eq. (3.23) that one of the ψ^4 has the same axis of symmetry, and that the two orthogonal functions will correspond to a twofold degenerate level, and will have symmetry axes that are not uniquely defined. Designating the nondegenerate state as state 1, we write

$$\psi_1{}^4=Y_{10}(\mathbf{\Omega}'), \tag{4.2}$$

$$P_2{}^4=P_3{}^4=\tfrac{1}{2}(1-P_1{}^4). \tag{4.3}$$

Using Eqs. (4.3), (3.21), and (3.12), one can write the orientational probability distribution as

$$\begin{aligned}\sum_\mu P_\mu{}^4|\psi_\mu{}^4|^2&=\frac{3}{4\pi}P_3{}^4+(P_1{}^4-P_3{}^4)\,|Y_{10}(\mathbf{\Omega}')|^2\\ &=\frac{1}{4\pi}+(P_1{}^4-P_3{}^4)(1/5\pi)^{1/2}Y_{20}(\mathbf{\Omega}'),\end{aligned} \tag{4.4}$$

which has the same symmetry axis as U^4. Results for the other sublattices will be identical, except for the directions of the axes of the orientational distributions, which will be arranged as in Fig. 1. It is easily seen that a rotation through 120° about the z' axis leaves sublattice 4 unchanged, and permutes cyclically sublattices 1, 2, 3 and the corresponding orientational distributions. It follows that the average charge distribution of the whole crystal has a 3-fold axis of symmetry in the z' direction, and that the same is true of U^4. However, a potential energy of the general form given in Eq. (3.19) has a threefold axis of symmetry only if it has full axial symmetry; thus U^4 has the symmetry properties originally assumed. In the same way, this can be seen to be true of U^1, U^2, and U^3—which completes the demonstration of self-consistency.

To proceed farther, to derive the P's, U_a, and F_a, it is necessary to carry out more detailed calculations that lead to self-consistent values of the probabilities P_1 and P_3, which must be the same for every sublattice. Instead of deriving the orientating potential energy U^4 for a molecule from the orientational distribution of its neighbors, we shall proceed directly to the calculation of its matrix elements $\mathfrak{U}_{\alpha\beta}{}^4$ by use of Eq. (3.31). For this purpose it is convenient to describe molecular couplings and the internal field in terms of the angles $\mathbf{\Omega}'$, while expressing the ψ's in terms of functions Φ and direction cosines γ related to the cubic axes of the crystal. Equation (3.18) remains valid in terms of the $\mathbf{\Omega}'$, and Eqs. (3.28)–(3.31) remain valid if one understands that in the definition of $\mathfrak{Y}_{\alpha\beta}{}^M$ [Eq. (3.27)] one has $Y_{2M}=Y_{2M}(\mathbf{\Omega}')$. The only property of these $\mathfrak{Y}$'s that we shall require is easily derived by direct integration:

$$\mathfrak{Y}_{\alpha\beta}{}^0=(1-\delta_{\alpha\beta})/(20\pi)^{1/2}. \tag{4.5}$$

Because of the axial symmetry of U^4, with this choice of angles one has $\kappa_M{}^4=0$ except for $M=0$, and only $M=0$ contributes to Eq. (3.31) for $\mathfrak{U}_{\alpha\beta}{}^4$. Since the molecules on sublattices 1, 2, and 3 can be carried into each other by rotations about the threefold [1,1,1] axis, these three sublattices will make equal contributions to U^4 and to $\mathfrak{U}_{\alpha\beta}{}^4$; the sum over j in Eq. (3.31) can then be restricted to molecules on sublattice 1, if a compensating factor 3 is introduced. Let $L_{Nl\nu}$ in Eq. (3.31) be expressed in terms of the γ's, using Eqs. (3.30) and (3.29). Omitting the unnecessary superscripts on the P's, one can then write the sum over ν as

$$\begin{aligned}\sum_\nu P_\nu{}^1\gamma_{\nu\alpha'}{}^1\gamma_{\nu\beta'}{}^1=(P_1-P_3)\gamma_{1\alpha'}{}^1\gamma_{1\beta'}{}^1\\ +P_3\sum_\nu \gamma_{\nu\alpha'}{}^1\gamma_{\nu\beta'}{}^1.\end{aligned} \tag{4.6}$$

From the properties of the direction cosines, it follows that the last sum is $\delta_{\alpha'\beta'}$. When the sum over α' and β' is carried out, this term contributes

$$\sum_{\alpha'}\sum_{\beta'}\delta_{\alpha'\beta'}\mathfrak{Y}_{\alpha'\beta'}{}^N=0,\quad \text{all } N, \tag{4.7}$$

as one sees with the aid of Eq. (4.5). One thus finds

$$\mathfrak{U}_{\alpha\beta}{}^4=\kappa_0\mathfrak{Y}_{\alpha\beta}{}^0=(1-\delta_{\alpha\beta})\kappa_0/(20\pi)^{1/2}, \tag{4.8}$$

with

$$\begin{aligned}\kappa_0=\kappa_0{}^4=(P_1-P_3)(20\pi/3)(70\pi)^{1/2}\\ \times\sum_{N=-2}^{+2}\ \sum_{\substack{j\text{ on}\\ \text{sublattice 1}}} G_N\Gamma_{4j}Y_{4N}{}^*(\mathbf{\Omega}_{4j}).\end{aligned} \tag{4.9}$$

Here Γ_{4j} and $\mathbf{\Omega}_{4j}$ denote Γ_{ij} and $\mathbf{\Omega}_{ij}$ where i is the central molecule on sublattice 4. The constants

$$\begin{aligned}G_N=C(224;0N)\sum_{\alpha\beta}\gamma_{1\alpha}{}^1\gamma_{1\beta}{}^1\mathfrak{Y}_{\alpha\beta}{}^N\\ =\tfrac{2}{5}C(224;0N)Y_{2N}(\mathbf{\Omega}_1{}^1)\end{aligned} \tag{4.10}$$

are easily found by use of Table I and II:

$$\begin{aligned}G_0&=-(2/175\pi)^{1/2}.\\ G_{\pm1}&=(\pm1+i/\surd3)/(105\pi)^{1/2},\\ G_{\pm2}&=(1/\surd3\pm i)/(105\pi)^{1/2}.\end{aligned} \tag{4.11}$$

Equations (2.18) will then determine the direction cosines $\gamma_{\nu\alpha}{}^4$. Consistency of these equations requires

$$\begin{vmatrix} -\lambda & \kappa_0 & \kappa_0 \\ \kappa_0 & -\lambda & \kappa_0 \\ \kappa_0 & \kappa_0 & -\lambda \end{vmatrix} = 0, \tag{4.12}$$

whence

$$\lambda = \sqrt{(20\pi)}\epsilon^4 = 2\kappa_0, -\kappa_0(\text{twice}). \tag{4.13}$$

Solution of Eqs. (2.18) with the nondegenerate values of ϵ^4 yields the direction cosines $\gamma_{1x}{}^4 = \gamma_{1y}{}^4 = \gamma_{1z}{}^4 = 1/\sqrt{3}$, in agreement with Eq. (4.2). This result, which follows from symmetry, is independent of T, even though the matrix elements of the orienting potential depend on the P's and thus on T.

For numerical calculations, we take $R = 3.75$ Å, $Q = 0.110\times10^{-16}$ electron cm^2 (see Ref. 27). If attention is restricted to nearest neighbor interactions, one requires only a single Γ_{ij}:

$$\Gamma = 0.903\times10^{-16}\ \text{erg} = k\times0.654\text{°K}, \tag{4.14}$$

where k is Boltzmann's constant. The sum over molecules in Eq. (4.9) is then easily evaluated; one finds

$$\epsilon_1 = -(38/3)\Gamma(P_1 - P_3) = -(38/3)\Gamma(\tfrac{3}{2}P_1 - \tfrac{1}{2}), \tag{4.15}$$

which must, by symmetry, be valid for all lattices. The result of including interactions of more widely separated molecules can be deduced from the calculations of Felsteiner,[26] who arrived at the order here considered while treating the classical problem of interacting quadrupoles on a fcc lattice at $T = 0$. By summing over all pairs of molecules within a radius of 300 Å of each other, he arrived at an orientational energy per molecule equal to $-kT$ at 28.9°K. Equation (3.15) shows that a corresponding treatment in the quantum-mechanical approximation would yield an orientational energy less by a factor 4/25. This will agree with the orientational energy implied by Eq. (4.15) for $T = 0$, $P_1 = 1$, which is

$$\tfrac{1}{2}\epsilon_1(T=0) = -19\Gamma/3, \tag{4.16}$$

is one uses a somewhat larger effective Γ,

$$\Gamma = k\times0.730\text{°K}. \tag{4.17}$$

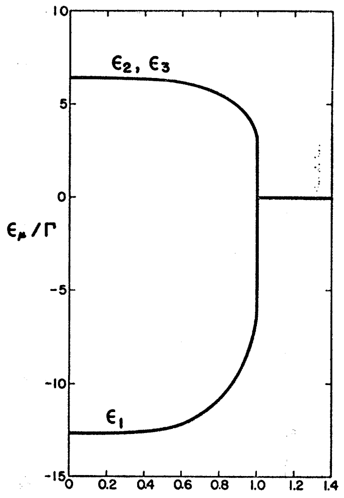

FIG. 3. Molecular energy levels in fcc. hydrogen. The upper level is doubly degenerate.

Summation over the other molecules in the lattice actually increases the multiplying constant, rather than Γ, but it will be convenient to absorb the increase into Γ.

The calculations made in this paper apply equally to solid para-D_2, except for modification of the value of Γ [Eq. (3.10)], which arises primarily from the difference in the lattice spacing. The change should be proportional to $1/R^5$, or to $V^{-5/2}$, where ν is the volume per mole. This increases Γ by a factor of 1.257, to

$$\Gamma_{D_2} = k\times0.918\text{°K}, \tag{4.18}$$

for the case of a summation over all molecules in the lattice.

One can determine self-consistent values of the P's and ϵ's by solving Eq. (4.15) simultaneously with Eq. (2.13), remembering Eq. (3.22). Alternatively, one can find the self-consistent P's by choosing them to minimize the free energy per molecule [Eq. (2.9)]

$$F_{\text{var}}/N = \tfrac{1}{2}\sum_\mu P_\mu\epsilon_\mu + kT\sum_\mu P_\mu \ln P_\mu. \tag{4.19}$$

In terms of

$$\rho = 1 - P_1, \tag{4.20}$$

this becomes

$$F_{\text{var}}/\text{N} = -(19/3)\Gamma[1 - 3\rho + (9/4)\rho^2] + kT\{\rho\ln\rho + (1-\rho)\ln(1-\rho) - \rho\ln2\}. \tag{4.21}$$

This problem is of the form considered by Strässler and

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[27] *Note added in proof.* This value for Q has been commonly used for many years in discussions of solid hydrogen. It appears to have been derived by combining the value of the electronic quadrupole moment experimentally determined by N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1952), with the nuclear contribution to the quadrupole moment computed as though the nuclei were fixed at their equilibrium separation. The electronic contribution represents an average over nuclear separations, and it is desirable to compute the nuclear contribution in the same way. To derive better values for Q, one may use the theoretical values for the one-electron distribution given by L. Wolniewicz, J. Chem. Phys. **45**, 515 (1966):

$$\begin{aligned}\langle 3z'^2 - r^2\rangle &= 0.1628\times10^{-16}\ \text{cm}^2 \text{ for } H_2,\\ &= 0.1578\times10^{-16}\ \text{cm}^2 \text{ for } D_2.\end{aligned}$$

Wolniewicz also gives for the nuclear separation in the case of H_2

$$\tfrac{1}{2}\langle R^2\rangle = 0.2976\times10^{-16}\ \text{cm}^2.$$

Using the estimate of N. Ramsey, Phys. Rev. **87**, 1077 (1952), that this quantity is smaller in D_2 by the factor 0.976, one obtains

$$\begin{aligned}Q &= 0.1348\times10^{-16}\ \text{electron cm}^2 \text{ for } H_2,\\ &= 0.1327\times10^{-16}\ \text{electron cm}^2 \text{ for } D_2.\end{aligned}$$

Use of these values would raise the values of Γ and T_c quoted in the text by 50% in the case of H_2 and 45% in the case of D_2.

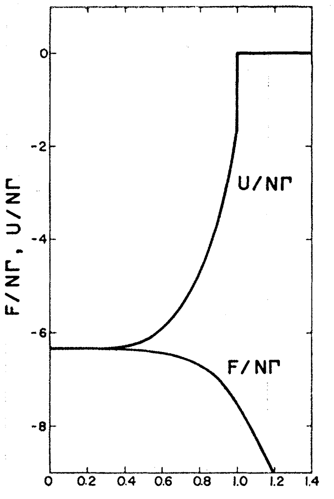

FIG. 4. Internal energy U and free energy F, per molecule, in fcc. hydrogen.

Kittel.[28] Their arguments lead easily to the conclusion that at $T=0$ one has an ordered phase with $P_1=1$. As T increases, P_1 falls, reaching the value $\frac{2}{3}$ at a temperature T_c defined by

$$kT_c = 19\Gamma/4\ln 2. \tag{4.22}$$

At this point, a first-order transition occurs as P_1, P_2, P_3 abruptly assume the common value $\frac{1}{3}$ characteristic of the orientationally disordered phase, which is stable at all higher T.

The computed value of T_c is 4.48°K for ortho-H_2 if one sums only over the interactions of next neighbors, and 5.07°K if one uses Felsteiner's more complete summation. In the case of para-D_2 with the complete summation, one obtains $T_c=6.37$°K.

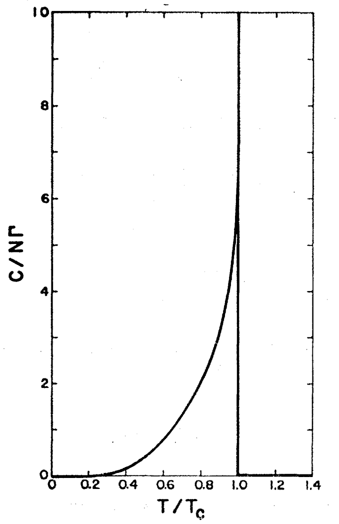

FIG. 5. Thermal capacity per molecule in fcc. hydrogen.

The remaining results of the calculation are presented in a form that will be unchanged by modification of the effective Γ. Figures 3, 4, and 5 present, respectively, ϵ_μ/Γ against T/T_c, $U/N\Gamma$ and $F/N\Gamma$ against T/T_c, and $C/N\Gamma$ against T/T_c.

V. CONCLUSION

It does not appear that neglect of admixture of functions with higher J into the unperturbed functions with $J=1$ is a significant source of error in this work. For a potential of the form given by Eq. (4.1), the Schrödinger equation for the rotational motion of the hydrogen molecules can be solved exactly.[23] The problem reduces to solving an oblate spheroidal wave equation, and the level perturbations thus calculated differ, in the case of H_2, by less than one percent from the ϵ's computed here. The difference will be greater in the case of D_2, for which the separation of rotational levels is roughly half as great, but the approximation is still a good one.

The transition temperatures computed by assuming quadrupole-quadrupole coupling of all pairs of molecules, with the larger value of Q quoted in Ref. 27, are higher than the observed (extrapolated) transition temperatures in ortho-H_2 and para-D_2 by more than a factor of 2. It is characteristic of the internal field approximation that it yields too high a transition temperature, and the results of this calculation are also affected by other approximations, such as neglect of lattice vibrations and of other types of orientational coupling. The discrepancy is probably primarily due, however, to the fact that a fixed fcc lattice is assumed here, whereas the actual transition involves a change to a hcp lattice. To discuss the occurrence of such a transition it is necessary to consider the properties of hcp solid hydrogen. This will be the subject of a companion paper.

ACKNOWLEDGMENTS

One of us (H.M.J.) wishes to express appreciation for the hospitality of the quantum theory group of the University of Florida during the period in which the paper was written.

APPENDIX: PROOF THAT $F_a \geq F$

The proof that $F \leq F_a$, as defined by Eqs. (2.5) to (2.9) and computed with any orthonormal functions $\psi_\mu{}^i$ and probabilities $P_\mu{}^i$, will follow the pattern used by Girardeau.[20] The formalism can be simplified because of the distinguishability of the rotators.

To begin, we assume that the $\psi_\mu{}^i$ form a complete orthonormal set for each i. One can then define the

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[28] S. Strässler and C. Kittel, Phys. Rev. **139**, A758 (1965).

operators $A_{\nu\mu}{}^{i}$ by

$$A_{\nu\mu}{}^{i}\psi_{\rho}{}^{i}=\psi_{\nu}{}^{i}\delta_{\mu\rho}. \tag{A1}$$

Acting on any function of the crystal coordinates, expanded in terms of the complete orthonormal set of functions $\Psi_{\{\mu\}}$, this will act only on the factors depending on $\mathbf{\Omega}_i$, changing the quantum number μ to ν, where μ occurs, and otherwise deleting the term. Let

$$w_{\nu\lambda}{}^{i}=\langle\psi_{\nu}|H_i|\psi_{\lambda}\rangle, \tag{A2}$$

$$w_{\nu\lambda;\nu'\lambda'}{}^{ii'}=\langle\psi_{\nu}{}^{i}\psi_{\nu'}{}^{i'}|V_{ij}|\psi_{\lambda}{}^{i}\psi_{\lambda'}{}^{i'}\rangle. \tag{A3}$$

Then one can write

$$H=\sum_{i\nu\lambda} w_{\nu\lambda}{}^{i}A_{\nu\lambda}{}^{i}+\tfrac{1}{2}\sum_{i\nu\lambda}\sum_{i'\nu'\lambda'} w_{\nu\lambda;\nu'\lambda'}{}^{ii'}A_{\nu\lambda}{}^{i}A_{\nu'\lambda'}{}^{i'}. \tag{A4}$$

It follows from Peierls's inequality[29] that

$$\begin{aligned} Z=&\sum_{\{\mu\}}\langle\Psi_{\{\mu\}}|e^{-\beta H}|\Psi_{\{\mu\}}\rangle\\ &\geqslant\sum_{\{\mu\}}\exp[-\beta\langle\Psi_{\{\mu\}}|H|\Psi_{\{\mu\}}\rangle]=Z'. \end{aligned} \tag{A5}$$

Only the diagonal terms in H (those with $\nu=\lambda$, $\nu'=\lambda'$) contribute to the latter sum. These make up the operator

$$H_{\text{diag}}=\sum_{i\nu} w_{\nu}{}^{i}A_{\nu\nu}{}^{i}+\tfrac{1}{2}\sum_{i\nu}\sum_{i'\nu'} w_{\nu\nu'}{}^{ii'}A_{\nu\nu}{}^{i}A_{\nu'\nu'}{}^{i'}, \tag{A6}$$

where the w's are the quantities defined in Eqs. (2.5) and (2.6). The $\Psi_{\{\mu\}}$ form a complete set of eigenfunctions of H_{diag}. It follows that

$$Z'=\sum_{\{\mu\}}\langle\Psi_{\{\mu\}}|\exp(-\beta H_{\text{diag}})|\Psi_{\{\mu\}}\rangle \tag{A7}$$

is the exact partition function for a system with Hamiltonian H_{diag}.

We now write

$$H_{\text{diag}}=H_0+H_1, \tag{A8}$$

where

$$H_0=\sum_{i\mu}\epsilon_{\mu}{}^{i}A_{\mu\mu}{}^{i}-\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}P_{\mu}{}^{i}P_{\nu}{}^{j}, \tag{A9}$$

$$H_1=\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}(A_{\mu\mu}{}^{i}-P_{\mu}{}^{i})(A_{\nu\nu}{}^{j}-P_{\nu}{}^{j}), \tag{A10}$$

with

$$\epsilon_{\mu}{}^{i}=w_{\mu}{}^{i}+\sum_{j\nu} w_{\mu\nu}{}^{ij}P_{\nu}{}^{j}, \tag{A11}$$

the P's being arbitrary constants. Following a method due to Bogoliubov (see Girardeau, footnote 13), one can then show that, for any choice of the P's,

$$F=-\frac{1}{\beta}\ln Z\leqslant-\frac{1}{\beta}\ln Z'\leqslant F_{\text{var}}, \tag{A12}$$

where

$$F_{\text{var}}=-\frac{1}{\beta}\ln\operatorname{Tr}\{\exp(-\beta H_0)\}+\frac{\operatorname{Tr}\{H_1\exp(-\beta H_0)\}}{\operatorname{Tr}\{\exp(-\beta H_0)\}}. \tag{A13}$$

The traces in these equations are easily evaluated in terms of the basis $\Psi_{\{\mu\}}$, since all $\Psi_{\{\mu\}}$ are eigenfunctions of both H_0 and H_1. One finds

$$\begin{aligned} \operatorname{Tr}\{\exp(-\beta H_0)\}=&\sum_{\{\mu_i\}}\exp\Big(-\beta\Big[\sum_{i\mu}\epsilon_{\mu}{}^{i}\delta_{\mu\mu_i}\\ &\qquad-\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}P_{\mu}{}^{i}P_{\nu}{}^{j}\Big]\Big)\\ =&\prod_{i}\Big\{\sum_{\mu_i}\exp(-\beta\epsilon_{\mu_i}{}^{i})\Big\}\\ &\times\exp\Big(-\beta\Big[-\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}P_{\mu}{}^{i}P_{\nu}{}^{j}\Big]\Big). \end{aligned} \tag{A14}$$

Similar manipulations show that

$$\begin{aligned} \frac{\operatorname{Tr}\{A_{\mu\mu}{}^{i}\exp(-\beta H_0)\}}{\operatorname{Tr}\{\exp(-\beta H_0)\}}&=\frac{\operatorname{Tr}\{\delta_{\mu\mu_i}\exp(-\beta H_0)\}}{\operatorname{Tr}\{\exp(-\beta H_0)\}}\\ &=\frac{\exp(-\beta\epsilon_{\mu}{}^{i})}{\sum_{\mu}\exp(-\beta\epsilon_{\mu}{}^{i})}\equiv N_{\mu}{}^{i}, \end{aligned} \tag{A15}$$

$$\frac{\operatorname{Tr}\{A_{\mu\mu}{}^{i}A_{\nu\nu}{}^{j}\exp(-\beta H_0)\}}{\operatorname{Tr}\{\exp(-\beta H_0)\}}=N_{\mu}{}^{i}N_{\nu}{}^{j}. \tag{A16}$$

One thus finds

$$\begin{aligned} F_{\text{var}}=&-\frac{1}{\beta}\sum_{i}\ln\Big\{\sum_{\mu}\exp(-\beta\epsilon_{\mu}{}^{i})\Big\}-\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}P_{\mu}{}^{i}P_{\nu}{}^{j}\\ &+\tfrac{1}{2}\sum_{i\mu}\sum_{j\nu} w_{\mu\nu}{}^{ij}(N_{\mu}{}^{i}-P_{\mu}{}^{i})(N_{\nu}{}^{j}-P_{\nu}{}^{j}). \end{aligned} \tag{A17}$$

Remembering the dependence of the ϵ's and N's on the P's, one finds

$$\begin{aligned} \frac{\partial F_{\text{var}}}{\partial P_{\rho}{}^{k}}=&\sum_{i\mu} N_{\mu}{}^{i}w_{\mu\rho}{}^{ik}-\sum_{i\mu} w_{\mu\rho}{}^{ik}P_{\mu}{}^{i}\\ &+\sum_{i\mu}\sum_{j\mu} w_{\mu\nu}{}^{ij}(N_{\mu}{}^{i}-P_{\mu}{}^{i})\frac{\partial}{\partial P_{\rho}{}^{\mu}}(N_{\nu}{}^{j}-P_{\nu}{}^{j}). \end{aligned} \tag{A18}$$

It is evident that F_{var} will be stationary to variation of all the P's if $P_{\mu}{}^{i}=N_{\mu}{}^{i}$—that is, if the P's satisfy an equation having the form of Eq. (2.13). The lowest stationary value of F_{var}, say $(F_{\text{var}})_P$, will then be given by the first two terms of Eq. (A17), and will have the form of Eq. (2.14).

The problems of optimizing F_{var} and F_a by varying the constants $P_{\mu}{}^{i}$ are thus the same, and the results are formally the same. The significant difference here is

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[29] R. E. Peierls, Phys. Rev. 54, 918 (1938).

that in discussing F_{var} it has been assumed that the $\psi_\mu{}^i$ and $\Psi_{\{\mu\}}$ form complete orthonormal sets, whereas in the case of F_a it is desired to permit the sets $\{\psi_\mu{}^i\}$ to be incomplete. Such an incomplete set can be constructed by omitting from a complete set certain functions $\psi_\rho{}^i$. Now let F_{var} be computed using for the P's nonoptimal values: zero for the P's corresponding to the omitted ψ's, and for the other P's solutions of Eq. (2.10) as constructed with the incomplete set of ψ's. Use of these nonoptimal values yields $(F_a)_P$, but certainly increases the value of F_{var}. Finally, use of nonoptimal values of the P's in computing F_a yields

$$F_a \geqslant (F_a)_P \geqslant (F_{\text{var}})_P \geqslant F.$$

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Dependence of the Diffusion Coefficient on the Fermi Level: Zinc in Gallium Arsenide

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The experimental variation of the diffusion coefficient D with Zn concentration C_s has been determined at 1000, 900, 800, and 700°C from radioactive ^{65}Zn diffusion profiles by a Boltzmann-Matano analysis. With interstitial Zn as the dominant diffusing species and its concentration controlled by the interstitial-substitutional equilibrium in which the singly ionized interstitial donor reacts with a neutral Ga vacancy to form a singly ionized substitutional acceptor and two holes, the effective diffusion coefficient is described by $D=D^*C_s{}^2\gamma_{\text{p}}{}^2[1+(C_s/2\gamma_{\text{p}})(d\gamma_{\text{p}}/dC_s)]$, where γ_{p} is the hole activity coefficient. The term D^* equals $2D_i/K_1p_{\text{As}4}{}^{1/4}$, where D_i is the interstitial diffusion coefficient, K_1 the reaction equilibrium constant, and $p_{\text{As}4}$ the As$_4$ pressure. The relationship between γ_p and the Fermi level E_f is given by $\gamma_p=(A/p)\exp(E_f/kT)$, where A is a constant dependent only on temperature and p is the hole concentration. This derivation for D has extended previous analyses to include both the built-in field and the nonideal behavior of holes which occurs when the impurity level broadens into an impurity band and merges with the valence band to form impurity-band tails at high Zn concentrations. The observed nonmonotonic dependence of the Zn diffusion coefficient on its concentration is a consequence of the nonideal behavior of holes at high concentrations. Quantitative comparison of D with the experimental concentration dependence has permitted the determination of γ_p and E_f as functions of the hole concentration.

I. INTRODUCTION

FROM the study of Zn diffusion in GaAs by Cunnell and Gooch,[1] the noncomplementary error function shape of the Zn-concentration–versus–distance curves was clearly demonstrated. The resulting diffusion coefficients as a function of Zn concentration revealed a concentration-dependent diffusion coefficient (see Ref. 2 and Sec. III B for a description of the determination of the diffusion coefficient D from the diffusion profile by the Boltzmann-Matano method). Longini[3] contributed significantly to the understanding of the diffusion mechanism by suggesting an interstitial-substitutional model in which the more rapidly diffusing interstitial donor dominates the diffusion process at high-substitutional concentrations. Weisberg and Blanc[4] considered the interstitial-substitutional diffusion suggested by Longini for a fully ionized substitutional acceptor and the interstitial species as either (a) neutral, (b) a single donor, or (c) a double donor. They found that the singly ionized interstitial donor gave the best fit to the 1000°C diffusion profiles of Cunnell and Gooch, which meant that the diffusion coefficient varied as the square of the substitutional Zn concentration.

It should be noted that in their diffusion experiments Cunnell and Gooch used a two-zone heating system to reduce the vapor pressure of the Zn (which also reduces the partial pressure of arsenic vapor species), and obtained diffusion profiles only for surface concentrations between 2 and 8×10^{19} cm^{-3} which is considerably lower than the pseudobinary solubility of 3.5–4.0$\times10^{20}$ cm^{-3}.[5,6] Data over a more extensive range of concentrations were provided by the diffusion studies of Kendall

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