

## Search for Stable Orientational Orders in Rigid-Lattice Models of fcc Orthohydrogen

Hubert M. James\*

*Department of Physics, Purdue University, Lafayette, Indiana 47907*

(Received 1 May 1970)

An iterative method is applied to the search for stable and metastable orders in rigid-lattice models of fcc ortho- $H_2$  with various amounts of quadrupole-quadrupole coupling: unshielded coupling between all molecules, shielded coupling beyond first-neighbor molecules, and coupling between first neighbors or first and second neighbors only. The model with nearest-neighbor couplings gives results that are decidedly different from the others in that the order with space group  $Pa3$  becomes less stable than one with space group  $P4_2/mnm$  as  $T$  rises, and in the very small difference in the free energies of the stable order and three metastable orders. The  $P4_2/mnm$  order is probably without physical significance, since it is destabilized when the model contains any physically reasonable amount of coupling between farther neighbors. The existence of complicated metastable phases with relatively low free energy persists in all models, and suggests that theoretical methods for the study of ortho- $H_2$  may be inadequate if they place too great a dependence on the assumption of  $Pa3$  order, particularly in the treatment of the model with only first-neighbor coupling, or of the order-disorder transition in any model.

### I. INTRODUCTION

The orientational ordering of nearly spherical molecules in crystals by multipole-multipole electrostatic interactions offers a problem of surprising complexity. In the case of  $H_2$ , the electric quadrupole terms in the orientational coupling are much larger than the contributions of valence and van der Waals interactions,<sup>1</sup> and exploratory calculations with rigid-lattice models commonly take account only of the quadrupole-quadrupole (QQ) coupling. The orientational ordering of cubic and hexagonal arrays of quadrupoles under their mutual interactions has been extensively studied from the classical point of view.<sup>2-5</sup> A quantum theory of solid ortho- $H_2$  or para- $D_2$ , using a rigid-lattice model and the internal-field approximation,<sup>6,7</sup> shows that classical results are easily translated into quantum-theoretical results for these systems. The ground-state wave function is

$$\Psi = \prod_i Y_{1,0}(\vec{\Omega}_i), \quad (1)$$

where  $Y_{1,0}$  is the normalized surface harmonic and  $\vec{\Omega}_i$  stands for the spherical angles  $\theta_i$ ,  $\varphi_i$ , defined for each molecule  $i$  with respect to a polar axis in the equilibrium direction for the corresponding molecule in the classical model. Because of the libration of the molecules about their equilibrium orientations, the contribution of the QQ coupling to the average energy in the quantum model is less than that in the corresponding classical model by just a factor of  $\frac{4}{25}$ . It follows that classical and quantum treatments of a rigid-lattice model of ortho- $H_2$  will predict the same orientational order

for the crystal at  $T=0^\circ\text{K}$ . At higher  $T$ , however, quantum effects may be dominant, and a quantum-statistical treatment of ortho- $H_2$  is essential.

In the case of fcc ortho- $H_2$ , which is stable at the lowest temperatures, the orientational order predicted for  $T=0^\circ\text{K}$  has the molecules librating about equilibrium directions along the threefold axes of the lattice. This order, illustrated in Fig. 1(a), has the space group  $Pa3$ . This structure has been supported by neutron-diffraction studies<sup>8</sup> of the equivalent para- $D_2$  (83% pure) at  $1.9^\circ\text{K}$ , but difficulties in understanding the Raman<sup>9</sup> and far-infrared<sup>10</sup> spectra of  $H_2$  and  $D_2$  at about  $1.6^\circ\text{K}$  have led Hardy, Silvera, and McTague to suggest<sup>9</sup> that the actual point group may not be  $Pa3$ , but a less symmetrical one such as  $R\bar{3}$ . This is not excluded by the theoretical studies mentioned above, which have shown merely that, for a rigid-lattice model and in the internal-field approximation, the  $Pa3$  structure is self-consistent at all  $T$ , that it is the most stable structure at  $T=0^\circ\text{K}$ , and that it is more stable than orientational disorder for  $T$  up to a transition temperature  $T_c$  that is  $6.85\Gamma/k$  for a model with only next-neighbor interactions, and  $7.65\Gamma/k$  for a model that includes unshielded QQ interactions between all pairs of molecules. (Here  $\Gamma$  is the usual coupling constant  $6Q^2/25R^5$  for nearest neighbors.) The problem has therefore been reexamined, using an iterative numerical procedure developed in the study of hcp ortho- $H_2$ , where it proved to be a powerful means for identifying complex stable or metastable orientational orders.<sup>11</sup>

The new study showed immediately that a model

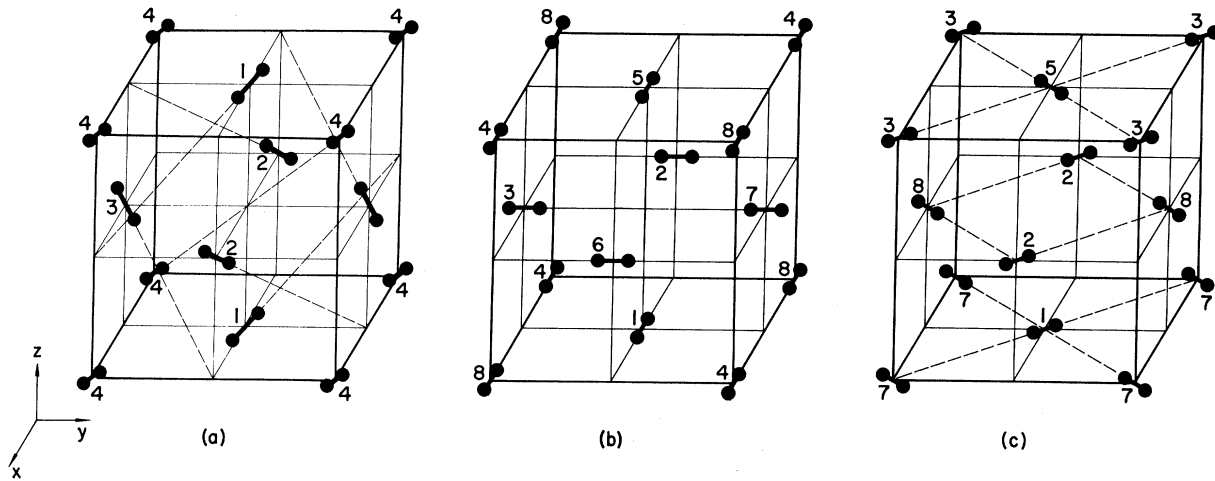


FIG. 1. (a) Equilibrium orientations of molecules in  $Pa3$  order; sublattice numbering for 4 sc sublattices. (b) Equilibrium orientations of molecules in  $P4_2/mnm$  order; sublattice numbering for 8 fcc sublattices. (c) Equilibrium orientations of molecules in  $I4_1/acd$  order; sublattice numbering for 8 tetragonal sublattices.

of fcc ortho- $H_2$  with only nearest-neighbor QQ coupling does exhibit another orientational ordering of the molecules, shown in Fig. 1(b), with point group  $P4_2/mnm$ . This is more stable than the  $Pa3$  order for  $T > 5.6\Gamma/k$ , and is metastable at lowest  $T$ . In addition, the model can assume two other orientational orderings of comparable stability over nearly the whole range of  $T < T_c$ , and there are indications of still other metastable orderings with higher free energy. These results may in part reflect the special characteristics of the internal-field approximation, but their nature and complexity suggests that the true behavior of a model with nearest-neighbor coupling may be less simple than has hitherto been anticipated; they also raise questions concerning the adequacy of other approximate treatments of this model, such as libron theory, when these start from the assumption of  $Pa3$  order.

Inclusion in the model of QQ couplings between molecules beyond nearest neighbors tends to destabilize the other orders with respect to the  $Pa3$  order. These results, which have been briefly described and discussed elsewhere,<sup>12</sup> suggest that a model with farther-neighbor QQ couplings may show a behavior that is both more realistic and simpler than that of the model with only nearest-neighbor couplings.

From another point of view, the results illustrate the potential usefulness of a careful examination of self-consistent solutions of the internal-field problem, even when they do not correspond to stable phases of the system. The multiplicity of stable and metastable self-consistent orderings of the molecules, and the sensitivity of the results

to the couplings included in the model, provide a reasonable basis for judgment as to what couplings must be included in a model that is to be studied in detail by more powerful methods.

This paper begins with a brief general description of the iterative method for solution of the effective-field problem, with some emphasis on the significance of metastable self-consistent orientational orders. Sections III and IV give detailed information about the calculations on fcc ortho- $H_2$ . Section V presents selected numerical results that appear to be sufficient for most purposes. Full numerical data on the several orders found in the various models, at all  $T$ , are too bulky for publication here; further information on specific points will be provided on request to the author. Section VI concludes the paper with comments on the physical significance of the results and their apparent implication of possible inadequacy of the model with only nearest-neighbor coupling.

## II. ITERATIVE PROCEDURE

The internal-field approximation involves both wave-mechanical and statistical approximations. One assumes that the orientational couplings acting on each molecule  $i$  can be represented by an average orientational potential energy  $U^i(\vec{\Omega}_i)$ , from which one can derive the orientational wave functions  $\psi_\mu^i(\vec{\Omega}_i)$  and the orientational energies  $\epsilon_\mu^i$  for that molecule. In treating solid ortho- $H_2$  it is customary and usually sufficient to restrict attention to zero-order solutions of this problem with  $J=1$ ; then  $\mu$  runs over only three values, and

$$\psi_{\mu}^i(\vec{\Omega}_i) = Y_{10}(\Theta_{\mu}^i), \quad (2)$$

where  $\Theta_{\mu}^i$  is the angle between the molecular axis and the symmetry axis of the function  $\psi_{\mu}^i$ . From the functions  $\psi_{\mu}^i$  one can construct a basis set of orientational wave functions for the crystal,

$$\Psi_{\{\mu\}} = \prod_i \psi_{\mu_i}^i(\vec{\Omega}_i). \quad (3)$$

The assumed independence of the molecules, subject only to the average potential energy of their interaction, implies that the probability of occurrence of state  $\Psi_{\{\mu\}}$  is a product of single-molecule probabilities,

$$P_{\{\mu\}} = \prod_i P_{\mu_i}^i, \quad (4)$$

where

$$P_{\mu_i}^i = \exp(-\beta\epsilon_{\mu_i}^i) / \sum_{\mu} \exp(-\beta\epsilon_{\mu_i}^i). \quad (5)$$

More precisely, one adds the assumption of random phases, assuming that the density matrix in terms of the basis  $\Psi_{\{\mu\}}$  is diagonal, with its diagonal elements given by Eq. (5). On this assumption, one can calculate the average energy of interaction between each molecule  $i$ , with orientation  $\vec{\Omega}_i$ , and all other molecules in the crystal. If these energies are identical with the original  $U^i(\vec{\Omega}_i)$ , this internal-field description of the crystal will be termed self-consistent.

Iterative procedures are commonly applied in the search for self-consistent descriptions of systems. In the present context, it is natural to divide the molecular lattice into sublattices, treating all molecules on each sublattice as equivalent. A calculation at given  $T$  can begin with arbitrarily chosen  $\epsilon_{\mu}^i$  and  $\psi_{\mu}^i$  for the molecules on each sublattice. One can compute<sup>11</sup> (by high-speed computer) the corresponding  $U^i$  for some chosen sublattice, and from this in turn derive new choices for the  $\epsilon_{\mu}^i$  and  $\psi_{\mu}^i$  for that sublattice. One can then go on to treat the other sublattices similarly, one after another, over and over, using at each step a newly computed field to derive a new orientational distribution, which is in turn used to derive a new field. If the process eventually converges, it will have determined a self-consistent orientational distribution for all molecules.<sup>13</sup> Any self-consistent distribution will be termed an order.

The order produced by a convergent iterative process will, in general, depend on the chosen sublattice structure and on the starting conditions. If the starting conditions possess some element of symmetry that is maintained throughout the calculation, one may arrive at an order from which the iterative process would otherwise diverge. In other cases, convergence of the process on a particular order may occur only because of restric-

tions implied by the chosen sublattice structure. An order will be termed unstable unless it can be approached by the iterative procedure from any sufficiently nearby distribution of whatever symmetry, in every sublattice structure in which it can be described. It seems unlikely that unstable orders have physical significance or much formal interest.<sup>14</sup> All orders described in this paper have passed tests for stability to small randomly chosen distortions in sublattice structures that would permit their disappearance if they were unstable. While a limited number of tests of this sort can not be conclusive, it seems unlikely that any of these orders are unstable.

The orientational free energy  $F$  of any self-consistent order is an extremal with respect to variations of the  $\psi_{\mu}^i$  within the manifold  $\mathcal{J} = 1$ , and an absolute minimum with respect to choice of the  $P_{\{\mu\}}$  subject to Eq. (4).<sup>7</sup> It is easily seen that, if the crystal model includes no interactions between molecules on the same sublattice, the  $F$  associated with successive orientational distributions in the iterative process will never increase<sup>15</sup>; it thus approaches the  $F$  of the final order monotonely from above. Couplings within a single sublattice cause only minor deviations from monotone convergence. Since  $F$  is an extremal for the final order, it approaches its limiting value much more rapidly than does the orientational distribution. In the computer output one can recognize the emergence of a familiar orientational order through the approach of the calculated  $F$  to the corresponding limit when the order is still undiscernible in a tabulation of mean molecular orientations.

The computed  $F$  for any order at any  $T$  is an upper limit on the exact orientational free energy

$$F = -kT \ln Z \quad (6)$$

of the model at that temperature,  $Z$  being the exact partition sum. The order with lowest  $F$  provides the best upper limit on  $F$ , and presumably the best available description of the behavior of the model, subject to the approximations employed. This order will be called the stable order (for the given  $T$ ); the orders with higher  $F$  that are not unstable will be called metastable. Whether they correspond to what one might call metastable phases of the model is arguable. If one carries out a series of iterative calculations at successively lower (or higher)  $T$ , using the final result of one calculation as the starting point for the next, one can follow an order that is stable in one range of  $T$  into a temperature range in which it is only metastable, much as one can extend observations of the properties of liquids into temperature ranges in which they are supercooled (or superheated). At any rate, it seems clear that metastable orders

with  $F$  near that of the stable order deserve attention in the further development of the theory.

### III. SUBLATTICES USED IN CALCULATIONS ON

#### fcc ORTHO- $H_2$

In studying fcc ortho- $H_2$ , the molecular lattice was divided into sublattices in ten different ways.

The first four sublattice structures are most easily described using coordinate axes parallel to the edges of the unit cube. Table I gives for each of four cases the primitive vectors that define the relative positions of molecules of a single sublattice. The relations of the sublattices to each other are indicated for the first three cases by Figs.

1(a)–1(c), respectively. These show the position of at least one molecule of each sublattice, except that one must understand that in Fig. 1(c) the molecules of sublattice 6 lie above molecules of sublattice 2 by the length  $a$  of the cube edge, as do the molecules of sublattice 8 above those of sublattice 4. This specification of the relations between the numbered sublattices is essential for a full understanding of the orders indicated by Table V. Since all orders to be dealt with here can be described in terms of these three sublattice structures, it is not necessary to indicate the way in which the sublattices were numbered in the other cases.

Examination of the sublattices in the first two cases will show that every molecule is at a center of inversion for every sublattice. It follows that every order that can be described in terms of these two sublattice structures must have every molecule at a center of inversion. This is not true of most of the other sublattice structures, and the molecules in the  $I4_1/acd$  order illustrated in Fig. 1(c) are not at centers of inversion. This is the only such order encountered in the present work.

The other sublattice structures were chosen to permit representation of any periodicity that might arise from the  $\dots ABCABC\dots$  repetition of close-packed planes in the fcc lattice. They are described in Table I in terms of primed coordinates such that the  $(x', y')$  plane is a close-packed plane. Each of these sublattices is made up of molecules from every third close-packed plane – all of them in the “layered” hexagonal structure, and one-fourth of them in the other cases. In two cases the unit cell can be taken to be right hexagonal and right orthorhombic prisms, respectively; with the other sublattices these prisms are sheared parallel to the close-packed planes. Calculations with these sublattice structures indicated the existence of self-consistent molecular orderings quite different from those discussed in this paper, but with free energies so high that they were not examined carefully. As concerns the more stable orders, these calculations confirmed the results obtained

with other sublattice structures, but added nothing new.

Convergence of the iterative process is slower the larger the number of sublattices. In planning the work it seemed safer to program the calculations for a variety of relatively simple sublattice structures than to attempt to devise any single sublattice structure that would afford all the desired flexibility. In retrospect, it is evident that all the essential results could have been attained relatively easily by use of the one division of the lattice into 32 simple cubic (sc) sublattices, except for some loss of confidence that all important possibilities had been explored.

### IV. LATTICE SUMS USED IN CALCULATIONS

The calculations followed the basic pattern indicated in Ref. 11, using the lattice sums  $D(I, J; \rho)$  defined in and below Eq. (10) of that paper. Equivalences in the relations between sublattices make it sufficient to compute the sums  $D(1, J; \rho)$ , which will here be written as

$$D_c(J, m) = \sum_{j(J)} \Gamma_j P_{4,m}(\cos \theta_j) \cos m \varphi_j, \quad (7)$$

$$D_s(J, m) = \sum_{j(J)} \Gamma_j P_{4,m}(\cos \theta_j) \sin m \varphi_j.$$

A molecule of sublattice 1 is taken as the origin, and the sums are carried over molecules  $j$  on sublattice  $J$ , out to some distance  $R$  from the origin. The spherical coordinates  $r_j$ ,  $\theta_j$ , and  $\varphi_j$  define the position of molecule  $j$  with respect to the usual coordinate axes parallel to the cube edges, and

$$\Gamma_j = \Gamma(d/r_j)^5. \quad (8)$$

The basic sums needed in calculations with 8 fcc sublattices are given in Table II; simple considerations of symmetry of the sublattices and of the surface harmonics show that all nonzero  $D$ 's differ from the  $D$ 's in that table by, at most, an easily determined sign. Values of the sums are given for  $R = d$  (nearest neighbors only),  $R = \sqrt{2}d$  (first and second neighbors), and for  $R = 40d$ . Inspection of the convergence of the sums as  $R$  increases shows that the values for  $R = 40d$  differ from sums extended over the whole lattice by no more than a few units in the last place given. The independently computed sums can be checked by the following relations. The fact that the quadrupoles on sublattice 1 will have the same interaction energy, whether they are all directed along the  $x$  axis or along the  $z$  axis, can easily be seen to imply that

$$D_c(1, 4) = 120 D_c(1, 0). \quad (9)$$

Similarly, one finds

$$D_c(5, 4) = 120 D_c(5, 0), \quad (10)$$

TABLE I. Primitive vectors for sublattices used in calculations on fcc ortho-H<sub>2</sub>. The type and number of similar sublattices is given for each case.  $x, y, z$  denote components parallel to the cube edges of the fcc lattice;  $x', y', z'$  denote components in a coordinate system in which the  $(x', y')$  plane is a close-packed plane and the  $x'$  axis is directed from one molecule toward a nearest neighbor, as in Fig. 2, Ref. 7.  $a$  is the cube edge and  $d = a/\sqrt{2}$ , the separation of nearest neighbors.

Sublattices		Primitive vectors for sublattice		
Type	Number		$(x, y, z)$	
sc	4	$(a, 0, 0)$	$(0, a, 0)$	$(0, 0, a)$
fcc	8	$(0, a, a)$	$(a, a, 0)$	$(a, 0, a)$
Tetragonal	8	$(a, 0, 0)$	$(0, a, 0)$	$(0, 0, 2a)$
sc	32	$(2a, 0, 0)$	$(0, 2a, 0)$	$(0, 0, 2a)$
			$(x', y', z')$	
Hexagonal (layered)	3	$(d, 0, 0)$	$(\frac{1}{2}d, \frac{1}{2}\sqrt{3}d, 0)$	$(0, 0, \sqrt{6}d)$
Hexagonal	12	$(2d, 0, 0)$	$(d, \sqrt{3}d, 0)$	$(0, 0, \sqrt{6}d)$
Orthorhombic	12	$(2d, 0, 0)$	$(0, \sqrt{3}d, 0)$	$(0, 0, \sqrt{6}d)$
Triclinic (tilted hex.)	12	$(2d, 0, 0)$	$(0, \sqrt{3}d, 0)$	$(d, 0, \sqrt{6}d)$
Monoclinic (tilted ortho.)	12	$(2d, 0, 0)$	$(0, \sqrt{3}d, 0)$	$(d, 0, \sqrt{6}d)$
Triclinic (tilted ortho.)	12	$(2d, 0, 0)$	$(0, \sqrt{3}d, 0)$	$(\frac{1}{2}d, \frac{1}{2}\sqrt{3}d, \sqrt{6}d)$

$$192 D_c(2, 0) = 72 D_c(4, 0) + D_c(4, 4), \quad (11)$$

$$120 D_c(2, 0) + 8 D_c(2, 2) - D_c(2, 4) = 0, \quad (12)$$

$$72 D_c(2, 0) + 8 D_c(2, 2) + D_c(2, 4) = 192 D_c(4, 0). \quad (13)$$

The above relations follow from rotational symmetries of the arrays and are valid for all choices of  $R$ . The fact that sublattice 1 differs from the entire lattice by a scale factor of 2 implies that, for  $R = \infty$ ,

$$D_c(1, m) + 4 D_c(2, m) + 2 D_c(4, m) + D_c(5, m) = 32 D_c(1, m) \quad (\text{all } m). \quad (14)$$

This relation is satisfied by the sums for  $R = 40d$  to within the estimated difference between these and the infinite sums.

Table II shows that second-neighbor interactions couple in pairs the sublattices related to each other like sublattices 1 and 5. Interactions of more widely separated molecules do not change the couplings between sublattices in any striking way, but they do introduce terms in the energy that depend only on the orientations of molecules on a single sublattice.

The basic sums needed in calculations with eight tetragonal lattices are given in Table III, and those needed in calculations with four sc sublattices are given in Table IV. Entries in Table IV can be derived from those in Table II, plus symmetry relations, by noting that fcc sublattices  $J$  and  $J+4$  together make up sc sublattice  $J$ ; they are also easily derived from the entries in Table III.

By making appropriate linear combinations of the columns in Tables II-IV one can obtain the sums needed in the treatment of models of ortho-H<sub>2</sub> in which different shielding factors are applied to first-neighbor interactions, second-neighbor interactions, and interactions of more widely separated pairs.

In calculations with other sublattice structures, only first- and second-neighbor interactions were included. Calculation of the sums is trivial, and the values will not be reproduced here.

TABLE II.  $D_x(J, m)/\Gamma$  [see Eq. (2)], evaluated for the 8 fcc sublattices defined by Table I and Fig. 1(b). Here  $d_x, d_y, d_z$  give the displacement of a molecule on sublattice  $J$  from the corresponding molecule on sublattice 1. The range  $R$  of the summations is indicated above the entries in columns 5-7.

$x$	$J$	$d_x, d_y, d_z$	$m$	$R=d$	$R=\sqrt{2}d$	$R=40d$
c	1	0, 0, 0	0	0.0	0.0	-0.041574
c	1	0, 0, 0	4	0.0	0.0	-4.9889
c	2		0	-0.8125	-0.8125	-0.829082
c	2		1	-1.25	-1.25	-1.407329
c	2	$-\frac{1}{2}a, 0, \frac{1}{2}a$	2	18.75	18.75	18.56797
c	2		3	-52.5	-52.5	-59.1078
c	2		4	52.5	52.5	49.0539
c	4		0	0.75	0.75	0.718249
s	4	$\frac{1}{2}a, \frac{1}{2}a, 0$	2	-15.0	-15.0	-16.88795
c	4		4	-210.0	-210.0	-210.8976
c	5		0	0.0	0.618718	0.591036
c	5	$a, 0, 0$	4	0.0	74.246212	70.9244

TABLE III.  $D_c(J, m)/\Gamma$ , evaluated for the 8 tetragonal sublattice structure. Definitions as in Table II.

$J$	$d_x, d_y, d_z$	$m$	$R=d$	$R=\sqrt{2}d$	$R=40d$
1	0, 0, 0	0	0	0.265165	0.337765
1	0, 0, 0	4	0	74.246212	62.6318
2		0	-0.8125	-0.8125	-0.829082
2	$-\frac{1}{2}a, 0, \frac{1}{2}a$	2	18.75	18.75	18.56797
2		4	52.5	52.5	49.0539
3		0	0	0	-0.134594
3	$\frac{1}{2}a, \frac{1}{2}a, a$	4	0	0	4.9073
5		0	0	0.353553	0.211697
5	0, 0, $a$	4	0	0	3.3037
7		0	1.5	1.5	1.571092
7	$\frac{1}{2}a, \frac{1}{2}a, 0$	4	-420.0	-420.0	-416.8879

## V. RESULTS

The special virtue of the iterative method is the relative freedom it offers from initial assumptions about the orders that are to be dealt with. The more complex, and thus more flexible, sublattice structures were used primarily in a search for new orders by iterations starting from random molecular orientations and in testing known orders for stability. Nearly 300 runs from random starting conditions were made in all for the various sublattice structures and coupling assumptions. After stable or metastable orders were identified, their properties at various  $T$  were determined by runs from symmetrized starting conditions in the simplest possible sublattice structure.

The symmetries of the stable and metastable orders found in this work can be understood by examining Table V, which gives (for one particular  $T$ ) the direction cosines of the symmetry axes of the ground and excited orientational states of the molecules on each sublattice, in the simplest available sublattice structure.<sup>16</sup> The orientational eigenvalues  $\epsilon$  are also given for each of these states. Inequivalences of the molecules on the different sublattices are evident as inequalities of corresponding  $\epsilon$ 's. Axial symmetry of the effective field for any sublattice is evident in equality of two of the  $\epsilon$ 's; when this occurs the corresponding direction cosines are not uniquely determined. Figures 1(a)–1(c) show the most probable orientations of molecules in the ground state for the three simplest orders. In these cases the direction cosines are independent of  $T$ ; in all other cases they change as  $T$  changes.

### A. Model with Only Nearest-Neighbor Couplings

Comments on the course of the search for new orders will be restricted to the case of coupling

between nearest neighbors only. It was known that the cubic  $Pa3$  order was stable with respect to orientational disorder below  $kT/\Gamma = 6.85$ . Search for a new order was begun near the upper end of this range, where orders with high entropy would be most likely to be stable. With four sc sublattices, 24 out of 28 trials with  $kT/\Gamma$  ranging from 6.0 to 7.1 led to the tetragonal  $P4_2/mnm$  order, which is the stable order throughout this range. With 12 hexagonal sublattices, 14 trials at  $kT/\Gamma = 6.0$  led to the metastable  $Pa3$  order 10 times, and to the stable  $P4_2/mnm$  order only 4 times; in this sublattice structure the  $P4_2/mnm$  order seems to "nucleate" from a relatively small range of initial conditions. For  $kT/\Gamma$  between 6.85 and 7.15, where the  $Pa3$  order is less stable than orientational disorder but the  $P4_2/mnm$  order is not, all runs led to the  $P4_2/mnm$  order. Twenty-four runs at  $kT/\Gamma$  equal to 6.0 or 7.0, using the 12 orthorhombic sublattices in terms of which the  $Pa3$  order can not be described, led only to the  $P4_2/mnm$  order. Thirty-five runs with the 3 "tilted" sublattice structures led only to the  $P4_2/mnm$  order or to complex orders with free energies so high that they were not studied further. Attention was then shifted to lower  $T$ , runs being made at  $kT/\Gamma$  equal to 3.0 or 4.0. Here new metastable orders appeared. In 10 runs using 8 fcc sublattices the stable  $Pa3$  order appeared twice, the  $P4_2/mnm$  order appeared twice, a new monoclinic  $P2_1/b$  order appeared three times, and a new tetragonal  $I4/mcm$  order appeared three times. With 32 sc sublattices the corresponding frequencies of occurrence in 13 runs were 3, 2, 5, and 3. With 8 tetragonal sublattices, in terms of which one can not describe the  $P2_1/b$  and  $I4/mcm$  orders, in 10 runs the  $Pa3$  and  $P4_2/mnm$  orders each appeared 5 times. An order with space group  $I4_1/acd$ , which had been found to be metastable in models with all molecules coupled, was found to be unstable when only nearest-neighbor couplings are included.

TABLE IV.  $D_c(J, m)/\Gamma$ , evaluated for the 4 sc sublattice structure. Definitions as in Table II

$J$	$m$	$R=d$	$R=\sqrt{2}d$	$R=40d$
1	0	0.0	0.618718	0.549462
1	4	0.0	74.246212	65.9355
2	0	-1.625	-1.625	-1.658164
2	2	37.5	37.5	37.13594
2	4	105.0	105.0	98.1078
3	0	-1.625	-1.625	-1.658164
3	2	-37.5	-37.5	-37.13594
3	4	105.0	105.0	98.1078
4	0	1.5	1.5	1.436498
4	4	-420.0	-420.0	-421.7952

TABLE V. Data on stable and metastable orders at  $kT/\Gamma = 3.0$  for several coupling assumptions. Thermodynamic functions are given on a per-molecule basis. Orientational state energies  $\epsilon$  and direction cosines for most probable orientations are given for the various sublattices, in a sublattice structure indicated in each case.

$kT/\Gamma$	$U/NT$	$S/Nk$	$F/NT$	Sublattice	$\epsilon_1/\Gamma$	$\gamma_{x1}$	$\gamma_{y1}$	$\gamma_{z1}$	$\epsilon_2/\Gamma$	$\gamma_{x2}$	$\gamma_{y2}$	$\gamma_{z2}$	$\epsilon_3/\Gamma$	$\gamma_{x3}$	$\gamma_{y3}$	$\gamma_{z3}$	
<b><math>P_{e3}(T_h^6)</math></b>																	
Next-neighbor interactions; 4 sc sublattices [ see Fig. 1(a) ]																	
3.0	-6.2639	0.0268	-4.1364	1	-12.597	-0.5773	0.5773	0.5773	6.298	0.5773	0.5773	0.5773	6.298				
				2	-12.597	0.5773	-0.5773	0.5773	6.298	0.5773	0.5773	0.5773	6.298				
				3	-12.597	0.5773	0.5773	-0.5773	6.298	0.5773	0.5773	0.5773	6.298				Not unique
				4	-12.597	0.5773	0.5773	0.5773	6.298	0.5773	0.5773	0.5773	6.298				Not unique
<b><math>P_{e2}/mmm (D_{4h}^{14})</math></b>																	
Next-neighbor interactions; 4 sc sublattices																	
3.0	-6.1524	0.0383	-6.2672	1,4	-12.402	1.0	0.0	0.0	3.447	0.0	0.0	1.0	8.955	0.0	1.0	0.0	0.0
				2,3	-12.402	0.0	1.0	0.0	3.447	0.0	0.0	1.0	8.955	1.0	0.0	0.0	0.0
<b><math>I_{41}/acd (D_{4h}^{20})</math></b>																	
All interactions; 8 tetragonal sublattices [ see Fig. 1(c) ]																	
3.0	-5.8321	0.0546	-5.9960	1,2,3,4	-11.801	0.7071	0.7071	0.0	2.596	0.0	0.0	1.0	9.205	-0.7071	0.7071	0.7071	0.0
				5,6,7,8	-11.801	-0.7071	0.7071	0.0	2.596	0.0	0.0	1.0	9.205	0.7071	0.7071	0.7071	0.0
<b><math>P_{21}/b(C_{2h}^3)</math></b>																	
All interactions; 8 fcc sublattices																	
3.0	-6.0130	0.0363	-6.1219	1,3	-12.018	-0.7468	-0.3454	0.5683	4.615	-0.3921	0.9189	0.0432	7.403	0.5371	0.1906	0.8217	0.0
				2,8	-12.220	0.1562	0.9661	0.2057	4.294	0.8955	-0.2264	0.3832	7.926	0.4167	0.1244	-0.9005	0.0
				4,6	-12.018	-0.7468	0.5683	-0.3454	4.615	-0.3921	0.0432	0.9189	7.403	0.5371	0.8217	0.1906	0.0
				5,7	-12.220	0.1562	0.2057	0.9661	4.294	0.8955	0.3832	-0.2264	7.926	0.4167	-0.9005	0.1244	0.0
<b><math>I_{41}/mcm(D_{4h}^{18})</math></b>																	
Nearest-neighbor interactions; 8 fcc sublattices																	
3.0	-5.9632	0.3967	-6.0822	1	-11.692	0.7414	0.0	0.6711	5.646	0.6711	0.0	-0.7414	6.046	0.0	1.0	0.0	0.0
				2	-12.651	1.0	0.0	0.0	2.143	0.0	1.0	0.0	10.507	0.0	0.0	1.0	0.0
				3	-12.075	0.0	0.0	0.0	6.038	0.0	Not unique	0.0	6.038	0.0	Not unique	0.0	0.0
				4	-11.692	0.0	0.7414	0.6711	5.646	0.0	0.6711	0.7414	6.046	1.0	0.0	0.0	0.0
				5	-11.692	0.7414	0.0	-0.6711	5.646	0.6711	0.0	0.7414	6.046	0.0	1.0	0.0	0.0
				6	-12.651	0.0	1.0	0.0	2.143	1.0	0.0	0.0	10.507	0.0	0.0	1.0	0.0
				7	-12.075	0.0	0.0	0.0	6.038	0.0	Not unique	0.0	6.038	0.0	Not unique	0.0	0.0
				8	-11.692	0.0	-0.7414	0.6711	5.646	0.0	0.6711	0.7414	6.046	1.0	0.0	0.0	0.0
<b><math>C_2/m(C_{2h}^3)</math></b>																	
All interactions; 8 fcc sublattices																	
3.0	-5.9691	0.0412	-6.0926	1	-12.381	0.5486	0.0	0.8361	5.073	0.0	1.0	0.0	7.308	-0.8361	0.0	0.5486	0.0
				2	-10.202	0.9991	0.0	-0.0434	4.676	0.0434	0.0	0.9991	5.526	0.0	-1.0	0.0	0.0

TABLE V. (continued)

$C_2/m(C_2h)$	$kT/\Gamma$	$U/N\Gamma$	$S/Nk$	$F/N\Gamma$	Sublattice	$\epsilon_1/\Gamma$	$\gamma_{41}$	$\gamma_{51}$	$\gamma_{41}$	$\epsilon_2/\Gamma$	$\gamma_{42}$	$\gamma_{52}$	$\gamma_{42}$	$\epsilon_3/\Gamma$	$\gamma_{43}$	$\gamma_{53}$	$\gamma_{43}$	
All interactions; 8 fcc sublattices																		
3	-11.490	-0.3525	0.3049	0.8847	3.717	0.6390	0.7691	-0.0105	7.774	0.6837	-0.5616	0.4660						
4	-11.978	0.4743	0.6328	0.6120	3.895	0.5475	-0.7564	0.3579	8.083	0.6894	0.1653	-0.7052						
5	-13.844	0.9164	0.0	-0.4002	5.221	0.0	1.0	0.0	8.623	0.4002	0.0	0.9164						
6	-12.978	0.0	1.0	0.0	4.857	0.8708	0.0	-0.4916	8.121	0.4916	0.0	0.8708						
7	-11.490	-0.3525	-0.3049	0.8847	3.717	0.6390	-0.7691	-0.0105	7.774	0.6837	0.5616	0.4660						
8	-11.978	0.4743	-0.6328	0.6120	3.895	0.5475	0.7564	0.3579	8.083	0.6894	-0.1653	-0.7052						
$P\bar{1}(C_1)$																		
First- and second-neighbor interactions; 8 fcc sublattices																		
3.0	-5.5273	0.5920	-5.7050															
1	-11.187	0.5580	-0.0742	0.8253	5.172	0.4632	0.8534	-0.2376	6.015	-0.6867	0.5153	0.5122						
2	-9.638	0.9970	0.0616	-0.0470	4.380	-0.0048	0.6539	0.7566	5.258	0.0774	-0.7541	0.6522						
3	-11.183	-0.3713	0.3421	0.8632	3.930	0.5787	0.8123	-0.0780	7.253	0.7261	-0.4724	0.4996						
4	-11.540	0.4996	0.6212	0.6038	2.662	0.5215	-0.7722	0.3630	8.878	0.6917	0.1335	-0.7097						
5	-12.507	0.9231	0.0169	-0.3841	5.061	-0.1391	0.9459	-0.2928	7.446	0.3584	0.3238	0.8755						
6	-11.652	0.0049	0.9999	-0.0083	3.702	0.8967	-0.0080	-0.4425	7.950	0.4425	0.0053	0.8967						
7	-11.266	-0.3736	-0.2249	0.8999	2.942	0.4655	-0.8846	-0.0278	8.324	0.8023	0.4085	0.4352						
8	-10.650	0.4791	-0.6039	0.6370	2.403	0.5026	0.7837	0.3649	8.247	0.7196	-0.1454	-0.6790						

Table VI gives, for the  $Pa3$  and  $P4_2/mnm$  orders of this model, the full values of  $U$  and  $S$  per molecule and the change  $\Delta F$  in the free energy due to the orientational coupling. The free energies of the two orders become equal when  $kT/\Gamma = 5.6$ , and the transition from  $Pa3$  to  $P4_2/mnm$  order with rising  $T$  occurs with latent heat  $0.245N\Gamma$ . The transition from  $P4_2/mnm$  order to orientational disorder occurs at  $kT/\Gamma = 7.15$  with latent heat  $\sim 0.29N\Gamma$ .

Figure 2 shows the difference between the free energies of the various orders (including complete orientational disorder) and that of the  $Pa3$  order, as a function of  $T$ . Plots of the free energies of the several orders would resemble Fig. 3, except that the curves would be much more closely spaced. Since the base line corresponds to the free energy of the  $Pa3$  order, the  $P4_2/mnm$  order becomes stable where the corresponding curve dips below the base line; it ceases to be stable when that curve intersects the curve for the disordered phase. Both  $Pa3$  and  $P4_2/mnm$  order appear to be metastable at temperatures somewhat above that at which they become less stable than disorder, but no attempt has been made to determine their range of metastability. The range of metastability of the  $P2_1/b$  and  $I4/mcm$  phases is indicated (approximately) by the extent of the corresponding curves. One point in Fig. 2 gives the calculated free energy for the unstable  $I4_1/acd$  order.

To understand the scale of Fig. 2, one should remember that the computed value of  $\Gamma$  for the rigid-lattice model, without correction for dielectric shielding and other effects, is about  $0.7 \text{ cm}^{-1}$  or  $1.0k$  for  $H_2$ , and  $0.84 \text{ cm}^{-1}$  or  $1.2k$  for  $D_2$ . The effective values appear to be reduced by roughly 20% by factors not considered here.<sup>17</sup> The horizontal scale is thus, roughly, temperature in degrees absolute, and extends far above the observed transition temperatures, which are  $2.9^\circ \text{K}$  for  $H_2$  and  $3.9^\circ \text{K}$  for  $D_2$ .<sup>18</sup> On the vertical scale, one unit corresponds to about one-fourteenth of the heat of fusion per molecule of solid  $H_2$  at  $13.8^\circ \text{K}$ , about one-hundredth of the cohesive energy per molecule of solid  $H_2$ , and about one-twelfth of the computed energy of excitation of a libron.<sup>19</sup> The free energies per molecule of the four stable and metastable orders thus lie in a range that is about  $\frac{1}{40}$  of the libron excitation energy.

#### B. Model with All Molecules Coupled

Figure 4 shows  $F-F(Pa3)$  for the metastable orders of the rigid-lattice model when unshielded QQ interactions between all molecules are included. In the presence of farther-neighbor interactions the  $P4_2/mnm$  order is not even metastable, and there is no corresponding curve in Fig. 4. The free energy of the metastable  $P2_1/b$  order is raised rela-



TABLE VI. Contributions of orientational couplings to  $U$ ,  $S$ , and  $F$  for  $Pa3$  and  $P4_2/mnm$  orders, in a model with nearest-neighbor QQ couplings only.

$kT/\Gamma$	$Pa3$			$P4_2/mnm$		
	$U/N\Gamma$	$S/Nk$	$\Delta F/N\Gamma$	$U/N\Gamma$	$S/Nk$	$\Delta F/N\Gamma$
2.0	-6.3305	0.0016	-4.1364	-6.2441	0.0033	-4.0535
3.0	-6.2639	0.0268	-3.0483	-6.1524	0.0383	-2.9713
4.0	-5.9684	0.1096	-2.0122	-5.8063	0.1355	-1.9538
5.0	-5.2635	0.2648	-1.0944	-5.0424	0.3039	-1.0689
5.5	-4.6943	0.3730	-0.7036	-4.4502	0.4165	-0.6988
6.0	-3.9237	0.5068	-0.3730	-3.6748	0.5512	-0.3904
6.5	-2.8399	0.6799	-0.1181	-2.6481	0.7153	-0.1562
6.7	-2.2358	0.7714	-0.0432	-2.1314	0.7935	-0.0872
6.85	-1.5990	0.8653	-0.0007			
7.0				-1.1297	0.9396	-0.0163
7.13				-0.4454	1.0363	-0.0014

tive to that of the  $Pa3$  order, but it remains metastable to somewhat higher  $T$  than in the absence of farther-neighbor coupling. Some elements of symmetry of the  $I4/mcm$  order are lost, and the space group becomes  $C2/m$ ; the free energy remains about equal to that of the  $P2_1/b$  order. There appears a new order with space group  $I4_1/acd$ , with four molecules per unit cell, which is metastable until its free energy exceeds that of orientational disorder. (This order does not go continuously into orientational disorder, despite the near tangency of the corresponding curves in Fig. 4.)

### C. Models with Intermediate Coupling of Farther-Neighbor Molecules

The effect of farther-neighbor interactions in destabilizing the  $P4_2/mnm$  order was further explored

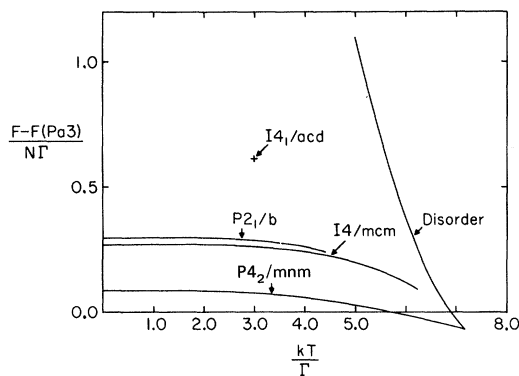


FIG. 2. Difference between the contribution of orientational coupling to the free energy of other orders and to that of the  $Pa3$  order, as a function of  $T$ , for the model with nearest-neighbor couplings only.

by calculations on models that include the full QQ interactions between nearest neighbors, but have interactions between other molecules reduced by a constant factor  $f$ . The temperature  $T_c$  of the transition to the disordered phase changes nearly linearly with  $f$ , rising from  $6.85\Gamma/k$  to  $7.65\Gamma/k$  for the  $Pa3$  order as  $f$  goes from 1 to 0 and falling from  $7.15\Gamma/k$  to about  $5.86\Gamma/k$  for the  $P4_2/mnm$  order. These transition temperatures become equal for  $f \approx 0.15$ . For larger  $f$  the  $P4_2/mnm$  order is not stable at any  $T$ ; it is metastable for  $f = 0.25$ , but not for  $f = 0.5$ .

### D. Model with First- and Second-Neighbor Coupling

Calculations have been made to determine whether second-neighbor coupling can reasonably replace

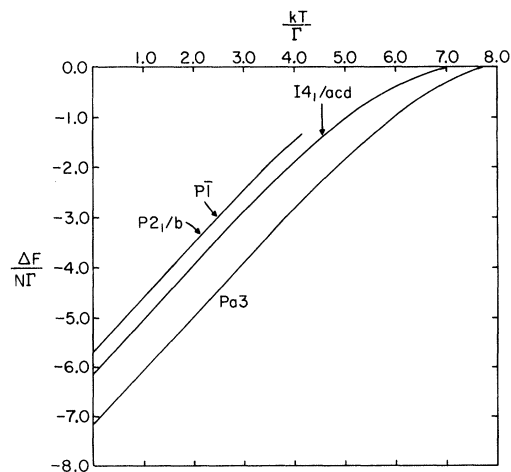


FIG. 3. Difference  $\Delta F$  between the orientational free energy of the orders and that of the disordered phase, as a function of  $T$ , for the model with QQ couplings between first and second neighbors.

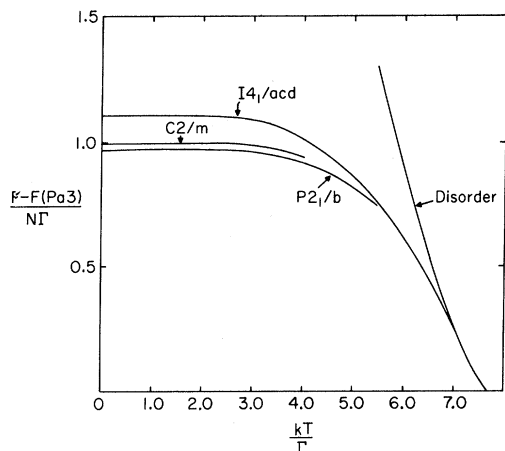


FIG. 4. Difference between the orientational free energy of the metastable orders and that of the stable  $Pa3$  order, as a function of  $T$ , for the model with unshielded QQ couplings between all molecules.

coupling to all farther neighbors. Table VII shows that the effect of this simplification of the model on the  $Pa3$  order is not very large. At low  $T$  the coupling energy is increased by about 1%, and  $kT_c/\Gamma$  is increased from 7.65 to 7.74. Comparison of Figs. 4 and 5 shows that the relation of the metastable  $I4_1/acd$  order to the  $Pa3$  order is little changed, while the  $P2_1/b$  order has its relative free energy increased moderately. Some symmetry elements of the  $C2/m$  order are lost (see Table V) and the space group becomes  $P\bar{1}$ , with only the translational symmetry of the fcc lattice plus inversion symmetry about each molecule.

#### VI. DISCUSSION

For all models of solid ortho- $H_2$  considered in this paper there exist a number of metastable or-

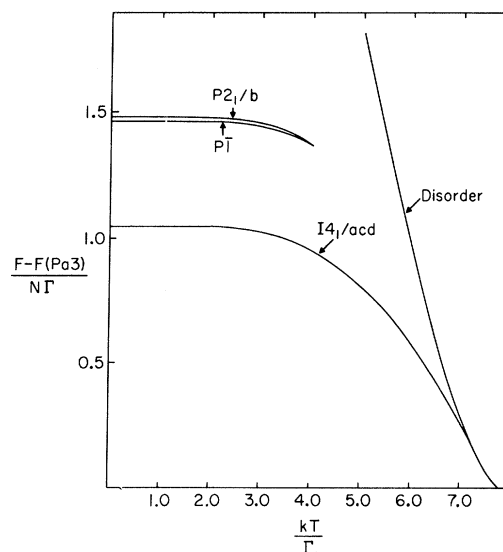


FIG. 5. Difference between the orientational free energy of the metastable orders and that of the stable  $Pa3$  order, as a function of  $T$ , for the model with QQ couplings between first and second neighbors.

ders with free energies relatively close to that of the  $Pa3$  order. The differences are of the same order as the calculated perturbation of the ground-state energy by terms neglected in the internal-field calculation.<sup>5</sup>

When only nearest-neighbor couplings are included the free-energy differences are particularly small. At  $T=0^\circ\text{K}$  the orientational free energy is simply the orientational coupling energy; the coupling energy per molecule is  $-6.33\Gamma$  for the  $Pa3$  order,  $-6.25\Gamma$  for the  $P4_2/mmm$  order,  $-6.06\Gamma$  for the  $I4_1/mcm$  order, and  $-6.04\Gamma$  for the  $P2_1/b$  order. For  $T > 5.6\Gamma/k$  the higher entropy of the  $P4_2/mmm$  order makes it the stable order, up to the

TABLE VII. Contributions of orientational couplings to  $U$ ,  $S$ , and  $F$  for the  $Pa3$  order, in models with unshielded QQ couplings between first and second neighbors, and between all molecules.

$kT/\Gamma$	Between first and second neighbors			Between all molecules		
	$U/N\Gamma$	$S/Nk$	$\Delta F/N\Gamma$	$U/N\Gamma$	$S/Nk$	$\Delta F/N\Gamma$
1.0				-7.1583	0.0000	-6.0597
2.0	-7.0687	0.0006	-4.8726	-7.1574	0.0005	-4.9612
3.0	-7.0331	0.0139	-3.7790	-7.1244	0.0129	-3.8672
4.0	-6.8439	0.0668	-2.7166	-6.9451	0.0629	-2.8024
5.0	-6.3548	0.1744	-1.7337	-6.4765	0.1660	-1.8136
6.0	-5.4174	0.3438	-0.8887	-5.5754	0.3289	-0.9571
6.5	-4.7153	0.4560	-0.5384	-4.9021	0.4365	-0.5983
7.0	-3.7834	0.5939	-0.2503	-4.0159	0.5676	-0.2989
7.5	-2.4212	0.7813	-0.0415	-2.7676	0.7394	-0.0738
7.65	-1.7652	0.8679	0.0001	-2.2374	0.8094	-0.0250
7.75				-1.7636	0.8709	0.0010

temperature at which orientational disorder takes over. Inclusion in the model of any physically reasonable amount of farther-neighbor interaction (which is certainly more than 15% of the unshielded QQ coupling) will destroy the stability of the  $P4_2/mnm$  order at any temperature and will considerably increase the stability of the  $Pa3$  order relative to all other orders discussed here. There is, therefore, no indication that the observations of Hardy and his collaborators on the Raman and infrared spectra can be explained in terms of the existence at low  $T$  of a stable order other than the  $Pa3$  order.

This does not mean that the appearance of metastable orders in these internal-field calculations is not of some broader theoretical interest. It seems likely that their existence will find expression in calculations carried out by more powerful methods, particularly for temperatures at which orientational order is showing a marked decrease. A linearized libron theory based on the assumption of  $Pa3$  order may well be adequate for the discussion of the optical properties of ortho- $H_2$  at very low temperatures, but use of a nonlinear generalization of such a theory in discussing the order-disorder transition, or even a situation in which the average number of librions is  $N/10$ , would appear to be more questionable. Low-lying metastable orders may also play an important role in perturbation calculations of the effects of other types of coupling between molecules.

One can expect a theoretical approach that ignores the possible existence of large local deviations from  $Pa3$  order to yield results that are not

sensitive to omission from the model of couplings between molecules other than nearest neighbors, since this is the case with the internal-field treatment of the  $Pa3$  order, considered alone. At the same time, it seems quite possible that the results obtained with more powerful and more accurate methods of calculation will show a sensitivity to the coupling assumption that is related to the change in spacing of the metastable orders found in the internal-field treatment. In other words, it seems possible that the model with only nearest-neighbor couplings will, when treated more accurately, display anomalous and even unrealistic behavior that is suppressed in treatments based on the assumption of  $Pa3$  order. Inclusion in the model of at least the couplings between second-neighbor molecules would appear to be a useful means of avoiding possible anomalous behavior.

In their discussion of the ordering of classical quadrupoles on an fcc lattice, with unshielded QQ coupling between all molecules, Nagai and Nakamura<sup>2</sup> did not identify the metastable  $C2/m$ ,  $P2_1/b$ , or  $I4_1/acd$  orders reported here; they did note the existence of the unstable  $P4_2/mnm$  order as one that makes the energy stationary, but they did not determine its energy. These omissions did not arise from any fundamental limitation in their procedure, but from its inconvenience for the exploration of possible complex orders, and from the fact that they were primarily interested in identifying the order with lowest energy. It can only be hoped that in the present work the examination of possibilities has been so broad that none of practical interest have been overlooked.

\*Research supported in part by National Science Foundation.

<sup>1</sup>T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).

<sup>2</sup>O. Nagai and T. Nakamura, Progr. Theoret. Phys. (Kyoto) **24**, 432 (1960).

<sup>3</sup>A. I. Kitaigorodskii and K. V. Mirskaya, Kristallografiya **10**, 162 (1965) [Soviet Phys. Crystallogr. **10**, 121 (1965)].

<sup>4</sup>J. Felsteiner, Phys. Rev. Letters **15**, 1025 (1965); Phys. Letters **28A**, 288 (1968).

<sup>5</sup>H. Miyagi and T. Nakamura, Progr. Theoret. Phys. (Kyoto) **37**, 641 (1967).

<sup>6</sup>J. C. Raich and H. M. James, Phys. Rev. Letters **16**, 173 (1966).

<sup>7</sup>H. M. James and J. C. Raich, Phys. Rev. **162**, 649 (1967).

<sup>8</sup>K. F. Mucker, S. Talhouk, P. M. Harris, D. White, and R. A. Erickson, Phys. Rev. Letters **16**, 799 (1966); K. F. Mucker, P. M. Harris, D. White, and R. A. Erickson, J. Chem. Phys. **49**, (1968).

<sup>9</sup>W. N. Hardy, I. F. Silvera, and J. P. McTague, Phys. Rev. Letters **22**, 297 (1969).

<sup>10</sup>W. N. Hardy, I. F. Silvera, K. N. Klump, and O.

Schnepf, Phys. Rev. Letters **21**, 291 (1968).

<sup>11</sup>H. M. James, Phys. Rev. **167**, 862 (1968).

<sup>12</sup>H. M. James, Phys. Rev. Letters **24**, 815 (1970); **24**, 970 (E) (1970). In this preliminary publication the  $P4_2/mnm$  order was correctly described, but it was erroneously identified as belonging to the space group  $Cmmm$ . The author is indebted to Professor A. B. Harris for calling this error to his attention.

<sup>13</sup>An alternative procedure is to derive  $U^i$  for all sublattices from the initially chosen  $\epsilon_\mu^i$  and  $\psi_\mu^i$ , and from these  $U^i$  to derive a complete new set of  $\epsilon_\mu^i$  and  $\psi_\mu^i$ . This is appropriate when it is desired to maintain some particular symmetry of the  $U^i$  through all stages of the calculation. It should, however, be avoided when one starts from randomly chosen orientational distributions in seeking possible orderings with unknown symmetry, since it may not lead to convergence on any single set of internal fields, but to a cyclic alternation between several physically meaningless sets of fields. Changing the  $U^i$  and  $\psi_\mu^i$  of the molecules on one sublattice at a time is normally sufficient to prevent such cycling, even when the sublattices are dealt with in a regular cyclic order, but the author has preferred to have the sublattices dealt with in a random sequence. This has always led to convergence

of the iterative calculation.

<sup>14</sup>Compare, for instance, the existence of self-consistent solutions of Hartree-Fock equations that do not correspond to any physically significant solution of the exact Schrödinger equation. S. I. Pekar, *Zh. Eksperim. i Teor. Fiz.* **18**, 525 (1948).

<sup>15</sup>For this to be true, it is of course essential to calculate  $F$  using equations valid for any distribution [ such as Eq. (14) of Ref. 11 ], rather than equations valid only for

self-consistent distributions [ such as Eq. (13) of Ref. 11 ].

<sup>16</sup>Corresponding data for other temperatures are available on request to the author.

<sup>17</sup>A. B. Harris, *Phys. Rev. B* **1**, 1881 (1970).

<sup>18</sup>A. F. Schuch, R. L. Mills, and D. A. Depatie, *Phys. Rev.* **165**, 1032 (1968).

<sup>19</sup>J. C. Raich and R. D. Ethers, *Phys. Rev.* **168**, 425 (1968).

## Self-Consistent Local Orbitals for Lithium Halide Crystals<sup>†</sup>

A. Barry Kunz

*Department of Physics and Materials Research Laboratory,  
University of Illinois, Urbana, Illinois 61801*

(Received 25 May, 1970)

Using the Adams-Gilbert local-orbital theory, it has been possible to obtain approximate self-consistent local orbitals for the fcc lithium halide crystals. In this formalism, terms to first order in interatomic overlap are included. Nearest neighbors are considered exactly in this formalism, and more distant neighbors in a point-ion model. The method of Roothaan is used to obtain the solutions. All relativistic effects are neglected in this calculation

### I. INTRODUCTION

Because of the introduction of localized-orbital theories by Adams,<sup>1</sup> Gilbert,<sup>2</sup> and Anderson,<sup>3</sup> self-consistent Hartree-Fock solutions for ground-state wave functions of polyatomic systems have become possible. The author has taken the theory of Gilbert, expanded the environment in powers of interatomic overlap, and retained terms to first order in interatomic overlap.<sup>4</sup> This seems justified for most ionic or insulating solids, since the overlaps are typically of the order 0.1 or less.<sup>5</sup> In the

original paper by the author, self-consistent orbitals for the LiH crystal were reported. In the present paper orbitals are obtained for LiF, LiCl, LiBr, and LiI using the analytic Hartree-Fock technique of Roothaan<sup>6</sup> in a somewhat modified form.

These localized orbitals, which the author obtains for the ground state of the lithium halide crystal, should prove very useful for band-structure calculations. The preliminary results for LiCl crystal have been used with great success by the author in computing a band structure.<sup>7</sup> The author

TABLE I. The values of  $A_{kj}$  and  $Z_{kj}$  are given for the  $s$  levels of the  $\text{Li}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions.

$J$	$\text{Li}^+$		$\text{F}^-$		$\text{Cl}^-$		$\text{Br}^-$		$\text{I}^-$	
	$A_{oj}$	$Z_{oj}$	$A_{oj}$	$Z_{oj}$	$A_{oj}$	$Z_{oj}$	$A_{oj}$	$Z_{oj}$	$A_{oj}$	$Z_{oj}$
1	0	2.69	0	10.040	0	18.9832	0	37.3527	0	56.5239
2	0	4.00	0	8.3691	0	14.7941	1	33.1430	1	26.1681
3	0	2.00	0	5.5505	1	14.7181	2	17.2808	2	24.7445
4			1	4.9546	1	9.6220	2	16.3407	2	12.7500
5			1	3.3675	1	6.7665	2	8.4198	3	10.0218
6			1	1.9804	2	6.2190	2	6.6235	3	5.2591
7			1	1.1869	2	3.2450	3	6.6182	3	3.3269
8					2	2.1679	3	3.4730	4	3.0142
9					2	1.3550	3	2.1970	4	2.2501
10							3	1.4859	4	1.4859
11									4	1.1889