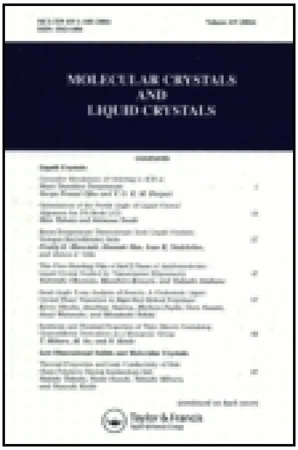

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Orientational Order Parameters in Solid Hydrogen: A Density Matrix Approach

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Orientational Order Parameters in Solid Hydrogen: A Density Matrix Approach†

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We consider the description of the orientational degrees of freedom of ortho-H_2 molecules in terms of density matrices and the irreducible tensorial operators associated with unit angular momentum. The range of allowed values for the orientational order parameters is determined from the positivity conditions imposed on the density matrix.

Keywords: hydrogen, orientational-order, density-matrix, relaxation

I. INTRODUCTION

Several groups[1–20] have carried out extensive studies of solid ortho-para hydrogen mixtures at low temperatures in recent years. The interest in these mixtures is that they represent a random array of interacting quantum rotors which has an interesting analogy with the spin glasses.[21] In solid H_2 the orientations of the molecules play a role analogous to the magnetic dipole moments in magnetic spin glasses such as $Eu_xSr_{1-x}S$.[22] The ortho-H_2 molecules with orbital angular momentum $J = 1$ interact via their electric quadrupole moments while the para species with $J = 0$ (i.e. spherically symmetric) serve as inert diluants. At low temperatures the $J = 1$ molecules align along local axes to minimize their interaction energy but in random dilute mixtures ($X_{\text{ortho}} < 55\%$) only short range ordering with a random variation of molecular alignments from site to site is observed. The low temperature state for low concentrations has been referred to as

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a quadrupolar glass[6] but no true phase transition to the glassy regime has been observed.[1,16,17]

In the so-called "quadrupolar glass" the quantum rotors cannot in general be described by pure states and a density matrix formalism is needed to describe the orientational degrees of freedom. The purpose of this article is to determine the precise limitations on the local order parameters (molecular alignment etc.) from the quantum mechanical conditions imposed on the density matrix and to discuss the implications for the analysis of NMR experiments. Some of the considerations for the spin-1 density matrix description have been given elsewhere,[23-29] but solid H_2 is a special case because the orbital angular momentum is quenched.[6,27] Harris and Berlinsky[30] have discussed the classical density matrix for diatomic molecules. In the following sections we review the density matrix formalism for unit angular momentum and then discuss the case for solid ortho-para hydrogen mixtures.

II. Density Matrix Formalism

The most general description of the degrees of freedom of an assembly of quantum rotors with angular momentum $J = 1$ is given by the product of single particle 3 × 3 density matrices ρ_i for each site i. The ρ_i are completely described by

1. the molecular dipole moments $\langle J_x \rangle_i$, $\langle J_y \rangle_i$, $\langle J_z \rangle_i$, and
2. the quadrupole moments $\langle J_z^2 \rangle_i$, $\langle J_x J_y \rangle_i$, $\langle J_y J_z \rangle_i$ . . . . . of which only 5 are independent variables.

Instead of Cartesian components we consider for general J a set of irreducible tensorial operators π_{LM} with $0 \leqq \mathrm{L} \leqq 2J$ and the associated multipole moments

$$t_{lm} = Tr(\rho\pi_{LM}) \tag{1}$$

For simplicity we have dropped the site index i. The expansion of the single particle density operator in terms of the multipole moments is given by

$$\rho = \frac{1}{(2J + 1)} \sum_{L=0}^{2J} \sum_{M=-L}^{L} (2L + 1) t_{LM}^{*} \pi_{LM} \tag{2}$$

There are three conditions imposed on ρ: Hermiticity and both weak and strong positivity conditions.

For all Hermitean operators Q, the expectation values $\langle Q \rangle = Tr(\rho Q)$ must be real. ρ is therefore Hermitean and

$$t_{LM} = (-)^M t^*_{L-M}$$

$\pi_{00} = \mathbb{1}_3$, the 3 × 3 unit matrix operator and $t_{00} = 1$.

The weak positivity conditions are given by

$$\frac{1}{2J+1} \leqq Tr\rho^2 \leqq 1 \tag{3}$$

The lower bound corresponds to the case when all the eigenvalues of ρ^2 are equal and the upper bound to the case when one eigenvalue is unity and all others are zero.

The eigenvalues of ρ must be positive definite because they represent the probabilities of realizing some given state and this leads to the strong positivity conditions

$$0 \leqq \lambda_n \leqq 1$$

where λ_n is the nth eigenvalue. These conditions place the strongest limitations on the allowed values for the multipole moments and thus on the allowed values of the local order parameters for ortho-H$_2$ molecules in the solid mixtures.

For the purpose of calculations it is useful to construct orthonormal matrix representations of the irreducible operators π_{LM} in the representation (JJ_z). For $J = 1$ these are given by the following 3 × 3 matrix operators with rows (and columns) labelled by the eigenvalues 1,0, -1 of J_z.

$$\pi_{10} = \frac{1}{\sqrt{2}} J_z = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{4(a)}$$

$$\pi_{11} = -\frac{1}{2} J_+ = -\frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} \tag{4(b)}$$

$$\pi_{20} = \frac{1}{\sqrt{6}} (3J_z^2 - J^2) = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{4(c)}$$

$$\pi_{21} = -\frac{1}{2}(J_zJ_+ + J_+J_z) = -\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{bmatrix} \qquad 4(d)$$

$$\pi_{22} = \frac{1}{2}J_+^2 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad 4(e)$$

$$\pi_{L,M} = (-)^M \pi^\dagger_{L,-M}$$

and

$$Tr(\pi_{LM}\pi^\dagger_{L'M'}) = \delta_{LL'}\delta_{MM'}$$

The quadrupole operators π_{2M} transform analogously to the spherical harmonics $Y_{2m}(\alpha,\beta)$ with respect to rotations of the coordinate axes.

The reference axes have remained arbitrary in the discussion so far and we are therefore free to choose local references axes that correspond to the local symmetry for each molecule. The natural choice for the z-axis is along the net component of the angular momentum at a given site, i.e. such that $\langle J_x\rangle = \langle J_y\rangle = 0$ with $\langle J_z\rangle \neq 0$. This is not appropriate for solid hydrogen because in the absence of interactions which break time reversal symmetry, the $\langle J_\alpha\rangle$ must vanish for all α in the solid. This is the so-called "quenching" of the orbital angular momentum.[31] Before we consider the case of quenching let us recall that the general form for $\rho_{J=1}$ is in the above notation

$$\begin{aligned} \rho &= \frac{1}{3}\pi_3 + \sum_n \mu_n \pi_{1n} + \sum_m Q_m \pi_{2m} \\ \mu_n &= \langle \pi^\dagger_{1n}\rangle \text{ and } Q_m = \langle \pi^\dagger_{2m}\rangle \end{aligned} \qquad (5)$$

are the dipole and quadrupole moments respectively. $\mu_0 = 1/\sqrt{2}\,\langle J_z\rangle$ is the only non-zero dipole moment. We are still free to choose the x and y axes in the plane normal to $0z$ and we will choose these axes such that Q_2 is real.

$$\text{i.e.}\quad Q_2 = \frac{1}{2}\langle J_x^2 - J_y^2\rangle \qquad (6)$$

and

$$\langle J_xJ_y + J_yJ_x\rangle = 0$$

Q_2 measures the departure from axial symmetry about the z-axis and is sometimes called the eccentricity.[32] It can be shown that Q_1 and Q_{-1} also vanish for this choice of local reference frame and the density matrix may be written as

$$\rho = \frac{1}{3}\pi_3 + \frac{1}{\sqrt{2}}\mu_0 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \begin{bmatrix} \frac{1}{\sqrt{6}}Q_0 & 0 & Q_2 \\ 0 & \frac{-2}{\sqrt{6}}Q_0 & 0 \\ Q_2 & 0 & \frac{1}{\sqrt{6}}Q_0 \end{bmatrix} \tag{7}$$

$$Q_0 = \frac{1}{\sqrt{6}}\langle 3J_z^2 - 2\rangle \tag{8}$$

is the alignment[32] along the z-axis. Experimentalists prefer order parameters such as the alignment to have unit amplitude for maximum alignment and it is therefore more natural to define the *alignment* as

$$\sigma = \langle 1 - 3/2\, J_z^2\rangle = -\sqrt{3/2}\, Q_0. \tag{9}$$

The only other intrinsic quadrupolar order parameter is the *eccentricity*

$$\eta = \langle J_x^2 - J_y^2\rangle = 2Q_2 \tag{10}$$

which also has a maximum amplitude of unity. In terms of these more familiar parameters we now have

$$\rho = \frac{1}{3}\pi_3 + \frac{1}{2}\mu_z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \begin{bmatrix} -\frac{1}{3}\sigma & 0 & \frac{1}{2}\eta \\ 0 & \frac{2}{3}\sigma & 0 \\ \frac{1}{2}\eta & 0 & -\frac{1}{3}\sigma \end{bmatrix} \tag{11}$$

The three eigenvalues of ρ are

$$\lambda_1 = \frac{1}{3} + \frac{2}{3}\sigma$$

and

$$\lambda_{2,(3)} = \frac{1}{3} - \frac{1}{3}\sigma\,(\pm)\,\frac{1}{2}\sqrt{\mu_z^2 + \eta^2} \qquad (12)$$

The strong positivity conditions, $\lambda_n \geqq 0$, are therefore seen to restrict the allowed values of the local order parameters σ,η and μ to the interior of a cone (see Figure 1) in the 3D parameter space. (Where there is no ambiguity we drop the subscript z on μ_z.) The vertex of the cone is located at $\sigma = 1$, $\mu = \eta = 0$, corresponding to the pure state $|\psi\rangle = |J_z = 0\rangle$, and the base of the cone is defined by the circle $\sigma = -1/2$, $\mu^2 + \eta^2 = 1$ which corresponds to the pure state $|\psi\rangle = \cos\gamma\,|1\rangle + \sin\gamma\,|-1\rangle$ with $\langle J_z\rangle = \cos 2\gamma$ and $\langle J_+^2\rangle = \sin 2\gamma$. (The polar angle γ generates the points on the circle of the cone's baseplate.)

The results shown in Figure 1 are identical to those obtained by Minnaert[25] using the Eberhard-Good theorem[33] and the conditions imposed on the terms $S_n = \mathrm{Tr}\rho^n$ for general J. The underlying physics is however easier to understand in the present discussion in terms of the eigenvalues of the density matrix and their relation to probability amplitudes. In his analysis of the states of polarization of the deuteron, Lakin[23] also reached the same conclusions as Minnaert.[25] Having established the physical considerations which determine the limited range of allowed values for the order parameters, we now turn to the special case of solid hydrogen.

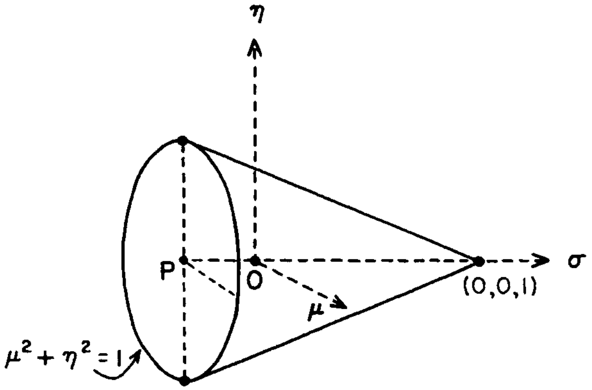

FIGURE 1 The allowed values of the order parameters $\mu = \langle J_z\rangle$ (net angular momentum), $\sigma = \langle 1 - 3/2\,J_z^2\rangle$ (the alignment) and $\eta = \langle J_x^2 - J_y^2\rangle$ (the eccentricity) for a spin-1 particle are restricted to the interior of a cone in parameter space with its vertex at ($\sigma = 1$, $\mu = \eta = 0$) and base defined by the circle $\sigma = -1/2$, $\mu^2 + \eta^2 = 1$ with center P at $(0, 0, -1/2)$.

III. APPLICATION TO SOLID HYDROGEN

There are two distinct molecular species of hydrogen, ortho- and parahydrogen, corresponding to the two ways of realizing a totally antisymmetric wave function. The para form has an antisymmetric nuclear spin wave function ($I_{\text{total}} = 0$) and a symmetrical orbital wave function (J even) while the ortho form has a symmetrical nuclear function ($I_{\text{total}} = 1$) and an antisymmetrical orbital function (J odd). The separation of the rotational energy levels is given by $E_J = BJ(J + 1)$ with $B = 85.37$ K and in the solid at low temperatures only the lowest J values, $J = 0$ for para-H_2 and $J = 1$ for ortho-H_2, need be considered. Although para-H_2 in the spherically symmetric $J = 0$ state is the true ground state, the conversion of the ortho species to the para form is very slow. It is a bimolecular process with a rate constant of 1.5% per hour. This slow conversion enables the experimenter to explore a continuous range of concentrations by simply allowing the samples to age while held at low temperature.

At high temperatures the ortho molecules are free to rotate but at low temperatures the anisotropic forces between the molecules lift the rotational degeneracy and the molecules align themselves with respect to one another to minimize their interaction energy. For high ortho concentrations one observes a periodic alignment in a Pa_3 configuration with four interpenetrating simple cubic sub-lattices,[1] the molecules being aligned parallel to a given body diagonal in each sub-lattice. The body diagonals are the local symmetry axes z_α for each sub-lattice and the order parameters, $\sigma_\alpha = \langle 1 - 3/2\, J_{z\alpha}^2 \rangle$, are the same at each site. $\sigma_\alpha = 1$, apart from a small correction due to zero-point librations,[4] and the molecules may to a good approximation be described in terms of the pure states $|\phi_i\rangle = |J_{z_{\alpha i}} = 0\,\rangle$ for each site i.

The long range periodic order for the molecular alignments is lost below a critical concentration of approximately 55% and the NMR studies indicate that there is only short range orientational ordering with a broad distribution of local symmetry axes and local order parameters throughout the sample. This purely local ordering has been referred to as a quadrupolar glass in analogy with the spin glasses, but unlike the dipolar spin glasses, there is no well defined transition from the disordered (para-orientational) state to the glass regime.

It is important to realize that in the glass-like regime with the observed broad distribution of order parameters, the ortho molecules cannot be described in terms of pure states. The reason for this is that inside the manifold $J = 1$, particles in a pure state can only take one of two limiting cases for their alignment; either $\sigma = 1$ with $\eta = 0$, or $\sigma = -1/2$ with $\eta = \pm 1$.[27] A density matrix formalism must be used to describe the ortho molecules in the glass regime where there is a large number of sites with intermediate values of σ.[4] There is some confusion in the literature concerning this point. In a recent review[1] of the properties of solid hydrogen it was claimed that negative values of σ had been ruled out as unphysical following arguments given in Van Kranendonk's book[34] but this is not strictly correct.[35] Van Kranendonk's remarks refer to considerations of the pure states $|J = 1, J_z = 0\rangle$ and $|J = 1, J_z = \pm 1\rangle$ *only*. He does not discuss either the density matrix approach or the formulation of the intrinsic quadrupolar order parameters σ and η needed to describe the orientational degrees of freedom of the ortho-H_2 molecules. Harris and Meyer[35] do point out that negative values of σ are not highly probable. There are however, limitations on the allowed values of σ and η for a given set of principal axes (chosen to coincide with the local symmetry axes) and we will now describe them in detail.

It is generally believed that the orbital angular momentum J is quenched[31] in the solid so that $\langle J_\alpha \rangle$ vanishes for all components α. The reason for this quenching (following the arguments of Van Vleck[31]) is that in the solid the electronic distribution of a given molecule may (to a first approximation) be regarded as being in an inhomogeneous electric field which represents the effect of the other molecules. This inhomogeneity removes the spatial degeneracy of the molecular wave function which must therefore be real and the expectation value of the orbital angular momentum $\langle i\hbar\, \partial/\partial\phi \rangle$ must accordingly vanish. Bethe[36] has shown that it is possible that the orbital angular momentum may only be partially quenched in some solids. In solid hydrogen it is believed that the dipole moments $\langle J_z \rangle$ are less than 10^{-4} otherwise they would lead to detectable NMR line shifts through the spin-rotational coupling $H_{SR} = -ah\vec{I}\cdot\vec{J}$ where $a = 114$ kHz.[37]

The quenching of the angular momentum in solid H_2 has two consequences for the limits on the allowed values for the order parameters. *Firstly*, from the discussion in Section I, it is seen that the allowed values of σ and η now lie within a triangle bounded by the three lines (Figure 2).

$$\frac{1}{3} + \frac{2}{3}\sigma \geqq 0$$

$$\frac{1}{3} - \frac{1}{3}\sigma \pm \frac{1}{2}\eta \geqq 0$$

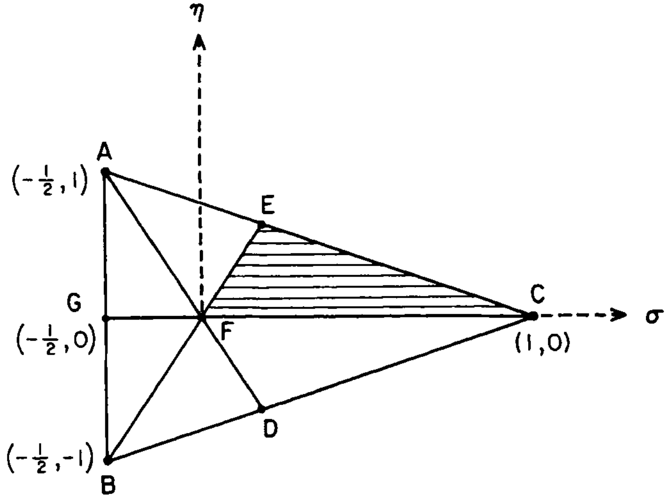

FIGURE 2 The allowed values of the orientational order parameters $\sigma = \langle 1 - 3/2\, J_z^2\rangle$ and $\eta = \langle J_x^2 - J_y^2\rangle$ for a spin-1 particle whose angular momentum is quenched are restricted to the interior of a triangle with vertices ($\sigma = 1$, $\eta = 0$) and ($\sigma = -1/2$, $\eta = \pm 1$). Not all points inside the triangle are physically indistinguishable and we need only consider the hatched region of ΔCEF. All other allowed values for (σ,η) can be generated by a suitable relabeling of the principal axes (x,y,z).

which represent the strong positivity conditions for the eigenvalues of ρ when the angular momentum is quenched. The allowed values of (σ,η) are therefore constrained to $-1/2 \leqq \sigma \leqq 1$ and $|\eta| \leqq 1 \pm 2/3\sigma$. *Secondly* and more importantly, because $\langle J_\alpha\rangle = 0$ for all α, we are now free to choose the Z-axis which was previously fixed by the net component of the angular momentum. The natural choice for the local reference axes is now the set of principal axes for the quadrupolar tensor

$$Q_{\alpha\beta} = \left\langle \frac{1}{2}(J_\alpha J_\beta + J_\beta J_\alpha) - \frac{1}{3} J^2 \delta_{\alpha\beta} \right\rangle$$

The choice of principal axes is not unique, however, because after finding one set we can always find another five by relabeling axes. This means that not all of the points in the "allowed" portion of the (σ,η) plane are inequivalent and we will show that we only need to consider the hatched region (triangle CFE) in Figure 2 bounded by the lines $\eta = 0$ and $\eta = 2\sigma$. All other areas of the triangle of allowed values can be obtained from the triangle CFE by a suitable relabeling of the axes. (This is not the only choice that can be made for a "*primitive*" area of inequivalent values of (σ,η). Another choice is illustrated in Figure 3 and is discussed below.)

One point that is not generally understood is that the pure states

$$\Psi_c = |J_z = 0\rangle \qquad \text{and}$$

$$\Psi_A = \frac{1}{\sqrt{2}}(|J_z = 1\rangle + |J_z = -1\rangle)$$

are *NOT* inequivalent.[27] (The labels A through F refer to the special points on the triangle of allowed values shown in Figure 2 and the corresponding state functions are listed in Table 1. The state Ψ_A can be obtained from Ψ_C by a rotation of the axes by $3\pi/2$ about the x-axis. The rotation operator

$$R_x\left(\frac{3\pi}{2}\right) = \exp\left(-\frac{i}{\hbar}\frac{3\pi}{2}J_x\right)$$

$$= 1_3 + \frac{i}{\hbar}J_x - \left(\frac{J_x}{\hbar}\right)^2 \tag{13}$$

and

$$R_x\left(\frac{3\pi}{2}\right)\Psi_C = e^{i\pi/2}\Psi_A \tag{14}$$

The rotation $R_x(3\pi/2)$ corresponds to the relabeling of the axes $(x,y,z) \rightarrow (x,-z,y)$ which leaves the state F invariant and maps D onto the point G in parameter space.

We can furthermore show that the rotation $R_x(3\pi/2)$ is a 1:1 mapping of the following triangular regions of parameter space onto one another

$$\Delta\text{CDF} \rightarrow \Delta\text{AGF},$$

$$\Delta\text{CEF} \rightarrow \Delta\text{AEF}, \tag{15}$$

and

$$\Delta\text{BDF} \rightarrow \Delta\text{BGF}$$

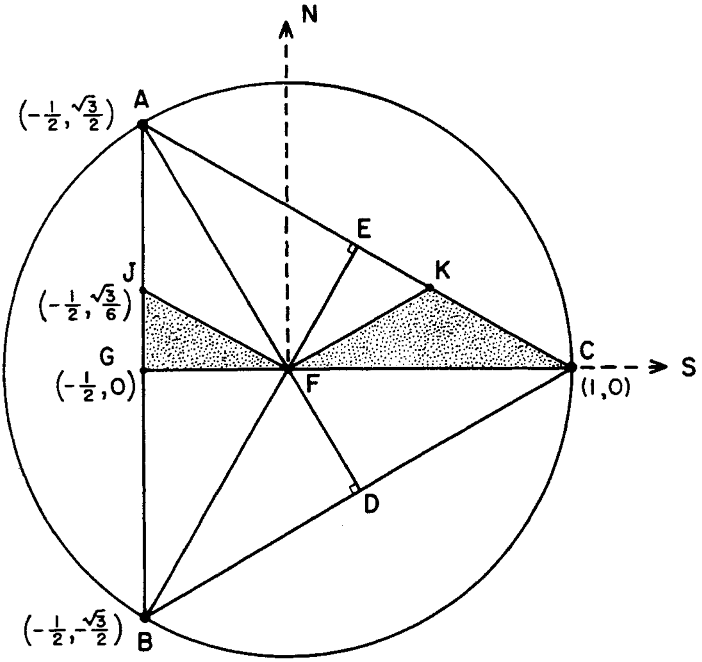

FIGURE 3 Diagram of allowed orientational order parameters for the orthonormal set $S = \sigma = \langle 1 - 3/2 J_z^2 \rangle$, $N = \sqrt{3}/2\ \eta = \sqrt{3}/2 \langle J_x^2 - J_y^2 \rangle$. Relabeling of the principal axes (x,y,z) corresponds to reflection in one or other of the bisectors BE, AD or CG of the triangle of allowed values.

This is seen by considering the transformation

$$\rho'\ (\sigma',\eta') = R_x^{\dagger}\left(\frac{3\pi}{2}\right)\ \rho(\sigma,\eta)\ R_x\left(\frac{3\pi}{2}\right)$$

using the matrix representation

$$R_x\left(\frac{3\pi}{2}\right) = \begin{bmatrix} \frac{1}{2} & \frac{i}{\sqrt{2}} & -\frac{1}{2} \\ \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\ -\frac{1}{2} & \frac{i}{\sqrt{2}} & \frac{1}{2} \end{bmatrix}$$

TABLE I

Special Points in Orientational Order Parameter Space. (see Figure 1)

Label	Parameters (σ,η)	Wave Function
A	$\left(-\frac{1}{2}, 1\right)$	$[\lvert 1\rangle + \lvert -1\rangle]/\sqrt{2}$
B	$\left(-\frac{1}{2}, -1\right)$	$[\lvert 1\rangle - \lvert -1\rangle]/\sqrt{2}$
C	$(1,0)$	$\lvert 0\rangle$
D	$\left(\frac{1}{4}, -\frac{1}{2}\right)$	$[\lvert 1\rangle - \lvert -1\rangle - \sqrt{2}\lvert 0\rangle]/2$
E	$\left(\frac{1}{4}, \frac{1}{2}\right)$	$[i(\lvert 1\rangle + \lvert -1\rangle) - \sqrt{2}\lvert 0\rangle]/2$
F	$(0, 0)$	$[(-1+i)\lvert 1\rangle + (1+i)\lvert -1\rangle - \sqrt{2}\lvert 0\rangle]/\sqrt{6}$
G	$\left(-\frac{1}{2}, 0\right)$	$[(-1+i)\lvert 1\rangle + (1+i)\lvert -1\rangle]/2$

$R_x\,(3\pi/2)$: $\psi_C \to \psi_A$, $\psi_D \to \psi_G$; ψ_B, ψ_F, ψ_E fixed.
$R_z\,(\pi/2)$: $\psi_A \to \psi_B$, $\psi_E \to \psi_D$; ψ_C, ψ_F, ψ_G fixed.

We find that this relabeling transforms the points (σ,η) into new points (σ',η') given by

$$\begin{bmatrix} \sigma' \\ \eta' \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{3}{4} \\ 1 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} \sigma \\ \eta \end{bmatrix} \tag{16}$$

which corresponds to the mapping given by Equations (15).

The results of the relabeling transformations are particularly easy to understand if instead of the parameters (σ,η) we consider the pair $(S = \sigma,\ N = \sqrt{3}/2\ \eta)$ which transform orthonormally when the axes are rotated. The parameter space (S,N) shown in Figure 3 has the three pure states at the vertices of an equilateral triangle which is circumscribed by a circle of unit radius. The rotation $R_x(3\pi/2)$ in real space simply corresponds to a reflection in (S,N) parameter space through the line BE with the transformed points given by

$$\begin{bmatrix} S' \\ N' \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} S \\ N \end{bmatrix} \quad - \tag{17}$$

Similarly, the relabeling $(x,y,z) \rightarrow (y,x,z)$ corresponds to a reflection through the line CG (i.e. $S = 0$). The entire area of allowed values in parameter space can therefore be mapped out starting only with the triangle ΔCFE by simply relabelling the principal axes. We therefore only need to consider the hatched region of parameter space shown in Figure 2 in order to describe *all* physically distinguishable orientational states for ortho-H$_2$ molecules in the solid state.

We can also consider other choices for the primitive areas in the orthonormal (S,N) parameter space. The choice of ΔCEF can be retained, or we may prefer to consider only states with the minimum values of the eccentricity N and the primitive set is then the sum of ΔCFK and ΔGFJ in Figure 3. This latter choice is equivalent to the first choice because ΔGFJ and ΔFEK are equivalent.

IV. INTERPRETATION OF NMR SPECTRA

The interpretation of the NMR spectra has been discussed in detail elsewhere.[1,16,17] The essential point is that the intramolecular nuclear dipole–dipole interaction H_{DD} can be written in terms of products of the irreducible tensorial operators π_{LM} in the manifold $J = 1$ with the corresponding nuclear spin operators N_{LM} in the manifold $I = 1$.

$$H_{DD} = hD \sum_M \pi_{2M} N^{\dagger}_{2M} \tag{18}$$

where $D = 173.06$ kHz.

In high magnet fields the field direction (say $0z$) is the natural quantization axis for the nuclear spins, and the secular component $(M = 0)$ of H_{DD} results in a fine structure for the NMR spectrum with *each* molecule contributing a doublet to the spectrum with frequencies

$$\Delta\nu_i = \pm \sqrt{3/2}\, D\, \langle\pi_{20}(i)\rangle_{0z}$$

The expectation value $\langle\pi_{20}\rangle_{0z}$ is evaluated with respect to the magnetic field axis, *NOT* the local molecular symmetry axis with respect to which the local order parameters (σ,η) are defined. Considering the transformation to the local frame we find

$$\Delta\nu_i = \pm D\left[-\sigma_i P_2(\cos\theta_i) + \frac{3}{4}\eta_i \sin^2\theta_i \cos 2\phi_i\right] \tag{19}$$

where (θ_i,ϕ_i) are the polar angles defining the orientation of the applied magnetic field with respect to the local molecular symmetry axes.

In the case where there is a broad distribution of order parameters and local symmetry axes it is not possible to deconvolute the NMR lineshapes uniquely.[12] One has instead assumed local axial symmetry at each site $(\eta_i = 0)$ and a powder distribution for the angles θ_i. The spectra can then be interpreted in terms of a broad distribution of local alignments σ.[1,4,12] This is unsatisfactory because there is no microscopic justification for assuming axial symmetry at each site.

We propose that the assumption of axial symmetry can be tested experimentally by examining the zero field NMR absorption spectrum. Although Reif and Purcell[38] have carried out zero field studies for the long range ordered phase where it is known that σ is constant and $\eta = 0$, it has not previously been considered for the glass phase.

In zero applied magnetic field the degeneracy of the nuclear spin levels is lifted only by the intramolecular spin–spin interactions,

$$H_{DD}(i) = hD\left[-\frac{1}{3}\sigma_i\,(3I_{zi}^2 - I^2) + \frac{1}{4}\eta_i(I_{+i}^2 + I_{-i}^2)\right] \tag{20}$$

The tensorial operators for the rotational degrees of freedom have been replaced by the expectation values σ,η. An applied radio-frequency field can induce magnetic dipole transitions between the nuclear spin levels in analogy with the so-called pure quadrupole resonance absorption (See Abragam, Chapter VII.[39]) The components I_{zi}, I_{+i}, I_{-i} of the nuclear spin are referred to the local molecular symmetry frame and the resonance frequencies are independent of the orientation of the crystal axes in space. The eigenstates of H_{DD} are $|I_z = 0\rangle$, and $|\pm\rangle = [|I_z = +1\rangle \pm |I_z = -1\rangle]/\sqrt{2}$. For each molecule i, three resonance lines can be expected corresponding to the transitions $|+\rangle \rightarrow |0\rangle$, $|-\rangle \rightarrow |0\rangle$ and $|+\rangle \rightarrow |-\rangle$ with frequencies $\nu_i^1 = D(-\sigma_i + 1/2\eta_i)$, $\nu_i^2 = D(-\sigma_i - 1/2\eta_i)$ and $\nu_i^3 = D\eta_i$, respectively. If axial symmetry is a good approximation, there is only one line at $\nu_i = -D\sigma_i$ and the detailed shape of the NMR absorption spectrum in zero field will be identical with that observed at high fields. On the other hand, if there is a significant departure from axial symmetry the high and zero field spectra will not be identical.

V. CONCLUSION

We have determined that in general the orientational degrees of ortho-H_2 molecules in the solid need to be described in terms of density matrices. The ortho molecules have unit angular momentum and the single particle density matrices are completely determined by five independent parameters (if the angular momentum is quenched). These parameters are

1. the three principal axes (x,y,z) for the quadrupole tensor,
2. the alignment $\sigma = \langle 1 - 3/2\, J_z^2\rangle$, and
3. the eccentricity $\eta = \langle J_x^2 - J_y^2\rangle$.

The positivity conditions for the density matrix show that the only allowed values of (σ,η) are those enclosed in a triangle in (σ,η) space whose vertices are the pure states $|J_z = 0\rangle$ and $|J_z = \pm 1\rangle$. Not all of these allowed values are physically indistinguishable because one may relabel the principal axes and we have shown that one can determine a simple primitive set of order parameters which are inequivalent by the choice $2\sigma \geqq \eta \geqq 0$. Orientational states with negative σ analogous to the classical probability distribution in the form of an oblate ellipsoid are not excluded on theoretical grounds.

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