Two-Libron Spectrum of Solid H_2 and D_2 [†]

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It is shown that the "two-libron" lines in the Raman spectrum of solid hydrogen result from the large cubic anharmonicity of the quadrupole-quadrupole Hamiltonian. A localized picture is used to describe the interaction of two librational excitations on neighboring molecules, and dynamic interactions with other molecules are treated perturbatively. In this approximation the average single-libron energy agrees with the anharmonic calculation in the accompanying paper. Using a value of the quadrupole-coupling constant obtained from the single-libron spectrum, the resulting two-libron energies and Raman transition probabilities are in excellent agreement with the observed spectrum.

I. INTRODUCTION

Over thirty years ago Pauling[1] suggested that the residual entropy observed in solid hydrogen at temperatures of order 10 K was due to the degeneracy associated with the orientations of the molecular axes. This interpretation was supported by the observation[2] of an anomaly in the specific heat of solid H_2 rich in the $(J = 1)$ species. These experiments were later extended to lower temperatures[3] where the peak in the specific heat indicated the presence of a new low-temperature phase for samples with $(J = 1)$ concentration above about 0.6. More recently, analogous experiments[4] have been performed on solid D_2 at high $(J = 1)$ concentration with similar results. It has only been in the past few years, however, that the properties of this orientationally ordered phase have been elucidated. In particular, the long-standing uncertainty about the crystal structure of solid hydrogen has been settled by the x-ray[5] and neutron-diffraction[6] work of Mills and White and collaborators. From this work it is clear that in the orientationally disordered phase both H_2 and D_2 crystallize in an hcp structure,[7] whereas the ordered phases occur with an fcc structure. These experiments were quite delicate, and it was therefore not possible to deduce unequivocally the orientations of the molecules in the low-temperature phase. However, theoretical calculations by Nagai and Nakamura[8] showed that, assuming the dominance of the electrostatic quadrupole-quadrupole (EQQ) interactions,[9] the classical ground state was probably one consisting of four sublattices, each sublattice consisting of molecules oriented preferentially along one of the four body diagonals. As James and Raich[10] showed, the corresponding quantum-mechanical ground state has equilibrium orientations coincident with those of the classical ground state. Although thermodynamic measurements[2-4,11,12] were consistent with this model, they did not provide a very sensitive test of the proposed sublattice structure.

Recently, Hardy *et al.*[13] have observed the elementary excitations (librons) of the system directly via Raman scattering. For both H_2 and D_2 the observed spectrum was found to contain five lines. In contrast, for the four-sublattice structure, space group $Pa\,3\,(T_h^6)$, the single-libron spectrum[14-19] should consist of three lines, one doubly degenerate and two triply degenerate.

Various explanations have been advanced for the presence of these two "extra" lines. Hardy *et al.*[13] suggested that either the structure is a rhombohedral distortion of the $Pa3$ structure, or else that the structure is $Pa3$, but that there is a strong coupling between the molecular rotations (librons) and the lattice vibrations. In addition, other sublattice configurations on an fcc lattice have been considered.[19,20] None of these explanations has provided even a qualitative fit to the data. The possibility of significant effects from a distortion seems unlikely. Although such a distortion has been inferred from x-ray data[21] for the analogous case of αN_2, it has no effect on the libron spectrum.[22] It is hard to see how the libron-phonon coupling could be strong enough to significantly alter the selection rules. Previous estimates[17,23,24] of this coupling have shown it to be perturbative. Finally, the two-layer structure proposed by James[25] on the basis of a nearest-neighbor model has been shown by him[20] to become unstable when further interactions are taken into account. In any event, the libron spectrum from this structure is very different from the observed spectrum.[19]

More recently, Nakamura and Miyagi[26] proposed that the two highest-frequency lines in the libron spectrum are the result of two-libron processes. However, the intensity for these processes was calculated to be only 2% of the one-libron intensity. This result is understandable, since the proposed mechanism depended on the existence of zero-point motion in the orientational system. This zero-point motion is analogous to, but smaller than, that in a three-dimensional Heisenberg antiferromagnet of

spin 1.[27,28] Elliott[29] has also noted the possibility of
an interpretation based on two-libron processes,
but he too did not suggest a plausible mechanism.
In this paper we show that the anharmonic libron-
libron interactions provide a mechanism for the
appearance of these two-libron states in the Raman
spectrum. As in the analogous case of the two-
magnon excitation,[30] the two librons are created on
neighboring lattice sites. Consequently, the posi-
tions of the peaks in the observed two-excitation
spectrum can be calculated within a localized
model. As reported previously,[31] the results of
such a calculation are in striking agreement with
the observed Raman spectrum.

Briefly, this paper is organized as follows. In
Sec. II we attempt to motivate the formalism used
for the calculation. Here we give order-of-magni-
tude estimates of the intensity, from which we con-
clude that the proposed mechanism involving an-
harmonicity is important. In Sec. III we describe
the formalism of the localized model. Several ap-
proximation schemes are discussed. In the most
refined of these, the effects of anharmonic libron-
libron interactions are the same as are found in a
libron calculation correct to first order in $1/z$.
(Here z is the number of nearest neighbors: for
an fcc lattice, $z=12$.) Here we also give the ef-
fective matrix element determining the intensity
of the two-libron processes. In Sec. IV we give
the numerical results of the various calculations,
and compare them to the observed Raman spec-
trum. We find excellent agreement between our
calculations and the experimental data using the
quadrupolar-coupling constant determined by
fitting the observed single-libron spectrum to cal-
culations which include anharmonic libron-libron
interactions. The interpretation and significance
of the single-libron spectrum will be discussed in
the accompanying paper.[32]

II. MOTIVATION

There is a very close analogy between spin waves
in an antiferromagnet and librational waves in
solid hydrogen.[27] Likewise, the two-libron pro-
cesses in solid hydrogen are analogs of the two-
magnon processes in antiferromagnets which have
been observed only recently.[30] These processes
represent one of the most convincing proofs of the
existence of magnon-magnon interactions. Simi-
larly, in solid hydrogen the two-libron processes
demonstrate the importance of libron-libron inter-
actions.

In both solid hydrogen and in insulating antifer-
romagnets the interactions between the elementary
excitations can be obtained by expanding the
Hamiltonian to higher order in the harmonic nor-
mal-mode amplitudes. Thus in both cases it is
possible to discuss the two-excitation states from

a fundamental point of view. For the antiferro-
magnet the exact microscopic mechanism whereby
the radiation field couples into these two-magnon
states is not known.[33] In solid hydrogen, on the
other hand, the relevant interactions between the
librons and the radiation field are known,[19] and con-
sequently the calculation of the two-libron Raman
spectrum described below is on a firm theoretical
basis.

As we shall see, the two-libron states observed
in the Raman spectrum result from the simulta-
neous creation of two librons on neighboring lattice
sites. In this respect the two-libron processes are
similar to the two-magnon processes.[30,33,34] As
pointed out by Elliott and Thorpe,[33,34] this way of
sampling the two-magnon density of states empha-
sizes states in which the two excitations are close
to one another. In contrast, the usual unweighted
two-magnon density of states for zero total momen-
tum of the two magnons has its peak at twice the
peak of the single-magnon density of states. The
observed two-magnon spectrum is calculated by
multiplying the usual two-magnon density of states
by a matrix element which shifts the peak in the
observed density of states. Elliot and Thorpe[33,34]
showed that although the shape of the observed
density of states can only be obtained by a detailed
calculation, the shifted peak in the density of
states coincides with the energy two localized ex-
citations would have on neighboring lattice sites.
Our idea is to treat the two-libron problem in
solid hydrogen in much the same way. We assume
that because the two librons are created on neigh-
boring sites, the peaks in the two-libron density
of states will coincide with the sharp energy levels
for two librons on neighboring sites. Such a lo-
calized picture unfortunately yields no estimate of
the width or shape of the two-libron lines. It is
clear, however, that because the momentum of
each libron is not restricted, these lines should
be much broader than the single-libron lines. Ex-
perimentally,[13] this is indeed the case.

The above considerations apply to most con-
ceivable two-libron processes, since the proba-
bility for creating two librons independently is
negligibly small. As mentioned above, the mech-
anism proposed by Nakamura and Miyagi[26] depends
on the orientational zero-point motion, and hence
is not effective. On the other hand, it was shown
earlier[19] that the anharmonic libron-libron inter-
actions are quite strong. In contrast to the mag-
netic case, where the magnon-magnon interactions
are mainly quartic in the magnon amplitudes, the
libron-libron interactions are predominantly cubic
in the libron amplitudes. As a result, the two-
libron states are strongly coupled into the single-
libron states, whereas in the magnetic case the
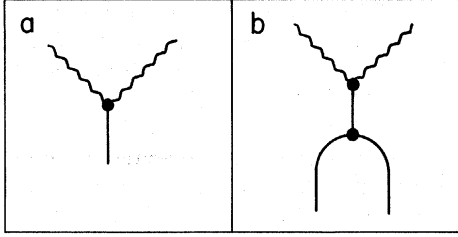two-magnon states are only very weakly coupled

FIG. 1. (a) One- and (b) two-libron Raman processes. The wiggly lines represent the incoming and outgoing photons and the solid lines represent librons. In the two-libron process a virtual libron decays via the cubic term into two final-state librons.

(e.g., by dipolar interactions) into the single-magnon states.

Even the crudest possible estimate confirms these ideas. In Fig. 1(a) we show the process responsible for the single-libron spectrum. The associated total intensity I_1 in the single-libron spectrum is then of order

$$I_1 \sim |\mathcal{K}_{\text{int}}|^2 , \qquad (2.1)$$

where $\mathcal{K}_{\text{int}}$ described the interaction between the librons and the photons.[19] In Fig. 1(b) we show the process responsible for the two-libron spectrum.[31] In this process a single libron is created by $\mathcal{K}_{\text{int}}$, and this single libron then breaks up into two librons under the cubic anharmonic libron-libron interaction V_3. The total intensity I_2 for this process is of order

$$I_2 \sim |V_3|^2 |\mathcal{K}_{\text{int}}|^2 |\Delta E|^{-2} , \qquad (2.2)$$

where ΔE is the average excitation energy of the intermediate state. The cubic anharmonic terms also lead to a shift in the single-libron energy $\Delta E^{(3)}$, which in second-order perturbation theory is of order[19]

$$\Delta E^{(3)} \sim |V_3|^2/\Delta E . \qquad (2.3)$$

Comparing Eqs. (2.1) and (2.2) we see that

$$I_2/I_1 \sim \Delta E^{(3)}/\Delta E . \qquad (2.4)$$

Using the results of Ref. 19 for $\Delta E^{(3)}$ and setting ΔE equal to the harmonic libron energy 21.2Γ, we estimate that the total intensity in the two-libron spectrum is about 20% as large as that in the single-libron spectrum, thus confirming the importance of the proposed mechanism.

III. FORMALISM

As Nakamura[9] has shown, the electrostatic quadrupole-quadrupole (EQQ) interactions are the most important orientational interactions between molecules in solid hydrogen. The Hamiltonian for this interaction is

$$\mathcal{K} = \frac{1}{2} \sum_{i,j} \mathcal{K}_{ij} , \qquad (3.1)$$

where[35]

$$\mathcal{K}_{ij} = \frac{20}{9} \pi (70\pi)^{1/2} \Gamma_0 \left(\frac{R_0}{R_{ij}}\right)^5$$

$$\times \sum_{M,N} C(224; M, N) \, Y_2^M(\hat{\Omega}_i) \, Y_2^N(\hat{\Omega}_j) \, Y_4^{M+N}(\hat{\Omega}_{ij})^* . \qquad (3.2)$$

Here $C(224; M, N)$ is a Clebsch-Gordan coefficient, $Y_J^M(\hat{\Omega})$ is a spherical harmonic in the phase convention of Rose,[36] and $\hat{\Omega}_i = (\theta_i, \varphi_i)$ and $\hat{\Omega}_{ij} = (\theta_{ij}, \varphi_{ij})$ specify the orientations of, respectively, the ith molecule and the intermolecular separation vector between molecules i and j relative to an axis fixed in the crystal. In Eq. (3.2) Γ_0 is the EQQ coupling constant, which is given, assuming a rigid lattice, as $\Gamma_0 = 6e^2 Q^2/25R_0^5$, where eQ is the molecular quadrupole moment and R_0 is the intermolecular separation. The main effect of phonons on the EQQ interaction is to renormalize Γ_0 to a somewhat smaller value,[24,37] and we shall therefore treat it as an emperically determined parameter, denoted Γ. Further- (than nearest-) neighbor interactions are included in Eq. (3.2) neglecting the effects of dielectric shielding.[24]

Following Raich and Etters[16] we write $\mathcal{K}_{EQQ}$ as

$$\mathcal{K}_{EQQ} = \frac{1}{2} \sum_{i,j} \sum_{M,N} \zeta_{ij}^{M,N} O_i^M O_j^N , \qquad (3.3)$$

where O_i^M are the operator equivalents of the spherical harmonics and are given as

$$O_i^0 = (J_{zi})^2 - \frac{2}{3} , \qquad (3.4a)$$

$$O_i^{\pm 1} = \pm (J_{zi} J_{\pm i} + J_{\pm i} J_{zi})/(2)^{1/2} , \qquad (3.4b)$$

$$O_i^{\pm 2} = \frac{1}{2} (J_{\pm i})^2 , \qquad (3.4c)$$

and the coefficients $\zeta_{ij}^{M,N}$ are defined by

$$\zeta_{ij}^{M,N} = \frac{20}{9} \pi (70\pi)^{1/2} A_M A_N \Gamma (R_0/R_{ij})^5$$

$$\times \sum_{M',N'} C(224; M', N') D_{M'M}^{(2)}(\chi_i)^* D_{N'N}^{(2)}(\chi_j)^* Y_4^{N'+M'}(\Omega_{ij})^* , \qquad (3.5)$$

where

$$A_0 = -\frac{3}{10}(5/\pi)^{1/2} , \qquad (3.6a)$$

$$A_{\pm 1} = \frac{1}{10}(15/\pi)^{1/2} , \qquad (3.6b)$$

$$A_{\pm 2} = -\frac{1}{10}(30/\pi)^{1/2} . \qquad (3.6c)$$

$D_{MM'}^{(2)}(\chi)$ is a rotation matrix,[36] and χ_i is the triad of Euler angles specifying the orientation of the local coordinate axes with respect to the crystal axes. The local coordinate axes for the ith molecule are chosen so that the z axis coincides with the equilib-

TABLE I. Quantization axes for the four sublattices with respect to the cubic crystal axes.

β^a	$\vec{\tau}_\beta{}^b$	Direction of z axis	Direction of x axis	Direction of y axis
1	$a/2(0,0,0)$	$[111]$	$[11\bar{2}]$	$[\bar{1}10]$
2	$a/2(1,1,0)$	$[\bar{1}\bar{1}1]$	$[112]$	$[110]$
3	$a/2(0,1,1)$	$[1\bar{1}1]$	$[1\bar{1}\bar{2}]$	$[110]$
4	$a/2(1,0,1)$	$[11\bar{1}]$	$[\bar{1}1\bar{2}]$	$[\bar{1}10]$

^{a}Here β labels the sublattice.

^{b}The position of a molecule on sublattice β can be written as $\vec{R} + \vec{\tau}_\beta$, where $\vec{R}$ is a lattice vector. Here $a = \sqrt{2}\,R_0$ where R_0 is the nearest-neighbor separation.

rium orientation of the ith molecule. The equilibrium orientation and local coordinate system for each of the four sublattices are given in Table I. The notation is discussed more fully in the accompanying paper.[32]

With this choice of axes, the mean-field ground state of $\mathcal{H}_{EQQ}$ is one in which $J_{zi} = 0$ for all molecules.[10] By expanding in terms of small deviations from this approximate ground state, one obtains a linear theory of libron waves similar to that of spin waves in a magnetic insulator.[27,28] It has been shown, however, that in so doing it is necessary to take into account the effects of further neighbors[18] and of anharmonic libron-libron interactions.[19,31] Accordingly, we ought to include such effects in the present calculation. In order to see how to do this in the simplest way, let us review the way in which these effects influence the calculations of the libron spectrum.

There are essentially two types of effects due to further-neighbor interactions. The first and most important effect is to modify the molecular field energy.[18,20] In the molecular field approximation one treats the truncated Hamiltonian $\mathcal{H}_{tr}$,

$$\mathcal{H}_{tr} = -\frac{2}{3} \sum_{i,j,M} \zeta_{ij}^{M,0} O_i^M \qquad (3.7a)$$

$$= -\frac{2}{3} \sum_i O_i^0 \sum_j \zeta_{ij}^{0,0} \qquad (3.7b)$$

$$= E_0 \sum_i \left(J_{zi}^2 - \frac{2}{3} \right), \qquad (3.7c)$$

where

$$E_0 = -\frac{2}{3} \sum_j \zeta_{ij}^{0,0}. \qquad (3.8)$$

Here we have used the symmetry of the space group to drop the terms with $M \neq 0$ in Eq. (3.7a). Assuming only nearest-neighbor EQQ interactions, one has

$$E_0^{nn} = 19\Gamma, \qquad (3.9)$$

whereas inclusion of further-neighbor interactions in the lattice sum of Eq. (3.8) yields

$$E_0 = 21.20\Gamma. \qquad (3.10)$$

The second effect of further-neighbor interactions is contained in the terms which have been dropped in writing the molecular field Hamiltonian. These terms, e.g., $\zeta_{ij}^{1,-1} O_i^1 O_j^{-1}$, describe processes in which excitations are delocalized. In second-order perturbation theory the molecular field energy is modified by processes in which excitations hop from one site to another and then hop back to the original site and also by fluctuations in which virtual pairs of librons appear. These effects give rise to shifts in the average libron energy of order $|\zeta_{ij}^{M,N}|^2$ [see Eq. (4.4) below]. Since $\zeta_{ij} \sim R_{ij}^{-5}$, we see that further-neighbor interactions are negligible in this context. Accordingly, we shall take account of further-neighbor interactions by using Eq. (3.10) for the unperturbed molecular field energy, but in all other contexts further-neighbor interactions will be ignored.

A tabulation of the coefficients $\zeta_{ij}^{M,N}$ for nearest-neighbor interactions is presented in Table II. This tabulation is for one particular pair of molecules. Coefficients describing the interactions between other pairs of molecules can be obtained from those in Table II by the transformations described in Appendix B of Ref. 19. It is clear from a consideration of the sublattice structure, however, that the operations of the space group $Pa\,3(T_h^6)$ take one specified pair of nearest-neighboring molecules into all other nearest-neighboring pairs of molecules. Hence, the energy-level schemes and Raman spectra of all such pairs are identical, and we shall consider only the pair whose coefficients are given in Table II.

We wish to describe the excitations of a pair of molecules when all the other molecules are in their molecular field ground state. More accurate treatments can be obtained by treating deviations from the molecular field ground state perturbatively. Thus we write the total Hamiltonian in the form

$$\mathcal{H}_{EQQ} = \epsilon^0 + \mathcal{H}_0 + V, \qquad (3.11)$$

where ϵ^0 is a constant fixing the zero of energy and

$$\mathcal{H}_0 = E_0 \sum_{k \neq 1,2} (J_{zk})^2 + \mathcal{H}_{12} - \frac{2}{3} \sum_{k \neq 1,2} \sum_M (\zeta_{1k}^{M,0} O_1^M + \zeta_{2k}^{M,0} O_2^M). \qquad (3.12)$$

Here we have labeled the molecules in the pair as 1 and 2 and the perturbation V is written as

$$V = V_{\text{pair-vac}} + V_{\text{vac-vac}}, \qquad (3.13)$$

where

$$V_{\text{pair-vac}} = 2 \sum_{k \neq 1,2} \sum_{M,N} [\zeta_{1k}^{M,N}(O_1^M + \tfrac{2}{3}\delta_{M0})$$

$$+ \zeta_{2k}^{M,N}(O_2^M + \tfrac{2}{3}\delta_{M0})](O_k^N + \tfrac{2}{3}\delta_{N0}), \qquad (3.14a)$$

$$V_{\text{vac-vac}} = \sum_{j,k \neq 1,2} \sum_{M,N} \zeta_{jk}^{M,N}(O_j^M + \tfrac{2}{3}\delta_{M0})(O_k^N + \tfrac{2}{3}\delta_{N0}). \qquad (3.14b)$$

TABLE II. Values of $\zeta_{12}^{M,N}/\Gamma$ for the $Pa3$ structure.

	$N=2$	$N=1$	$N=0$	$N=-1$	$N=-2$
$M=2$	$(-1.3472,-0.9622)^a$	$(-0.9444,0.2887)$	$(-0.9583,0.5773)$	$(-0.3889,0.4811)$	$(-0.0139,0.5773)$
$M=1$	$(-2.1944,-0.2887)$	$(-0.5556,0.2406)$	$(-1.4167,-0.2887)$	$(-0.7778,0.1443)$	$(-0.8611,0.4811)$
$M=0$	$(-2.2083,2.3094)$	$(-0.1667,-1.1547)$	$(-2.3750,0.0000)$	$(0.1667,-1.1547)$	$(-2.2083,-2.3094)$
$M=-1$	$(0.8611,0.4811)$	$(-0.7778,-0.1443)$	$(1.4167,-0.2887)$	$(-0.5556,-0.2406)$	$(2.1944,-0.2887)$
$M=-2$	$(-0.0139,-0.5773)$	$(0.3889,0.4811)$	$(-0.9583,-0.5773)$	$(0.9444,0.2887)$	$(-1.3472,0.9622)$

^{a}Here (x,y) denotes $x+iy$.

The Hamiltonian $\mathcal{H}_0$ of Eq. (3.12) has the following interpretation. It describes exactly, via the term $\mathcal{H}_{12}$, the interactions between the molecules in the pair 1 and 2. All other molecules librate in the rigid molecular field as represented by the first term in Eq. (3.12). In describing the interactions between a member of the pair and its neighbors outside the pair, we assume that the neighbors are in their molecular field ground state, in which case we obtain the last term in Eq. (3.12). The notation of Eq. (3.13) and (3.14) is intended to suggest a picture in which fluctuations about the molecular field ground state are classified as either vacuum-vacuum or pair-vacuum fluctuations. In this terminology molecules outside the pair in their molecular field ground state form the "vacuum." It will also prove convenient to decompose $\mathcal{H}_{12}$ into secular (viz., conserving the number of librons) and nonsecular terms:

$$\mathcal{H}_{12}=\mathcal{H}_{12}^{(0)}+V_{12}, \qquad (3.15)$$

with

$$\mathcal{H}_{12}^{(0)}=\sum_{\substack{M_1,M_2 \\ M_1',M_2'}}' |M_1,M_2\rangle\langle M_1,M_2|\mathcal{H}_{12}|M_1',M_2'\rangle\langle M_1',M_2'| . \qquad (3.16)$$

Here $|M_1,M_2\rangle$ denotes the state where the first molecule has $J_z=M_1$ and the second has $J_z=M_2$. We shall refer to this manifold of states as the pair subspace. In Eq. (3.16) the prime indicates that the sum is restricted to those values of M_1, M_1', M_2, and M_2' which satisfy $M_1^2+M_2^2=M_1'^2+M_2'^2$, so that

$\mathcal{H}_{12}^{(0)}$ conserves the number of librons. The same type of decomposition can be performed for the perturbation V of Eq. (3.14). The classification and effects of the secular and nonsecular terms are much the same as for the case of nuclear spin systems weakly coupled to a lattice.[38]

IV. CALCULATION

In this section we present the various approximations used to calculate the two-libron energy levels. The associated Raman intensities are calculated in Sec. V.

At first we shall completely neglect the fluctuations described by the term V in Eq. (3.11). Thus we consider a pair of molecules surrounded by molecules which are in their molecular field ground state. In this approximation the energy levels of the pair are found by diagonalizing the pair Hamiltonian $\mathcal{H}_{pair}$ given by

$$\mathcal{H}_{pair}=\mathcal{H}_{12}-\tfrac{2}{3}\sum_{k\neq1,2}\sum_M (\zeta_{1k}^{M,0}O_1^M+\zeta_{2k}^{M,0}O_2^M). \qquad (4.1)$$

The matrix $\mathcal{H}_{pair}$ is given in Table III in terms of the $\zeta_{ij}^{M,N}$. In order to get a rough idea of the type of results we are going to find, let us keep only the secular terms in $\mathcal{H}_{pair}$. Then the two-libron energies are found by diagonalizing the submatrix consisting of the upper left four rows and columns of the matrix shown in Table III. The results of this calculation are given in Table IV under the heading "secular". Even at this stage some effects of libron-libron interactions are included. For in-

TABLE III. The matrix $\mathcal{H}_{pair}$ in terms^a of $\zeta_{12}^{M,N}$.

	$(1,1)^b$	$(1,-1)$	$(-1,1)$	$(-1,-1)$	$(1,0)$	$(-1,0)$	$(0,1)$	$(0,-1)$	$(0,0)$
$(1,1)^b$	$42.4\Gamma+\zeta^{0,0}$	$\zeta^{0,2}$	$\zeta^{2,0}$	$\zeta^{2,2}$	$\zeta^{0,1}$	$\zeta^{2,1}$	$\zeta^{1,0}$	$\zeta^{1,2}$	$\zeta^{1,1}$
$(1,-1)$	$\zeta^{0,-2}$	$42.4\Gamma+\zeta^{0,0}$	$\zeta^{2,-2}$	$\zeta^{2,0}$	$\zeta^{0,-1}$	$\zeta^{2,-1}$	$\zeta^{1,-2}$	$\zeta^{1,0}$	$\zeta^{1,-1}$
$(-1,1)$	$\zeta^{-2,0}$	$\zeta^{-2,2}$	$42.4\Gamma+\zeta^{0,0}$	$\zeta^{0,2}$	$\zeta^{-2,1}$	$\zeta^{0,1}$	$\zeta^{-1,0}$	$\zeta^{-1,2}$	$\zeta^{-1,1}$
$(-1,-1)$	$\zeta^{-2,-2}$	$\zeta^{-2,0}$	$\zeta^{0,-2}$	$42.4\Gamma+\zeta^{0,0}$	$\zeta^{-2,-1}$	$\zeta^{0,-1}$	$\zeta^{-1,-2}$	$\zeta^{-1,0}$	$\zeta^{-1,-1}$
$(1,0)$	$\zeta^{0,-1}$	$\zeta^{0,1}$	$\zeta^{2,-1}$	$\zeta^{2,1}$	21.2Γ	0	$-\zeta^{1,-1}$	$-\zeta^{1,1}$	0
$(-1,0)$	$\zeta^{-2,-1}$	$\zeta^{-2,1}$	$\zeta^{0,-1}$	$\zeta^{0,1}$	0	21.2Γ	$-\zeta^{-1,-1}$	$-\zeta^{-1,1}$	0
$(0,1)$	$\zeta^{-1,0}$	$\zeta^{-1,2}$	$\zeta^{1,0}$	$\zeta^{1,2}$	$-\zeta^{-1,1}$	$-\zeta^{1,1}$	21.2Γ	0	0
$(0,-1)$	$\zeta^{-1,-2}$	$\zeta^{-1,0}$	$\zeta^{1,-2}$	$\zeta^{1,0}$	$-\zeta^{-1,-1}$	$-\zeta^{1,-1}$	0	21.2Γ	0
$(0,0)$	$\zeta^{-1,-1}$	$\zeta^{-1,1}$	$\zeta^{1,-1}$	$\zeta^{1,1}$	0	0	0	0	0

^{a}For simplicity we include the factors E_0 and $2E_0$ in the diagonal elements using Eq. (3.10) rather than (3.8).

Also $\zeta^{M,N}$ denotes $\zeta_{12}^{M,N}$.

^{b}Rows and columns are labeled by (M_1, M_2).

TABLE IV. Two-libron energies in units of Γ for various approximations.

Mean field	Diagonal	Secular	Pair	Fully anharmonic
42.40	40.03	44.97	45.39	36.56
42.40	40.03	41.84	41.88	33.40
42.40	40.03	37.55	38.41	30.02
42.40	40.03	35.77	36.02	27.68

stance, we see that the diagonal elements of $\mathcal{H}_{pair}$ are E_0 for the one-libron states and $2E_0 + \zeta_{12}^{0,0}$ for the two-libron states. The term $\zeta_{12}^{0,0}$ is negative and reduces the energy of neighboring excitations by about 6% as compared to that of separated librons. This term may therefore be thought of as the binding energy of librons. For comparison we have also included in Table IV estimates for the two-libron energies one obtains from mean-field theory, viz., $2E_0$, and from the diagonal elements of $\mathcal{H}_{pair}$ which include the libron binding energy.

The next approximation is obtained by diagonalizing the full 9×9 matrix $\mathcal{H}_{pair}$ and the results are given in Table IV under the heading "pair". By diagonalizing $\mathcal{H}_{pair}$ we allow admixing of the one- and two-libron states, but only within the pair. In terms of libron amplitudes, this type of admixture can only come from anharmonic interactions, of which the most important are the cubic terms. However, it is clear that our decomposition of the solid into a pair of molecules in a rigid background, or "vacuum," is artificial. In particular we expect that admixtures involving molecules outside the pair will also take place. Since most of the neighbors of one of the molecules in the pair are outside the pair, the phase space for such admixtures is larger than that for the admixtures within the pair. Thus it is not surprising that the results of the "pair" approximation do not differ drastically from those of the "secular" approximation. This argument does suggest that we should give a more complete treatment of admixtures due to anharmonicity.

To see how to do this, let us discuss briefly the effects of admixing and of the hopping of excitations, as described by the perturbation V in Eq. (3.11). In the first place the secular terms in V have the effect of broadening the sharp energy levels obtained in the localized picture. We shall ignore this effect, since the formalism we are using is not appropriate for the calculation of the shape of the two-libron density of states. Of more interest is the shift in energy caused by the nonsecular terms. Among these terms are those which contribute to the anharmonic shifts due to libron-libron interactions investigated in Refs. 19 and 32. Due to omission of these terms the average libron energies within the above approximations do not in-

clude anharmonic effects properly. Since these effects were found to be rather large,[19] we ought to use a scheme in which the average libron energy agrees with what was found from the libron calculation of Ref. 32. To do this we must treat $V_{pair-vac}$ in second-order perturbation theory.

If the off-diagonal elements of $\mathcal{H}_{pair}$ were zero, we would use the effect of those states in which one of the neighbors of the pair is excited to resolve the degeneracy among the two-libron states. According to second-order degenerate perturbation theory, the energy levels are obtained by diagonalizing the effective Hamiltonian $\mathcal{H}_{eff}^{(2)}$ which is nonzero only within the two-libron subspace, where it is defined as

$$\mathcal{H}_{eff}^{(2)} = (2E_0 + \zeta_{12}^{0,0})I^{(2)} + V_{eff}^{(2)} , \qquad (4.2)$$

where

$$V_{eff}^{(2)} = \sum_i ' \frac{V_{pair,vac}|i\rangle\langle i|V_{pair-vac}}{E^{(2)} - E_i} , \qquad (4.3)$$

where $I^{(2)}$ is the unit operator in the two-libron subspace, $E^{(2)}$ is a two-libron energy, and the prime over the summation indicates that secular terms are to be omitted. Let us discuss the possible intermediate states $|i\rangle$ in Eq. (4.3). By its definition $V_{pair-vac}$ can connect states in the pair subspace only to states $|i\rangle$ in which at least one of the neighbors is excited. Furthermore, since $V_{pair-vac}$ can only affect two molecules at a time, $|i\rangle$ cannot be a state for which there are no librons on both molecules of the pair. States with one libron inside the pair and one on a neighbor give rise to secular terms and hence are omitted. Thus the intermediate states $|i\rangle$ must be three-libron states. We shall approximate the difference $E_i - E^{(2)}$ by our best estimate of the average one-libron energy, including anharmonic effects which we shall call E_L. The value of E_L is given as[32,39]

$$E_L = E_0 - (1/E_L)\sum_j (2|\zeta_{ij}^{0,1}|^2 + |\zeta_{ij}^{2,1}|^2$$
$$+ |\zeta_{ij}^{2,-1}|^2 - \tfrac{1}{4}|\zeta_{ij}^{1,1}|^2 - \tfrac{1}{4}|\zeta_{ij}^{1,-1}|^2) , \qquad (4.4a)$$

$$E_L \approx 16.13\Gamma , \qquad (4.4b)$$

and we shall soon see that the local formulation we use leads to the same result. Similarly, to resolve the degeneracy of the one-libron states we diagonalize the effective Hamiltonian $\mathcal{H}_{eff}^{(1)}$ which is nonzero only in the one-libron subspace, where it is defined as

$$\mathcal{H}_{eff}^{(1)} = E_0 I^{(1)} + V_{eff}^{(1)} , \qquad (4.5)$$

where

$$V_{eff}^{(1)} = \sum_j ' \frac{V_{pair-vac}|j\rangle\langle j|V_{pair-vac}}{E^{(1)} - E_j} \qquad (4.6)$$

and $I^{(1)}$ is the unit matrix in the one-libron subspace. Again, the prime on the summation in Eq.

(4.6) indicates the secular terms are to be omitted. This time the intermediate states $|j\rangle$ may be either two- or three-libron states, for which we shall approximate the energy denominator $E_j - E^{(1)}$ by E_L and $2E_L$, respectively. Finally, the ground state will also be shifted by an amount V_G by these same effects. Thus, in order to calculate the energies relative to the ground state we have added the term $- V_G$ to the diagonal elements of $\mathcal{K}_{\rm eff}^{(2)}$ and $\mathcal{K}_{\rm eff}^{(1)}$, where

$$V_G = -\sum_k E_k^{-1} |\langle 0|V_{\rm pair\text{-}vac}|k\rangle|^2 . \qquad (4.7)$$

Here $|0\rangle$ is the molecular field ground state, and $|k\rangle$ is a state in which one of the pair and a neighboring molecule are excited. Again we approximate the energy denominator for these terms by $2E_L$.

In order to judge the degree to which we have included anharmonic effects we may compare the average diagonal element of $\mathcal{K}_{\rm eff}^{(1)}$, which we denote $E_{\rm diag}$, with the average libron energy calculated within the libron formalism E_L. Evaluating Eqs. (4.6) and (4.7) we find that

$$E_{\rm diag} = E_0 - \frac{1}{2E_L}\sum_{i=1}^{2}\sum_{j\neq1,2}(2|\zeta_{ij}^{0,1}|^2 + |\zeta_{ij}^{2,1}|^2$$
$$+ |\zeta_{ij}^{2,-1}|^2 - |\zeta_{ij}^{1,1}|^2 - |\zeta_{ij}^{1,-1}|^2) . \qquad (4.8)$$

Comparing this result to that for E_L given in Eq. (4.4) we see that here the terms for which $j=1$ or $j=2$ are missing. Since these terms are taken into account exactly by our treatment of the pair subspace, this type of difference between E_L and $E_{\rm diag}$ is not significant. It is of interest to determine the cause of the remaining discrepancy involving the terms in $|\zeta_{ij}^{1,1}|^2$ and $|\zeta_{ij}^{1,-1}|^2$. The result of Eq. (4.4) was obtained by grouping terms in perturbation theory according to their order in $1/z$, where z is the number of nearest neighbors, here $z=12$. The motivation for this scheme was twofold: First, it explicitly identifies an expansion parameter, so that the status of various approximations is clarified; and second, it is likely that spurious kinematic effects of the boson formalism used disappear when such a grouping is used.[40] This scheme does not correspond exactly to the ordinary grouping in perturbation theory, since terms first order in $1/z$ come from both second- and third-order perturbation theory. Hence to obtain equivalent results from the localized and libron-wave schemes we must include in the former calculation certain third-order terms. These terms are of the form

$$E^{(3)} \sim \sum_{\substack{i=1,2;k \\ j\neq1,2}}\sum_{m,n}\frac{\mathcal{K}_{jk}|m\rangle\langle m|\mathcal{K}_{ij}|n\rangle\langle n|\mathcal{K}_{jk}}{(E-E_m)(E-E_n)} , \qquad (4.9)$$

where $|m\rangle$ and $|n\rangle$ are states containing two virtual librons, and in the libron-wave calculation are represented by the diagram of Fig. 2. In evaluating this term in the localized scheme, we exclude certain terms, for instance those in which j refers to molecules within the pair, because these terms are already treated completely in $\mathcal{K}_{\rm pair}$. Since these restrictions in the summation lead to effects of higher order in $1/z$, we may treat them in any convenient approximate way. Since about $1/z$ or $\frac{1}{12}$ of the terms are missing, we use the results of Ref. 32 to write

$$E^{(3)} \approx -\frac{11}{12}[(3/4E_L)\sum_j(|\zeta_{ij}^{1,1}|^2 + |\zeta_{ij}^{1,-1}|^2)] . \qquad (4.10)$$

Thus to make contact with the libron formalism we add $E^{(3)}$ to the single-libron energies and $2E^{(3)}$ to the two-libron energies. This approximation now agrees with the anharmonic libron-wave calculation, and hence we shall refer to it as the "fully anharmonic" theory. This agreement is interesting because it supports the belief that use of the $1/z$ expansion eliminates spurious kinematic terms, since there are no such terms in the localized picture. To summarize, the results of the fully anharmonic theory are thus found by diagonalizing the effective Hamiltonian

$$\mathcal{K}_{\rm eff} = \mathcal{K}_{\rm pair} + V_{\rm eff}^{(2)} + V_{\rm eff}^{(1)} - V_G(I^{(1)} + I^{(2)})$$
$$+ E^{(3)}(I^{(1)} + 2I^{(2)}) , \qquad (4.11)$$

which is given in Table V.

We may make some comments on the physical effects manifested in Tables III–V. It is quite clear, for instance, that the anharmonic shifts are important. However, comparison of Tables III and V shows that the most important difference between $\mathcal{K}_{\rm eff}$ and $\mathcal{K}_{\rm pair}$ is in their diagonal elements. In other words the main effect of anharmonicity is to renormalize the libron energy E_0. Accordingly, it is not surprising that even the secular approximation gives nearly the correct splittings within the two-libron manifold. In contrast the average two-libron energy is drastically reduced by the inclu-
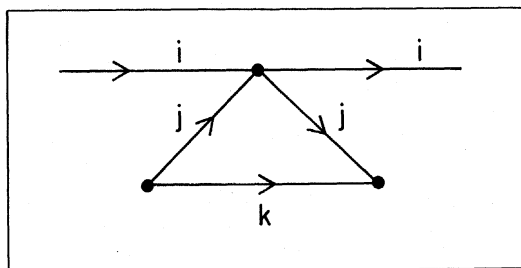

FIG. 2. Third-order diagram for the average libron energy. As explained in the accompanying paper, this diagram gives a contribution of order $(1/z)^0$. The lattice sum over sites j and k gives factors of z which cancel the factors of z implicit in the energy denominators.

TABLE V. Matrix H_{eff} in units of Γ.

	(1, 1)[a]	(1, −1)	(−1, 1)	(−1, −1)
(1, 1)	31.135	(−2.510, 1.894)[b]	(−0.834, 0.865)	(−0.743, −1.129)
(1, −1)	(−2.510, −1.894)	31.135	(0.170, 0.544)	(−0.834, 0.865)
(−1, 1)	(−0.834, −0.865)	(0.170, −0.544)	31.135	(−2.510, 1.894)
(−1, −1)	(−0.743, 1.129)	(−0.834, −0.865)	(−2.510, −1.894)	31.135
(1, 0)	(−0.167, 1.155)	(0.167, 1.155)	(0.389, −0.481)	(0.944, −0.289)
(−1, 0)	(−0.944, −0.289)	(−0.389, −0.481)	(−0.167, 1.155)	(0.167, 1.155)
(0, 1)	(−1.417, 0.289)	(−0.861, −0.481)	(1.147, 0.289)	(2.194, 0.289)
(0, −1)	(−2.194, 0.289)	(−1.417, 0.289)	(0.861, −0.481)	(1.417, 0.289)
(0, 0)	(−0.556, −0.241)	(−0.778, −0.144)	(−0.778, 0.144)	(−0.556, 0.241)

	(1, 0)[c]	(−1, 0)	(0, 1)	(0, −1)	(0, 0)
(1, 1)	(−0.167, −1.155)	(−0.944, 0.289)	(−1.417, −0.289)	(−2.194, −0.289)	(−0.556, 0.241)
(1, −1)	(0.167, −1.155)	(−0.389, 0.481)	(−0.861, 0.481)	(−1.417, −0.289)	(−0.778, 0.144)
(−1, 1)	(0.389, 0.481)	(−0.167, −1.155)	(1.417, −0.289)	(0.861, 0.481)	(−0.778, −0.144)
(−1, −1)	(0.944, 0.289)	(0.167, −1.155)	(2.194, −0.289)	(1.417, −0.289)	(−0.556, −0.241)
(1, 0)	16.368	(0.039, −0.206)	(0.832, −0.154)	(0.636, −0.241)	0
(−1, 0)	(0.039, 0.206)	16.368	(0.640, 0.241)	(0.832, 0.154)	0
(0, 1)	(0.832, 0.154)	(0.640, −0.241)	16.739	(0.530, 0.087)	0
(0, −1)	(0.640, 0.241)	(0.832, −0.154)	(0.530, −0.087)	16.739	0
(0, 0)	0	0	0	0	0

[a]Rows and columns are labeled by (M_1, M_2).
[b]Here (x, y) denotes $x + iy$.
[c]Row headings given above apply to all 9 elements in the row.

sion of anharmonic effects.

V. TWO-LIBRON RAMAN INTENSITIES

In this section we calculate the Raman intensities in the two-libron Raman spectrum. The interaction between the radiation field and the molecular rotations responsible for the Raman spectrum in solid hydrogen is [19]

$$\mathcal{H}_{int} = -\tfrac{1}{2}\sum_i \vec{E}(i) \cdot \overleftrightarrow{\alpha}(i) \cdot \vec{E}(i) , \qquad (5.1)$$

where $\overleftrightarrow{\alpha}(i)$ is the polarizability of the ith molecule, $\vec{E}(i)$ is the external electric field at the ith site, and the sum is over all molecules in the solid. The spherical components of the anisotropic part of the polarizability may be written in terms of the anisotropy of the polarizability referred to the molecular axes as

$$\alpha_M^{(2)}(i(\beta)) = \kappa \overline{\alpha} (\tfrac{8}{15}\pi)^{1/2} \sum_N D_{MN}^{(2)}(\chi_\beta)^* \, Y_2^N(\hat{\omega}_i). \qquad (5.2)$$

Here ω_i specifies the orientation of the ith molecule relative to its equilibrium orientation, κ is the anisotropy of the polarizability, $\overline{\alpha}$ is the average polarizability, and $D_{MN}^{(2)}(\chi_i)$ is a rotation matrix whose argument is the triad of Euler angles describing the equilibrium orientation of the ith molecule relative to the crystal axes. A more complete definition of these symbols is given in Ref. 19. We replace the spherical harmonics by the operator equivalents:

$$Y_2^N(\hat{\omega}_i) = A_N O_i^N . \qquad (5.3)$$

Also the electric field is written in terms of photon creation and annihilation operators as [41]

$$E_M(\vec{r}, \tau) = i \sum_{\vec{k}, \tau} \left(\frac{4\pi\hbar\omega_{\vec{k}\tau}}{2V}\right)^{1/2} \epsilon_M(\vec{k}, \tau)$$

$$\times \{\alpha_{\vec{k}\tau} \exp[i(\vec{k} \cdot \vec{r} - \omega_{\vec{k}\tau} t)]$$

$$- \alpha_{\vec{k}\tau}^\dagger \exp[-i(\vec{k} \cdot \vec{r} - \omega_{\vec{k}\tau} t)]\} , \qquad (5.4)$$

where ϵ_M is the Mth spherical component of the unit polarization vector for the photon mode of wave vector $\vec{k}$ and polarization index τ.

We shall discuss the intensity in the Raman spectrum with reference to the unperturbed libron states. The relative intensity for Raman transitions involving the creation of a single libron is given in first-order time-dependent perturbation theory as

$$I_{\vec{q},\rho}(\omega) = |\langle \vec{q}\rho | \mathcal{H}_{int} | 0 \rangle|^2 \delta(\hbar\omega - E_{\vec{q},\rho}) . \qquad (5.5)$$

Here $|\vec{q}, \rho\rangle$ denotes a state of the orientational system containing a single libron of wave vector $\vec{q}$ and mode index ρ and $E_{\vec{q},\rho}$ is the orientational energy of the final single-libron state. Neglecting zero-point motion this process can only create a single libron, because the operators O_i^M can only create a single libron out of the molecular field ground state. As Nakamura and Miyagi [26] have shown, this is no longer true when zero-point effects are included, and

they find a small two-libron intensity due to zero-point motion. If we neglect this effect, then integrating Eq. (5.5) over all frequencies gives the total single-libron intensity in the Raman spectrum. The sum over final states can then be done by closure. If we average over photon polarizations as for a powder sample, then the result is

$$I_1 = C_0 \sum_{M,M'} \sum_{i,j} D^{(2)}_{M,M'} (\hat{\omega}_{ij})^* \langle 0 | Y_2^{M'}(\hat{\omega}_j) Y_2^M(\hat{\omega}_i)^* | 0 \rangle ,$$

(5.6)

where C_0 is a weak function of the angle between the incident and scattered photons and $\hat{\omega}_{ij}$ is the set of Euler angles which carry the local axes of molecule i into those of molecule j.

It is clear that if we take account of final-state interactions, we shall find some probability of two-libron processes. In such a process the single-libron created in Eq. (5.5) spontaneously decays into two librons under the action of the cubic anharmonicity. This process is shown graphically in Fig. 1. The effective matrix element for this process is [42]

$$\sum_i \langle t | V | i \rangle \langle i | \mathcal{K}_{\text{int}} | 0 \rangle E_i^{-1} .$$

(5.7)

Here $|t\rangle$ is a final state with two-librons and the sum is over all intermediate states $|i\rangle$ containing a single libron. Thus we can reasonably approximate the energy denominator by the single-libron energy E_L so that the relative intensity for this process is given as

$$I_2(\omega) = E_L^{-2} \sum_t \left| \sum_i \langle t | V | i \rangle \langle i | \mathcal{K}_{\text{int}} | 0 \rangle \right|^2 \delta(\hbar\omega - E_t).$$

(5.8)

Let us denote by $\hat{V}$ that part of V which has matrix elements corresponding to a net increase of one in the number of librons. Then we could as well write $\hat{V}$ for V in Eq. (5.8). However, the notation $\hat{V}$ is convenient for the calculation of the total intensity I_2 of the two-libron Raman spectrum. The total intensity is found by integrating Eq. (5.8) over all frequencies, in which case the sum over final states can be done by closure, and we find that

$$I_2 = E_L^{-2} \langle 0 | \mathcal{K}_{\text{int}} \hat{V}^\dagger \hat{V} \mathcal{K}_{\text{int}} | 0 \rangle .$$

(5.9)

We substitute the expression in Eq. (5.1) for $\mathcal{K}_{\text{int}}$ and carry out the calculations assuming a powder average. This calculation is complicated, but resembles closely that in Ref. 19, and so we quote only the final result:

$$I_2 = C_0 E_L^{-2} \sum_{M,M'} \sum_{i,j} D^{(2)}_{M,M'}(\hat{\omega}_{ij})^*$$

$$\times \langle 0 | Y_2^{M'}(\hat{\omega}_j) \hat{V}^\dagger \hat{V} Y_2^M(\hat{\omega}_i)^* | 0 \rangle . \quad (5.10)$$

Numerical evaluation of Eqs. (5.6) and (5.10) yields

$$I_2/I_1 = 0.21 , \qquad (5.11)$$

in good agreement with the estimate given in Eq. (2.4).

The next step is to calculate the intensity of each of the individual two-libron Raman processes. At this point we found it convenient to use first-order time-dependent perturbation theory, [43] using the wave functions calculated either within the pair approximation or within the fully anharmonic approximation. In this approach the two-libron levels are Raman active by virtue of having a small admixture of single-libron states. We write the two-libron wave functions Ψ_j as

$$|\Psi_j\rangle = \sum_{M_1, M_2} a_j^{M_1 M_2} |M_1, M_2\rangle , \qquad (5.12)$$

and the intensity for the jth two-libron state is given by

$$I_j^{(2)} = \tfrac{1}{2} N_M z | \langle \Psi_j | \mathcal{K}_{\text{int}} | 0 \rangle |^2 , \qquad (5.13)$$

where the factor $\tfrac{1}{2} N_M z$ results from the sum over all pairs, and N_M is the number of molecules. If we again assume a powdered sample, Eq. (5.13) can be expanded as

$$I_j^{(2)} = \tfrac{1}{2} N_M z C_0 \sum_{\substack{M_1, M_2 \\ M_1', M_2'}} \sum_{\substack{N, N' \\ k, l}} a_j^{M_1 M_2} a_j^{M_1' M_2'}{}^* D^{(2)}_{NN'}(\hat{\omega}_{kl})^*$$

$$\times \langle M_1', M_2' | Y_2^N(\hat{\omega}_k)^* | 0 \rangle \langle 0 | Y_2^{N'}(\hat{\omega}_l) | M_1, M_2 \rangle ,$$

(5.14)

which we write in the form

$$I_j^{(2)} = \tfrac{1}{2} N_M z C_0 \sum_{\substack{M_1, M_2 \\ M_1', M_2'}} a_j^{M_1 M_2} a_j^{M_1' M_2'}{}^* \Lambda_{M_1', M_2'}^{M_1, M_2} .$$

(5.15)

The matrix $\Lambda_{M_1', M_2'}^{M_1, M_2}$ has the value

$$\Lambda_{1,0}^{1,0} = \Lambda_{0,1}^{0,1} = \Lambda_{-1,0}^{-1,0} = \Lambda_{0,-1}^{0,-1} = 1 , \qquad (5.16a)$$

$$\Lambda_{0,1}^{1,0} = \Lambda_{-1,0}^{0,-1} = \tfrac{2}{9} e^{2\pi i/3} , \qquad (5.16b)$$

$$\Lambda_{1,0}^{0,1} = \Lambda_{0,-1}^{-1,0} = \tfrac{2}{9} e^{-2\pi i/3} , \qquad (5.16c)$$

$$\Lambda_{0,-1}^{1,0} = \Lambda_{-1,0}^{0,1} = \Lambda_{1,0}^{-1,0} = \Lambda_{0,1}^{0,-1} = -\tfrac{5}{9}, \qquad (5.16d)$$

with all other elements being equal to zero. A formula similar to Eq. (5.15) applies if $|\Psi_j\rangle$ is a one-libron state, except that now we sum over all individual molecules:

$$I_j^{(1)} = \tfrac{1}{2} N_M C_0 \sum_{\substack{M_1, M_2 \\ M_1', M_2'}} a_j^{M_1 M_2} a_j^{M_1' M_2'}{}^* \Lambda_{M_1', M_2'}^{M_1, M_2} .$$

(5.17)

Here the factor $\tfrac{1}{2} N_M$ is due to the fact that we may consider the crystal as consisting of $\tfrac{1}{2} N_M$ pairs of molecules.

The values of $I_j^{(2)}$, in units in which the total inten-

TABLE VI. Energies and Raman intensities of the two-libron processes.

	A: Using $\mathcal{H}_{pair}$		B: Using $\mathcal{H}_{eff}$	
	E_j/Γ	$I_j^{(2)}/I_{tot}$[a]	E_j/Γ	$I_j^{(2)}/I_{tot}$[a]
1	45.5	0.035	36.6	0.033
2	41.9	0.004	33.4	0.008
3	38.4	0.077	30.0	0.097
4	36.0	0.056	27.7	0.075
	Total	0.172		0.213

[a]Here I_{tot} is the total intensity from all one- and two-libron processes.

sity for all processes is one, is given in Table VI, first using the eigenstates of $\mathcal{H}_{pair}$ and then using the eigenstates of $\mathcal{H}_{eff}$. Both calculations yield a total two-libron intensity in agreement with our calculations, Eq. (2.4) and (5.11), based on effective matrix elements.

VI. DISCUSSION AND CONCLUSION

A. Discussion

Let us now compare the results of our calculations with the experimental data. Since the single-libron Raman spectrum displays the sharper features, and since the theory of the single-libron spectrum is on firmer ground than the two-libron spectrum, we shall use the same values of the effective EQQ coupling constant Γ_{eff} as were used to fit the single-libron spectrum, viz., $\Gamma_{eff} = 0.56$ cm^{-1} for H_2 and $\Gamma_{eff} = 0.78$ cm^{-1} for D_2. The experimental data is shown in Figs. 3 and 4, along with the
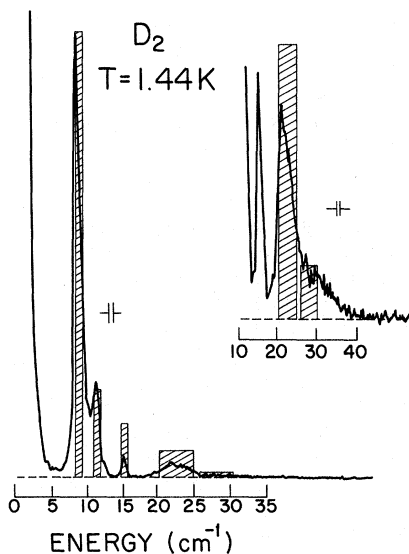
FIG. 3. Comparison between the calculated and observed Raman spectrum of solid D_2 of Ref. 13. The theoretically predicted lines are indicated by bars whose areas are proportional to the calculated intensities.
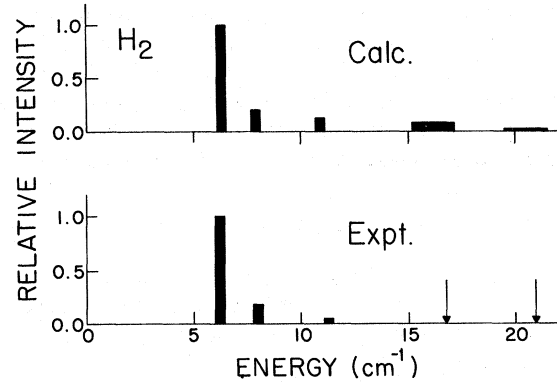
FIG. 4. Schematic comparison of the theoretical and observed Raman spectrum of solid H_2. The areas of the bars are proportional to the intensities.

results of the fully anharmonic theory. As is apparent from the figures, the fully anharmonic theory is in striking agreement with the experimental data. The data show that the two-libron spectrum consists of two lines, the lower of which may perhaps have some structure. We identify this line with the unresolved sum of the two lowest lines in Table VI, which have a total intensity of about 17% of I_{tot} and a center of gravity at 29.0Γ. The upper line in the two-libron spectrum is rather weak, having an intensity of perhaps 3–5% of I_{tot} for D_2 and corresponds to our line at 36.6Γ. The fourth line which we predict at 33.0Γ is too weak to be observed.

In comparing the experimentally determined values of Γ_{eff} with theory it is necessary to take account of the fact that the experiments were done on samples containing about a 3% impurity of $(J = 0)$ molecules. As a result, the experiments determine the concentration-dependent average libron energy $E_L(x)$, where x is the concentration of $(J = 1)$ molecules. The $(\partial p/\partial T)_V$ measurements of Ref. 12 gave

$$E_L(x) = k_B[38.9x - 19.0] \text{ K} \qquad (6.1a)$$

$$= E_L(1)[2.0x - 1.0] \qquad (6.1b)$$

for $x \approx 1$. Thus, due to the 3% $(J = 0)$ impurity we have that $\Gamma = 1.06\Gamma_{eff}$. As a result, the Raman data give $\Gamma = 0.59$ cm^{-1} for H_2 and $\Gamma = 0.83$ cm^{-1} for D_2. A discussion of the significance of these values and their relation to other determinations of Γ is given in the accompanying paper.[32]

Although our calculations do not enable us to make any quantitative statements about the energy widths of the various libron modes, we can make some qualitative observations. First of all, it is clear that the two-libron excitations must have a larger energy width than the single-libron excitations. The latter have width only insofar as anharmonicity leads to a damping of the elementary excitations.

The two-libron states would have a kinematic width even in the absence of damping, since only the total momentum of the two librons is quantized. Thus we expect a root-mean-square (rms) energy width in the two-libron states of order $\sqrt{2}B$, where B is the rms bandwidth for single-libron excitations, defined as

$$B^2 = \hbar^2 \left[\langle \omega^2 \rangle - \langle \omega \rangle^2 \right], \qquad (6.2)$$

where the brackets indicate an average over the Brillouin zone. Neglecting further-than-nearest-neighbor interactions, we have from Ref. 19 that

$$(B/19\Gamma)^2 \approx 1 - (0.9835)^2 \approx 0.04 , \qquad (6.3)$$

so that $B \approx \frac{1}{5}E_L$. Thus we expect a width in the two-libron states of order $\sqrt{2}B \approx 0.3E_L$.

We may compare this estimate with the experimental data shown in Fig. 4 for D_2. We note that the single-libron lines have a width which is only slightly larger than the experimental resolution width. In contrast the two-libron lines have an energy width $\Delta\omega$ of about 5 cm^{-1} which is about 5 times that of the single-libron lines, but agrees with the estimate $\Delta\omega \approx 0.3E_L \approx 4$ cm^{-1} for D_2.

B. Conclusion

We conclude then that the appearance of five lines rather than three in the Raman spectrum results from the presence of two-libron processes rather than from a distortion of the lattice or from libron-phonon interactions. The striking agreement between our calculations and the experimental data shows that our picture of libron-libron interactions is a valid one.

This work also suggests future studies of the libron spectrum in solid hydrogen. We are currently engaged in a more sophisticated calculation aimed at obtaining the shape of the two-libron density of states observed via Raman scattering. This calculation, using Green's-function methods, is similar to that used by Elliott and Thorpe[33] to calculate the shape of the observed two-magnon density of states in antiferromagnets. Our work also suggests that inelastic scattering of neutrons would provide a useful extension of the Raman data. Such experiments would also observe the two-libron density of states due to the presence of the large cubic anharmonicity. However, there is the additional advantage in such experiments that they could probe the two-libron states over their entire momentum range, rather than being confined to zero-total momentum as in the Raman experiments. The neutron experiments would have the additional advantage that they would remove any possible doubts as to the "magnetic" space group of solid hydrogen and they would furnish unequivocal upper limits for the non-EQQ interactions. It is even possible that such experiments could detect three-libron states.

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[1]L. Pauling, Phys. Rev. 36, 430 (1930).

[2]F. Simon, K. Mendelssohn, and F. Ruheman, Naturwiss. 18, 34 (1930); K. Mendelssohn, M. Ruheman, and F. E. Simon, Z. Physik. Chem. B 15, 121 (1930).

[3]R. W. Hill and B. W. A. Ricketson, Phil. Mag. 45, 277 (1954); B. W. A. Ricketson, thesis (Oxford University, England) (unpublished).

[4]G. Grenier and D. White, J. Chem. Phys. 40, 3015 (1964).

[5]R. L. Mills and A. F. Schuch, Phys. Rev. Letters 15, 722 (1965); A. F. Schuch and R. L. Mills, ibid., 16, 616 (1966).

[6]K. F. Mucker, S. Talhouk, P. M. Harris, and D. White, Phys. Rev. Letters 15, 586 (1965); K. F. Mucker, S. Talhouk, P. M. Harris, D. White, and R. A. Erickson, ibid. 16, 799 (1966); K. F. Mucker, P. M. Harris, D. White, and R. A. Erickson, J. Chem. Phys. 49, 1922 (1968).

[7]W. H. Keesom, J. deSmedt, and H. H. Mooy, Commun. Kamerlingh Onnes Lab. Univ. Leiden 19, 209d (1930).

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

[9]T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955).

[10]H. M. James and J. C. Raich, Phys. Rev. 162, 649 (1967).

[11]J. F. Jarvis, H. Meyer, and D. Ramm, Phys. Rev. 178, 1461 (1969).

[12]D. Ramm, H. Meyer, and R. L. Mills, Phys. Rev. B 1, 2763 (1970).

[13]I. F. Silvera, W. N. Hardy, and J. P. McTague, Discussions Faraday Soc. 48, 54 (1969).

[14]S. Homma, K. Okada, and H. Matsuda, Progr. Theoret. Phys. (Kyoto) 36, 1310 (1966); 38, 767 (1967).

[15]H. Ueyama and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 36, 784 (1967).

[16]J. C. Raich and R. D. Etters, Phys. Rev. 168, 425 (1968).

[17]F. G. Mertens, W. Biem, and H. Hahn, Z. Physik 213, 33 (1968).

[18]A. J. Berlinsky, A. B. Harris, and C. F. Coll, III, Solid State Commun. 7, 1491 (1969).

[19]C. F. Coll, III and A. B. Harris, Phys. Rev. B 2, 1176 (1970).

[20]H. M. James, Phys. Rev. Letters 24, 815 (1970).

[21]T. H. Jordan, H. W. Smith, W. E. Streib, and W. N. Lipscomb, J. Chem. Phys. 41, 756 (1964).

[22]J. E. Cahill and G. E. Leroi, J. Chem. Phys. 51, 1324 (1969); M. Brith, A. Ron, and O. Schnepp, ibid. 51, 1318 (1969).

[23]J. Van Kranendonk and V. F. Sears, Can. J. Phys. 44, 313 (1966).

[24]A. B. Harris, Phys. Rev. B 1, 1881 (1970).

[25]H. M. James, International Conference on Quantum Crystal, Aspen, 1969 (unpublished).

[26]T. Nakamura and H. Miyagi, Progr. Theoret. Phys. (Kyoto) 44, 833 (1970).

[27]A. B. Harris, J. Appl. Phys. 42, 1574 (1971).

[28]See F. Keffer, in Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, New York, 1966), Vol. XVIII/2; L. R. Walker, in Magnetism, edited by G. Rado and H. Suhl (Academic, New York, 1963), Vol. I.

[29]R. J. Elliott, Discussions Faraday Soc. 48, 7 (1969).

[30]P. A. Fleury, Phys. Rev. Letters 21, 151 (1968).

[31]C. F. Coll, III, A. B. Harris, and A. J. Berlinsky, Phys. Rev. Letters 25, 858 (1970).

[32]C. F. Coll, III and A. B. Harris, preceding paper, Phys. Rev. B 4, 2781 (1971).

[33]R. J. Elliott and M. F. Thorpe, J. Phys. C. 2, 1630 (1969).

[34]R. J. Elliott, M. F. Thorpe, G. F. Imbusch, R. Loudon, and J. B. Parkinson, Phys. Rev. Letters 21, 147 (1968).

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

[36]M. E. Rose, Elementary Theory of Angular Momentum (Wiley, New York, 1957).

[37]J. Noolandi and J. Van Kranendonk, Phys. Letters 30A, 258 (1969).

[38]A. Abragam, The Principles of Nuclear Magnetism (Clarendon, Oxford, 1962).

[39]The result in Ref. 19 is corrected by inclusion of the third-order terms in Ref. 32.

[40]A. B. Harris, Phys. Rev. Letters 21, 602 (1968).

[41]L. I. Schiff, Quantum Mechanics, 2nd ed. (McGraw-Hill, New York, 1955), Chap. XIV.

[42]L. I. Schiff, Quantum Mechanics, 2nd ed. (McGraw-Hill, New York, 1955), p. 202.

[43]These computations were checked by comparing their results with those obtained using the second-order time-dependent perturbation theory as in Eq. (5.8). In fact, the two approaches gave identical results only when self-consistent energy denominators were used in Eq. (5.8).