Anharmonic One-Libron Spectrum in Solid H_2 and D_2†

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A self-consistent, anharmonic approximation is used to compute the values of the libron energies as a function of the momentum along various symmetry directions in the first Brillouin zone. A density-of-states histogram is also presented, based on a calculation of the libron energies at 584 points in the irreducible section of the first Brillouin zone.

I. INTRODUCTION

It is by now well established that the electric quadrupole-quadrupole (EQQ) interaction is responsible for the orientational ordering of the molecules in solid ortho-hydrogen and para-deuterium at low temperatures.[1] Deviations from the fully aligned state occur when the molecules execute torsional oscillations about their equilibrium orientation. The normal modes associated with motion of this type have wavelike character and have been called librons.[2]

The dynamics of librational motion may be studied by expanding the EQQ Hamiltonian in terms of deviations from the fully aligned state. The Hamiltonian is then found to be highly anharmonic with the dominant anharmonic term being cubic in the deviations.

Coll and Harris[3] have shown how diagrammatic perturbation theory may be used to construct a dynamical matrix for the libron energies which is energy dependent. They then went on to compute the values of the libron energies at zero momentum ($k=0$) and the associated intensities for Raman scattering.

In this paper we extend the calculation of the libron energies throughout the Brillouin zone. Two methods were used to solve for the energies. First, along the symmetry directions, we used group theory to transform the dynamical matrix into block diagonal form. The resulting secular equations could then be solved easily on the computer. Second, the roots of the secular equation were found on the computer for arbitrary values of $\vec{k}$. Solutions according to this second method were found to agree with those of the first along the symmetry directions. This second method allowed us to compute the energies on a grid of points in the Brillouin zone and thus to construct the density of states.

II. THEORY

We consider the system in which ($J=1$) ortho-hydrogen or para-deuterium molecules are arranged at the lattice sites of a face-centered cubic (fcc) structure. At zero temperature the molecules assume an orientation which is determined primarily by the EQQ interaction. If the molecules are treated as classical quadrupoles the ordered state is found to be one in which the molecules are aligned along $\langle 111 \rangle$ axes.[4] When treated quantum mechanically it can be shown[5] that the ordered state is one in which each molecule is in the rotational state ($J=1$, $J_z=0$), where the z axis coincides with a $\langle 111 \rangle$ axis. We may visualize the fcc lattice as being made up of four interpenetrating simple-cubic sublattices. The equilibrium orientation of a molecule on sublattice 1, 2, 3, or 4 lies along $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, or $[11\bar{1}]$, respectively. The lattice structure is thus described as a simple-cubic Bravais lattice with four molecules per unit cell. The space group for this structure is designated $Pa3(T_h^6)$.

We look for the low-lying excitations of the system which we characterize by $\Delta M_J = \pm 1$. Since there are four molecules per unit cell we expect eight modes for each momentum $\vec{k}$. It is these $\Delta M_J = \pm 1$ type excitations which we refer to as librons.

For simplicity the discussion will be confined to zero temperature. In the molecular field approximation the eight libron modes are degenerate and have an energy

$$E_0 = 19\Gamma, \tag{1}$$

if only nearest-neighbor interactions are considered. Here Γ is the EQQ coupling constant.[2] If further-neighbor interactions are taken into account[6] then

$$E_0 = 21.20\Gamma. \tag{2}$$

By comparing the theoretical values of the anharmonic libron energies at $k=0$ to the experimental Raman spectra taken by Hardy, Silvera, and McTague,[7] one deduces the following empirical values of Γ[3]:

$$\Gamma = 0.56 \text{ cm}^{-1} \text{ for } H_2 , \tag{3a}$$

$$\Gamma = 0.78 \text{ cm}^{-1} \text{ for } D_2 . \tag{3b}$$

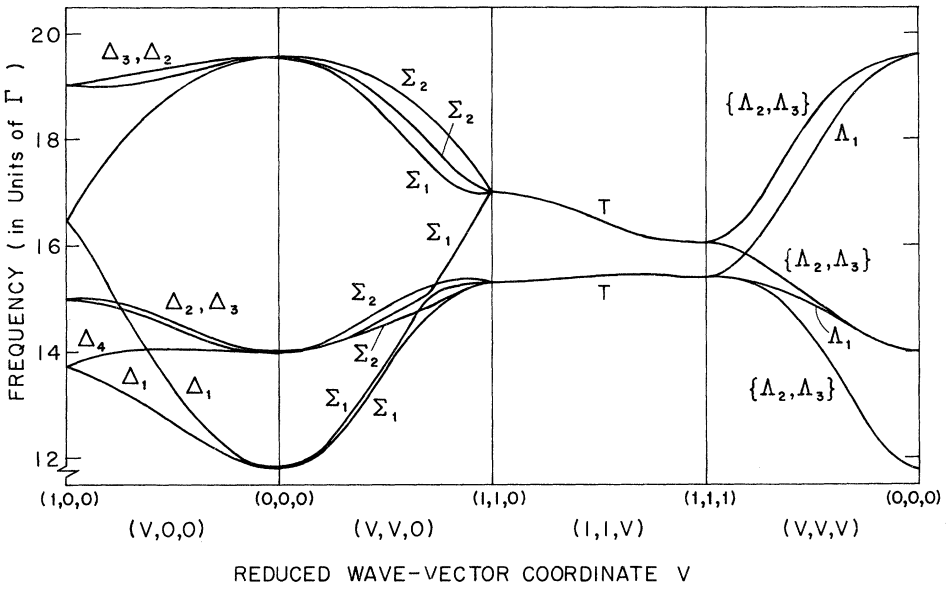

FIG. 1. Anharmonic libron dispersion curves along four symmetry directions. Curves are labeled by the irreducible representations according to which the wave functions transform.

In both the harmonic and the anharmonic approximations the Hamiltonian contains terms which do not conserve the number of librons.[3] In the harmonic case these terms can be transformed away using a Bogoliubov transformation.[8] The transformed cubic terms, however, are extremely unwieldy. Accordingly, when anharmonic effects are included, a formalism is used in which the Green's function is a 16×16 matrix and in which the non-number-conserving terms in the Hamiltonian cause a coupling between libron states which propagate forward and those which propagate backward in time, i.e., between "particles" and "holes."

It is shown in Ref. 3 that the libron energies correspond to the roots of the secular equation

$$\mathrm{Re\,Det}\left|(\underline{G}^0(z))^{-1}-\underline{M}(\vec{k},z)\right|=0\ . \tag{4}$$

Here $\underline{G}^0(z)$ is the 16×16 matrix Green's function for the molecular field Hamiltonian, and $\underline{M}(\vec{k},z)$ is the energy- and momentum-dependent self-energy matrix which contains both harmonic and anharmonic effects.[9]

III. RESULTS

The self-energy may be reduced to block diagonal form by appropriate transformations in several symmetry directions. These directions are the edge of the cube [the points $(1, 1, V)$ where $0\leq V\leq 1$]

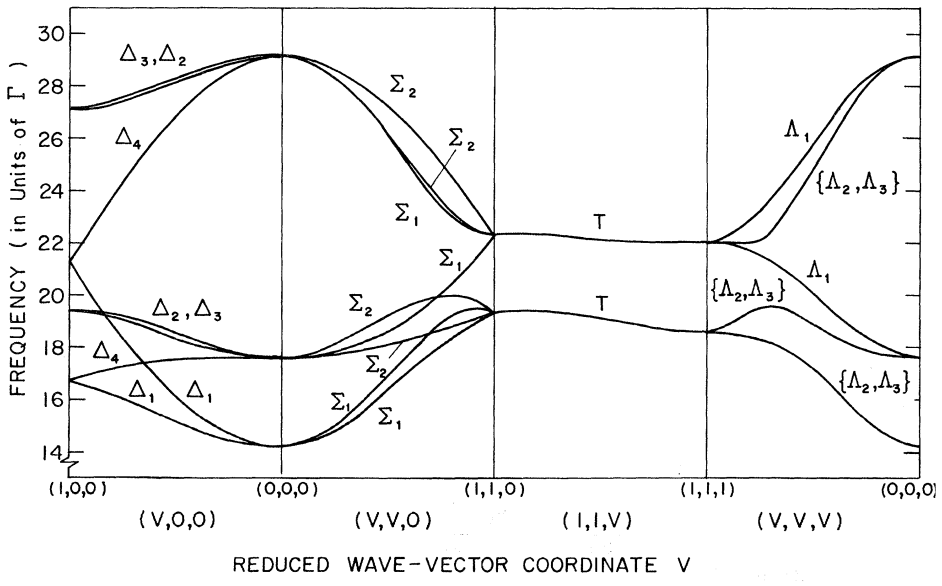

FIG. 2. Harmonic libron dispersion curves labeled as in Fig. 1. Note, however, the change of scale on the vertical axis.

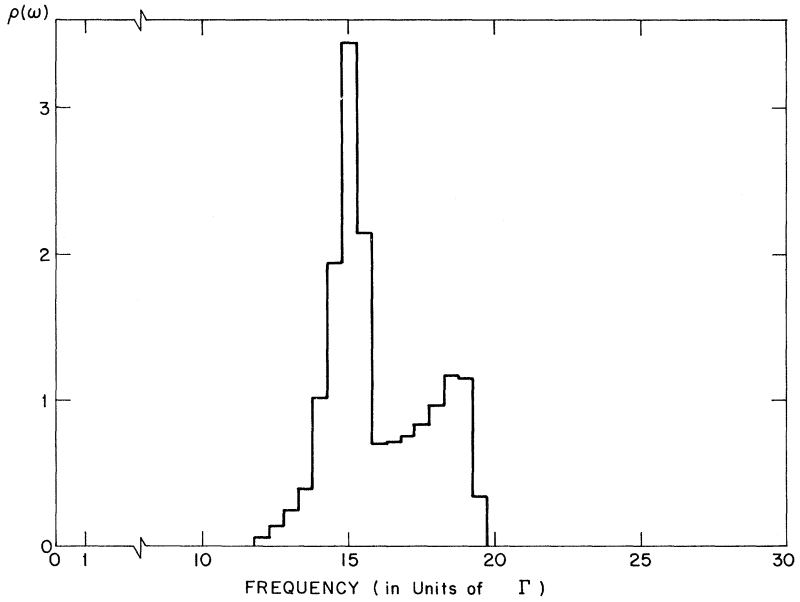

FIG. 3. Histogram representing the anharmonic density of states based on the values of the energies of the eight libron modes at 13 824 points in the Brillouin zone. The vertical axis $\rho(\omega)$ is defined as $1/N$ times the number of states per unit of frequency where N is the number of unit cells.

which we call T and, in addition, the directions $[100]-\Delta$, $[111]-\Lambda$, and $[110]-\Sigma$ where the symbols following the square brackets label the symmetry direction. For comparison we have also computed the dispersion curves for the harmonic Hamiltonian, including the effects of second neighbors[10] and taking E_0 as in Eq. (2).

The group-theoretical reduction of the 16×16 dynamical matrix $M(\vec{k}, z)$ leads to matrices of dimension (4×4), (6×6), (8×8), and (8×8) for Δ, Λ, Σ, and T, respectively. Thus it is still necessary to solve the simplified secular equations by computer. However, the saving in machine time is considerable.

The resulting dispersion curves are shown in Fig. 1 for the anharmonic case and Fig. 2 for the harmonic case. We note that the eight modes are split except along the Λ and T directions. The lines labelled $\{\Lambda_2, \Lambda_3\}$ are degenerate as a consequence of time-reversal symmetry. Along the T direction the energy bands "stick together"[11] as a result of the additional symmetry under the combined operations of the screw axis and time reversal. This gives two fourfold-degenerate lines

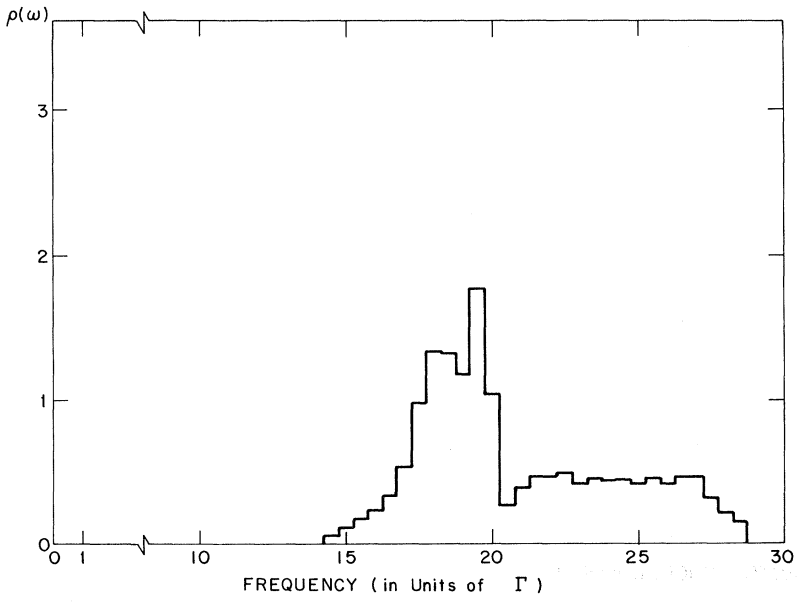

FIG. 4. Histogram representing harmonic density of states based on the values of the energies of the eight libron modes at 13 824 points in the Brillouin zone, with vertical axis as in Fig. 3.

where one might expect four twofold-degenerate lines if this extra symmetry did not exist. The small splitting in the nearly degenerate pairs of lines (Δ_2, Δ_3) is caused by second-neighbor interactions which have been included in the self-energy. This splitting occurs also in the harmonic approximation. An interesting result of the anharmonic calculation is the crossing of energy levels Λ_1 and $\{\Lambda_2, \Lambda_3\}$ which does not occur in the harmonic approximation.

In order to compute the libron energies at other points in the Brillouin zone we employed the tedious but straightforward method of searching for the zeros of the determinant of the full 16×16 matrix as indicated in Eq. (4). We did this for 584 values of the momentum by dividing the positive octant into $(12)^3$ cubes and computing the energies at the centers of the cubes in one-third of the octant. This amounts to calculating the libron energies at 13 824 equally spaced points in the full Brillouin zone. The resulting energies were used to construct a histogram of the density of states which is shown in Fig. 3. Figure 4 shows the density of states for the harmonic Hamiltonian. This was obtained by the relatively simple process of diagonalizing the quadratic part of the Hamiltonian for the selected values of $\vec{k}$. If we compare Figs. 3 and 4, we see that the main effect of anharmonicity is to shift down the high-energy modes while leaving the lower-energy modes relatively unchanged. The bandwith is reduced by a factor of almost a half from 15Γ to 8Γ while the bottom of the band is shifted down by only about 2Γ to 11.8Γ.

IV. COMMENTS

Our theoretical results for the libron density of states and the dispersion curves along the symmetry directions may be tested experimentally by means of inelastic neutron scattering. The experimental observations may be somewhat difficult, however, since the intensity from the inelastic scattering of neutrons by librons is expected to be much smaller than the intensity obtained in comparable experiments measuring inelastic scattering of neutrons by phonons.

In addition, the computational machinery which produced the libron energies throughout the zone will be used as part of a more elaborate calculation of the shape of the two libron portion of the Raman spectrum for which experimental results are already available.[7]

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[9]As shown in Ref. 3 anharmonic effects were included in the self-energy by means of an approximation which is essentially that of second-order perturbation theory.

[10]Dispersion curves along various symmetry directions and a density-of-states histogram have previously been calculated in the harmonic approximation with coupling between nearest neighbors only by F. G. Mertens, W. Biem, and H. Hahn, Z. Physik 213, 33 (1968); 220, 1 (1969).

[11]See, for example, V. Heine, *Group Theory in Quantum Mechanics* (Pergamon, New York, 1960), p. 284.