Because the rotational kinetic energy $6B_I \approx 500$ K is very large, the terms proportional to B_I in eqs. (24)–(26) dominate insofar as the angle-dependent parts of χ_{ij}^{02}, χ_{ij}^{20}, and χ_{ij}^{22} are concerned. Hence, we have the relatively simple approximate results

$$\chi_{ij}^{20} = -\chi_{ij}^{00}\left[\frac{\varphi_{2i}}{\varphi_{0i}} + \frac{H^{20}}{6B_I}\right], \qquad (27)$$

$$\chi_{ij}^{02} = -\chi_{ij}^{00}\left[\frac{\varphi_{2j}}{\varphi_{0j}} + \frac{H^{20}}{6B_I}\right], \qquad (28)$$

and

$$\chi_{ij}^{22} = -\chi_{ij}^{00}\left(\frac{H^{22}}{12B_I}\right). \qquad (29)$$

These functions are next substituted into eqs. (15), (22) and (23) to find u_i and φ_i by iteration until a self-consistent result is achieved.

4. Results

The result of primary interest here is E, the ground state energy per molecule; it is given by $E = \langle T \rangle + \frac{1}{2}\langle u \rangle$ where $\langle T \rangle$ is the expectation value of the translational and rotational kinetic energy and $\langle u \rangle$ is that of the single-particle effective field. Thus one finds E from φ_i and u_i,

$$E = N_1^{-1} \int \varphi_i^*(1,\omega_1)\left(-\frac{\mathbf{V}_1^2}{2m} + \frac{1}{2I}J_1^2\right.$$

$$\left. + u_i(1,\omega_1)\right)\varphi_i(1,\omega_1)\,\mathrm{d}^3r_1\,\mathrm{d}\omega_1. \qquad (30)$$

The energy is plotted as a function of molar volume in fig. 2. Curve A is experimental, while curve B is the result using potential E6 and not including any anisotropic interaction; curves C and D are found including V_{ani} with $\rho = \rho_t = 0.283$ Å and $\rho = \rho_e = 0.239$ Å, respectively. We see that there is a significant change in E for both of curves C and D and that it depends dramatically on the value of ρ. In particular, $\rho = \rho_e$ leads to very good agreement of theory and experiment for $V \lesssim 15$ cm^3. The quantitative agreement should not be taken too seriously for several reasons; first, one does not know with any precision what is the correct value of ρ, and the result is extremely sensitive to this parameter. Also, we have neglected states with $m \neq 0$; they should be included and will produce further lowering of the energy, perhaps increasing the
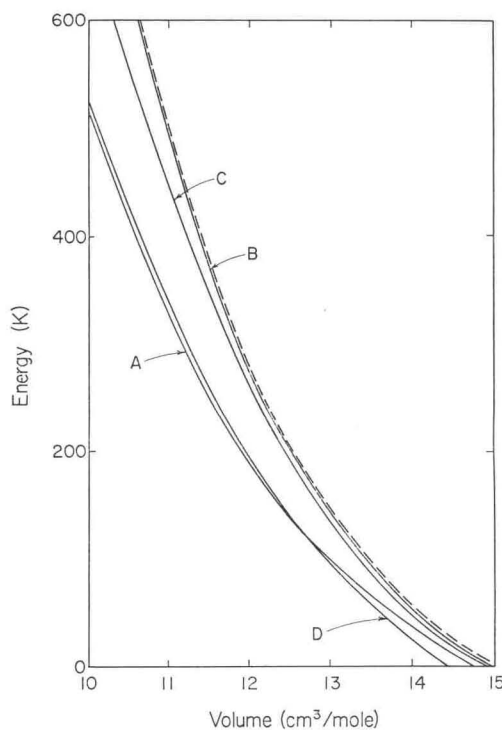

Fig. 2. Ground state energy E versus molar volume V.

magnitude of the correction ΔE_a (curve B minus C or D) by a factor of two to four. At the same time, there is also the possibility that the overall magnitude of β_1 used here is too large by about a factor of two. HARRIS (1970) has discussed some experimental evidence that suggests this. Analysis by EBNER and SUNG (1971a) of the measured λ-transition temperature in solid H$_2$ also suggests that β_1 should be smaller. A reduction of β_1 by a factor of two decreases $|\Delta E_a|$ by about a factor of four and approximately cancels the correction produced by including $m \neq 0$ states. We expect that this is a reasonable qualitative description of the actual situation.

Another interesting feature of the calculation is the size of φ_{2j}, which is to say, the amplitude for a molecule to be in the $l = 2$ state. For the case which produces curve D, this amplitude varies slowly between about 2 and 4% of the total amplitude for $V \gtrsim 11$ cm^3; it rises sharply to about 15% at $V = 10$ cm^3. This may signal the onset of a rotationally ordered state with the molecules oriented in a particular way at molar volumes only slightly smaller than 10 cm^3. We cannot make a more quantitative statement without including higher l values.

An ordered state of this kind has been predicted by RAICH and ETTERS (1972), but only at much smaller molar volume. The reason for the disagreement is that we are using a quantum crystal formalism rather than treating the molecules as quantum-mechanical rotators pinned to the lattice sites. In the latter picture, the part of V_{ani} involving V^{20} and V^{02} actually vanishes for nearest neighbors as a consequence of the symmetry of the point lattice, leaving only V^{22} as the contributing part of the anisotropic interaction. In our formalism, on the other hand, the particles have zero-point motion and also there are correlations between pairs of particles, as a result of which the effects of V^{02} and V^{20} do not vanish and actually produce more than 90% of ΔE_{a}. Thus these terms are by far the most important part of V_{ani} insofar as calculating the energy of the system is concerned.

In conclusion, we wish to summarize several basic features of the work presented here.

(1). The general approach is the same as in our previous calculations on quantum crystals; the overall agreement of these calculations with the experimental ground state energy and pressure in He^3, He^4 and H_2, and with the self-diffusion constant and activation energy in H_2 (EBNER and SUNG, 1972), indicates that the formalism is adequate for the calculation of many properties of quantum crystals. In the present work, it is extended to include the effect of anisotropic interactions such as exist between H_2 molecules.

(2). The actual computations have been simplified in several respects. For example, we have included V_{ani} only in the $l = 0, 2$ states, which means that the calculations are not valid below about $V = 10$ cm^3 where states of larger l become important. There is no difficulty in principle in extending the calculations to smaller volume; the numerical work, however, is formidable.

(3). Our results indicate that the anisotropic interaction does produce a significant lowering of the ground state energy in solid H_2 for $V \lesssim 15$ cm^3 and that its inclusion gives a corresponding improvement in the agreement of theory and experiment. One may also test the importance of V_{ani} by calculating e.g. the crystal field in solid H_2.

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