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GROUND STATE ENERGY OF SOLID MOLECULAR HYDROGEN AT HIGH PRESSURE

C. EBNER and C. C. SUNG

Department of Physics, Ohio State University, Columbus, Ohio 43210, U.S.A.

We review the present status of the theoretical equation of state of solid molecular hydrogen. Different quantum mechanical calculations by several groups lead to results which generally agree with each other but which disagree systematically with the measured pressure–volume curve at pressures larger than about 3000 atm. We present a new calculation of this curve including the effect of the anisotropic interaction between H_2 molecules within a completely quantum-mechanical formalism. Our results show that inclusion of this interaction removes the discrepancy between theory and experiment at high pressures and that a quantum-mechanical treatment is necessary to realize its full effect.

1. Introduction

Recent interest in the equation of state of solid molecular hydrogen stems in part from its application to problems in astrophysics. DEMARCUS (1958) has reviewed the experimental work of STEWART (1956) and the early theoretical work of DE BOER and BLAISSE (1948), KRONIG *et al.* (1946), and ABRIKOSOV (1954). More recently, considerable experimental progress has been made in finding the equation of state in the high pressure region ($P \approx 1$ Mbar) as described by GROSS (1970). Even at relatively small pressure, $P \approx 10^4$ bar, there is a sizeable discrepancy between theory and experiment. Consequently, application of the theoretical equation of state to problems such as the constitution of the outer layers of Jupiter and Saturn cannot be taken very seriously.

In the past few years, several more serious attempts have been made by KRUMHANSL and WU (1968, 1972) and by EBNER and SUNG (1970, 1971a) at calculating the P–V curve of solid H_2 using quantum-mechanical many-particle formalisms originally developed to find the equation of state of solid helium at relatively low pressures. For treatments of this problem see e.g. NOSANOW (1966). This approach is necessary in helium, first, because the combination of small atomic mass and an interatomic potential with a shallow attractive well leads to large zero-point motions of the atoms and requires a quantum-mechanical formalism, and, second, because the hard core in the potential introduces strong correlation effects into the motions of the atoms which means that we have a many-body problem. The work of EBNER and SUNG (1971b), among others, shows that the equations of state for He^3 and He^4 (the so-called "quantum crystals") can be computed with good accuracy at zero temperature ($T = 0$) if the single-particle wave functions and two-particle correlation functions are found self-consistently with some consideration given to three- and higher-particle correlation effects. Further, both our formalism and the numerical approximations we make in solving the equations should improve in accuracy with increasing pressure and decreasing molar volume V, in which limit solid helium becomes more classical as evidenced by decreasing amplitude of the zero-point motion.

Our approach should be even more valid when applied to solid hydrogen at high pressure because the attractive well in the intermolecular potential is almost four times deeper than for helium, producing more nearly classical behavior; that is, the zero-point motion is relatively smaller than in solid helium at the same pressure. In view of the success of "quantum crystal theories" in helium, it is a surprise that the same theories, when applied to solid hydrogen, produce appreciable disagreement with the measurements by STEWART (1956) of the P–V curve in the range of 10–20 kbar. Also, it is significant that quite different quantum crystal formalisms produce nearly identical P–V curves

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from a given intermolecular potential. These calculations are fairly consistent with the older, classical calculations and give theoretical pressures which are larger than the experimental ones for given V. The same comment holds for the semi-classical work of POLLOCK *et al.* (1972) and the variational Monte Carlo calculation of BRUCE (1972). In view of the success of these formalisms in solid helium, it seems safe to conclude that, excluding the possibility of large experimental errors, some important feature of the solid hydrogen problem has been overlooked.

One possible source of the difficulty lies in the intermolecular potential. There are several conventional choices which are discussed in some detail by KRUMHANSL and WU (1972). One is a Lennard–Jones 6–12 potential (LJ),

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

where r is the distance between the molecules' centers of mass. The two parameters ε and σ have been empirically determined from thermodynamic measurements on the gaseous phase. The generally accepted values prior to 1960 are $\varepsilon = 37.0$ K and $\sigma = 2.928$ Å, where we have set the Boltzmann constant equal to one. At that time, it was found that a better fit to the virial coefficients is obtained using $\varepsilon = 36.7$ K and $\sigma = 2.958$ Å. The difference between these is quite negligible insofar as calculations of the ground state energy E are concerned (recall that $P = -\partial E/\partial V$).

Another commonly used empirical interaction is a modified Buckingham exp-6 potential (E6),

$$V(r) = \begin{cases} \dfrac{\varepsilon_0}{1-(6/\alpha)}\left[\dfrac{6}{\alpha}\exp\left[\alpha\left(1-\dfrac{r}{r_\mathrm{m}}\right)\right] - \left(\dfrac{r}{r_\mathrm{m}}\right)^{6}\right], & r > r_\mathrm{max}, \\ \infty, & r < r_\mathrm{max}, \end{cases}$$

with $\varepsilon_0 = 38.0$ K, $r_\mathrm{m} = 3.339$ Å, $\alpha = 14.0$ and $r_\mathrm{max}/r_\mathrm{m} = 0.20$; these parameters are again determined from thermodynamic measurements in the gaseous phase. The E6 potential is superior to either LJ potential in the sense that it reproduces the measured second virial coefficient in gaseous hydrogen more faithfully. At the same time, because of the manner in which both potentials are obtained, the behavior in the hard core region is not particularly reliable. It is just this region which is most important in determining the energy at high pressure in the crystal. Any speculation concerning the reliability of the potential in the core region is probably not useful in the absence of more direct experimental information.

Another, and, we believe, the most important source of the discrepancy between experimental and theoretical pressures at small molar volume is the anisotropic part of the intermolecular interaction. The E6 and LJ potentials are isotropic and do not depend on the rotational states of the molecules. It is well known that this is an oversimplification and that the interaction does depend on the relative orientation of the molecules as described e.g. by HIRSCHFELDER *et al.* (1954). We shall call the orientation-dependent part V_ani; it becomes increasingly important at small interparticle separation and can produce a substantial change in the calculated P–V curve. The change in energy ΔE_a associated with the existence of V_ani first appears in second order, $\Delta E_\mathrm{a} = \mathrm{O}\,(V_\mathrm{ani}^2/B_I)$, where $B_I = 1/2I \approx 87$ K, I is the moment of inertia of a molecule and we use units such that $\hbar = 1$. The anisotropic interaction is small (about 1 K) at intermolecular distances corresponding to low P, but it increases sharply as the distance decreases and is responsible for a significant change in E and P for $V \lessapprox 15\ \mathrm{cm}^3$. The purpose of this paper is to calculate the energy change ΔE_a within the context of our quantum crystal formalism.

Since we have mentioned that both the classical and quantum mechanical approaches give qualitatively the same E, we should explain why it is necessary to make a quantum mechanical treatment of V_ani; this is especially true in view of some other recent efforts by KRUMHANSL and WU (1972), by NEECE *et al.* (1971), and by RAICH and ETTERS (1972) to include this part of the interaction in calculations of the energy.

(1) The individual molecules must be treated as quantum mechanical rotators rather than as classical objects which one can simply orient in certain directions without introducing any rotational kinetic energy. From a quantum-mechanical point of view, a molecule oriented along a particular direction is in some combination of excited angular momentum states. Now, since $B_I \approx 87$ K, the first excited rotational state costs $2B_I \approx 170$ K to produce, which is already much too large an energy to ignore in calculations of E.

(2) The zero-point motion of the molecules is also important because it strongly enhances the contribu-

tion of V_{ani} to the crystal energy. Indeed, that contribution to ΔE_{a} which is most important in the quantum calculation actually vanishes as a consequence of the crystal symmetry if the molecules are pinned precisely at lattice sites. We shall discuss this and related points further below.

The remainder of the paper is organized as follows: Section 2 contains a review of the quantum crystal formalism and of the anisotropic potential, while section 3 describes those modifications of our formalism which are necessary to handle V_{ani}; finally, in section 4 we present and discuss the results, assuming the crystal is 100% parahydrogen.

2. Review

2.1. *Quantum crystal formalism*

The self-consistent calculation given by EBNER and SUNG (1971b) of the ground state properties of quantum crystals can be summarized with several basic equations. First, the single-particle wave function $\varphi_i(1)$ of a particle localized around lattice position $\boldsymbol{R}_i$ is determined from the equation*

$$\left[-\frac{\nabla_1{}^2}{2m}+u_i(1)\right]\varphi_i(1)=\varepsilon\varphi_i(1), \tag{1}$$

where m is the mass of a hydrogen molecule and $u_i(1)$ is the single-particle self-consistent field which is taken in the harmonic approximation

$$u_i(1)=u_0+\frac{\alpha^4}{2m}(\boldsymbol{r}_1-\boldsymbol{R}_i)^2. \tag{2}$$

The symbols 1, 2, etc. stand for $r_1, r_2, \ldots$ The constants u_0 and α^2 are found by expanding the relation

$$u_i(1)=\sum_j{}'\int V(1,2)\,\chi_{ij}(1,2)\,\varphi_j^2(2)\,\mathrm{d}^3r_2 \tag{3}$$

in powers of $\boldsymbol{r}_i-\boldsymbol{R}_i$. The prime on the summation sign denotes that the summation is over all $j\neq i$; $V(1,2)$ is the interparticle interaction, and $\chi_{ij}(1,2)$ is the two-particle correlation function for particles 1 and 2 localized around sites i and j. This function is found from the two-particle equation

$$\left\{-\frac{\nabla_1{}^2}{2m}-\frac{\nabla_2{}^2}{2m}+u_i(1)+u_j(2)+V(1,2)-W_{ij}(1,2)\right.$$
$$\left.+\Delta_{ij}(1,2)-\lambda_0\right\}\varphi_i(1)\,\varphi_j(2)\,\chi_{ij}(1,2)=0, \tag{4}$$

where

$$W_{ij}(1,2)=\int V(1,\bar{2})\,\chi_{ij}(1,\bar{2})\,\varphi_j^2(\bar{2})\,\mathrm{d}^3\bar{r}_2$$
$$+\int V(\bar{1},2)\,\chi_{ij}(\bar{1},2)\,\varphi_i^2(\bar{1})\,\mathrm{d}^3\bar{r}_1, \tag{5}$$

and $\Delta_{ij}(1,2)$ contains some three-body correlation effects. It is approximated by $p(r_{12}-R_{ij})$, where p is chosen so that the condition

$$\int(\boldsymbol{r}_{12}-\boldsymbol{R}_{ij})\cdot\boldsymbol{R}_{ij}\,\chi_{ij}(1,2)\,\varphi_i^2(1)\,\varphi_j^2(2)\,\mathrm{d}^3r_1\,\mathrm{d}^3r_2=0 \tag{6}$$

is satisfied. Here $\boldsymbol{R}_{ij}=\boldsymbol{R}_i-\boldsymbol{R}_j$ and $\boldsymbol{r}_{12}=\boldsymbol{r}_1-\boldsymbol{r}_2$. The parameter p turns out to be non-zero only for nearest neighbors. Finally, the normalization of $\varphi_i(1)$ and $\chi_{ij}(1,2)$ is specified:

$$\int\varphi_i^2(1)\,\mathrm{d}^3r_1=1 \tag{7}$$

and

$$\int\chi_{ij}(1,2)\,\varphi_i^2(1)\,\varphi_j^2(2)\,\mathrm{d}^3r_1\,\mathrm{d}^3r_2=1. \tag{8}$$

Using eq. (1) and making some simple approximations, we may write the two-particle equation for χ_{ij} in the form

$$H_{00}\chi_{ij}(\xi)\equiv\left[-\frac{1}{m}\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}+v(\xi)\right.$$
$$+\frac{\alpha^2}{m}(\xi^2-R_{ij}^2)\frac{\mathrm{d}}{\mathrm{d}\xi}-W_{ij}(\xi)$$
$$\left.+p\,(\xi-R_{ij})\right]\chi_{ij}(\xi)=\lambda_1\,\chi_{ij}(\xi), \tag{9}$$

where $\xi=r_{12}$, $v(\xi)=V(1,2)$, and $W_{ij}(\xi)$ is an approximation form of $W_{ij}(1,2)$ in which it is averaged over all motions of particles 1 and 2 which can occur at constant r_{12}. These equations are solved simultaneously for χ_{ij}, φ_i and u_i.

Let us compare our method with three other recent calculations of the ground state energy in solid hydrogen. The first is the semi-classical approach of POLLOCK *et al.* (1972) in which the molecules are initially fixed on lattice sites $\boldsymbol{R}_j$ for the purpose of calculating the effective field around an individual site $\boldsymbol{R}_i$. This is

$$u_i^0(1)=\sum_j{}'v(|\,\boldsymbol{r}_1-\boldsymbol{R}_j\,|).$$

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* The units are such that $\hbar=k=1$.

The next step is to put in zero-point motion, which is done using the Domb–Salter approximation for the normal modes of the system. This method has the virtue of being very simple and is also such that finite temperature can be taken into account. At the same time, because of the rather extreme approximations made, the method should be checked against more sophisticated (and presumably more accurate) calculations. This has been done by the Cornell group who find it to be reliable at sufficiently small molar volume.

KRUMHANSL and WU (1972) have given a variational calculation of E in which short-range correlations are included by introducing a Jastrow-type pair-correlation function into the trial wave function. The expectation value of the Hamiltonian and the normalization integral are evaluated using a cluster expansion, a technique used in the quantum crystal problem by NOSANOW (1966). Nosanow chooses a two-particle correlation function $f(r_{12})$ such that the peak in the function is independent of molar volume; Krumhansl and Wu, on the other hand, choose a function such that the peak moves to a smaller value of r_{12} as the volume is decreased. In our formalism, the condition expressed by eq. (6) has the same effect on our correlation function χ_{ij}. As an example, in fig. 1 we plot $\chi_{ij}(r)$ for nearest neighbors at molar volumes of 10 and 23 cm^3 corresponding to nearest neighbor distances of 2.88 Å and 3.78 Å, respectively. Krumhansl and Wu introduce this behavior not only because it is physically reasonable, but also because it maintains good convergence of the cluster expansion at small molar volumes.

Finally, we mention the work of BRUCE (1972) which is also a variational calculation of E using a Jastrow-type pair correlation function in the trial wave function. Uncertainties associated with the cluster expansion are avoided by using Monte-Carlo methods to evaluate many-dimensional integrals. The procedure is the same as originally applied to solid helium by HANSEN and LEVESQUE (1968). From a theoretical point of view, it is encouraging that all of the above-described formalisms lead to comparable results for E in solid H_2 over a wide range of molar volume.

2.2. *Intermolecular interaction*

The interaction between a pair of parahydrogen molecules may be expanded as a sum over spherical harmonics; we shall approximate the sum by

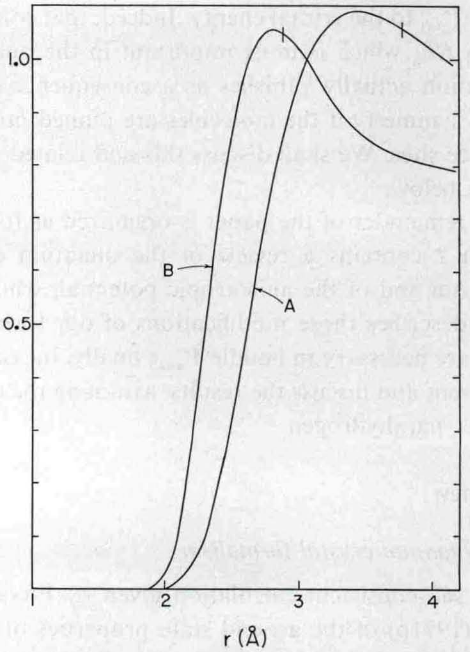

Fig. 1. Nearest-neighbor correlation functions $\chi(r)$ versus r. A: $V = 23$ cm^3 corresponding to a nearest-neighbor distance $a = 3.78$ Å; B: $V = 10$ cm^3 corresponding to $a = 2.88$ Å.

$$V(1, 2; \omega_1, \omega_2) = [V^{00}(1, 2)\, Y_0(\omega_1)\, Y_0(\omega_2)] + [V^{02}(1, 2)\, Y_0(\omega_1)\, Y_2(\omega_2) + V^{20}(1, 2)\, Y_2(\omega_1)\, Y_0(\omega_2) + V^{22}(1, 2)\, Y_2(\omega_1)\, Y_2(\omega_2)], \quad (10)$$

where Y_0 and Y_2 are the spherical harmonics for $l = 0$, $m = 0$, and $l = 2$, $m = 0$; ω_1 and ω_2 refer to the directions of the interatomic axes of molecules 1 and 2 relative to the c-axis of the hcp crystal. The first term on the right-hand side of eq. (10) is just the isotropic part of the interaction,

$$(Y_0)^2 V^{00} = \frac{1}{4\pi} V^{00}, \quad V^{00} = 4\pi v(r),$$

where v is e.g. the E6 potential described in section 1.

There is no reliable empirical determination of the anisotropic part of the interaction, V_{ani}. NAKAMURA (1955) has expanded the theoretical expression of DE BOER (1942), finding for molecules in the $l = 0$ and 2 states:

$$\sqrt{\tfrac{16}{5}\pi}\, B(r) \sqrt{\tfrac{4}{5}\pi} \sum_m [Y_{2m}(\omega_1)\, Y_{2,-m}(\Omega_{12}) + Y_{2m}(\omega_2)\, Y_{2,-m}(\Omega_{12})],$$

where

$$B(r) = \beta_1 \exp\left[-\frac{r-a_0}{\rho}\right] - \beta_2 \left(\frac{a_0}{r}\right)^6,$$

and Ω_{12} specifies the direction of $\boldsymbol{r}_{12}$ relative to the c-axis. The theoretical values of the parameters are $\beta_1 = 2.6\,\mathrm{K}, \beta_2 = 1.6\,\mathrm{K}$, and $\rho = 0.283$ Å; $a_0 = 3.75$ Å is the nearest neighbor distance in solid H_2 at $P = 0$. For computational simplicity, we retain only the $m = 0$ part of this interaction and have, upon comparison with eq. (10),

$$V^{20}(1,2) = V^{02}(1,2) = (\tfrac{8}{5}\sqrt{5})\pi\, B(r)\, P_2(\cos\theta_{12}), \quad (11)$$

where θ_{12} is the angle between $\boldsymbol{r}_{12}$ and the c-axis; P_2 is the Legendre polynomial of degree two. There is also an anisotropic potential proportional to $Y_2(\omega_1)\, Y_2(\omega_2)$. The dominant part of this is the electric quadrupole–quadrupole (EQQ) interaction which gives

$$V^{22}(1,2) = 20\pi\, \Gamma_0\, P_4(\cos\theta_{12}) \left(\frac{a_0}{r}\right)^5, \quad (12)$$

where $\Gamma_0 = 1$ K. Once again, we neglect terms with $m \neq 0$. Finally, there should also be terms in eq. (10) proportional to $Y_{2l}(\omega_1)$ and $Y_{2l}(\omega_2)$; the sum of all neglected terms is less than about 10% of V^{20} or V^{02} for all molar volumes treated here. In order to be consistent in this regard, we systematically ignore all terms involving $Y_4(\omega_1)$ and $Y_4(\omega_2)$ in what follows.

It is interesting to compare the exponential (valence) part of V_{ani} in eq. (11) with the corresponding part of the empirically determined E6 potential. The empirical constant $\rho_e = r_m/\alpha = 0.239$ Å is sufficiently different from the theoretical $\rho_t = 0.283$ Å to produce considerably different results in the calculations presented below if ρ_t is replaced by ρ_e. We shall comment further on this point in section 4.

3. Anisotropic formalism

The introduction of V_{ani} depending on the rotational state of the molecules produces an admixture of rotational states in the single-particle and correlation functions. When V_{ani} is taken in the form of eq. (10), then $\varphi_i(1)$ becomes

$$\varphi_i(1;\omega_1) = Y_0(\omega_1)\,\varphi_{0i}(1) + Y_2(\omega_1)\,\varphi_{2i}(1), \quad (13)$$

so that we now have two functions φ_{0i} and φ_{2i} to determine. Rotational states with $l > 2$ are ignored; this procedure is valid as long as the "anisotropy energy" is small compared to the excitation energy of these states.

Similarly, the single-particle self-consistent field now takes the form

$$u_i(1,\omega_1) = Y_0(\omega_1)\, Y_0(\omega_1)\, u_{0i}(1) + Y_0(\omega_1)\, Y_2(\omega_1)\, u_{2i}(1). \quad (14)$$

The Schrödinger equation for the single-particle function can be written as two equations:

$$\left(-\frac{\nabla_1{}^2}{2m} + u_{0i}\, Y_0{}^2\right)\varphi_{0i} + \tfrac{8}{7} u_{2i}\, Y_0{}^2\, \varphi_{2i} = \varepsilon\, \varphi_{0i}, \quad (15a)$$

$$\left(-\frac{\nabla_1{}^2}{2m} + 6B_I + u_{0i}\, Y_0{}^2 + (\tfrac{4}{21}\sqrt{5})\, u_{2i}\, Y_0{}^2\right)\varphi_{2i} + u_{2i}\, Y_0{}^2\, \varphi_{0i} = \varepsilon\, \varphi_{2i}, \quad (15b)$$

where we have used

$$Y_2\, Y_2 = (\tfrac{18}{35}\sqrt{\tfrac{5}{9}})\, Y_4\, Y_0 + (\tfrac{4}{21}\sqrt{5})\, Y_2\, Y_0 + \tfrac{8}{7}\, Y_0\, Y_0,$$

and Y_4 has been neglected, which is consistent with our approach of considering only the $l = 0$, 2 rotational states.

The general form of the correlation function $\chi_{ij}(1,2;\omega_1,\omega_2)$ is

$$\begin{aligned}\chi_{ij}(1,2;\omega_1,\omega_2) = 4\pi\, [&\chi_{ij}^{00}(1,2)\, Y_0(\omega_1)\, Y_0(\omega_2) \\ &+ \chi_{ij}^{20}(1,2)\, Y_2(\omega_1)\, Y_0(\omega_2) \\ &+ \chi_{ij}^{02}(1,2)\, Y_0(\omega_1)\, Y_2(\omega_2) \\ &+ \chi_{ij}^{22}(1,2)\, Y_2(\omega_1)\, Y_2(\omega_2)] \quad (16)\end{aligned}$$

in our approximation. We remark that χ_{ij} is part of the two-particle Green's function which has been factored into single-particle and correlation functions. This separation is not unique, and the form of χ_{ij} in eq. (16) is a consequence of our previous treatment (Ebner and Sung, 1971b).

The self-consistent field is given by the same equation as before

$$u_i(1,\omega_1) = \\ = \sum_j{}' \int V(1,2)\, \chi_{ij}(1,2;\omega_1,\omega_2)\, |\varphi_j(2,\omega_2)|^2\, \mathrm{d}^3 r_2\, \mathrm{d}\omega_2. \quad (17)$$

The equation of motion for χ_{ij} is similar to eq. (4),

$$H_{ij}\, \chi_{ij}\, \varphi_i\, \varphi_j = \lambda_0\, \chi_{ij}\, \varphi_i\, \varphi_j, \quad (18)$$

where

$$
\begin{aligned}
H_{ij} = {} & -\frac{\nabla_1{}^2}{2m} - \frac{\nabla_2{}^2}{2m} + \frac{1}{2I} J_1{}^2 + \frac{1}{2I} J_2{}^2 \\
& + V(1,2;\omega_1,\omega_2) + u_i(1,\omega_1) + u_j(2,\omega_2) + \varDelta_{ij}(1,2) \\
& - \int \chi_{ij'}(1,\bar{2};\omega_1,\bar{\omega}_2)\, V(1,\bar{2})\, |\varphi_j(\bar{2},\bar{\omega}_2)|^2\, \mathrm{d}^3\bar{r}_2\, \mathrm{d}\bar{\omega}_2 \\
& - \int \chi_{ij}(\bar{1},2;\bar{\omega}_1,\omega_2)\, V(\bar{1},2)\, |\varphi_i(\bar{1},\bar{\omega}_1)|^2\, \mathrm{d}^3\bar{r}_1\, \mathrm{d}\bar{\omega}_1 ,
\end{aligned}
\tag{19}
$$

where $J_1{}^2$ and $J_2{}^2$ are the internal angular momentum operators for molecules 1 and 2. The simultaneous solution of these equations plus the single-particle equation and the self-consistency condition eq. (17) is a formidable numerical problem. Since our interest at this time is primarily to examine the effect of the anisotropic interaction on the energy in the molecular phase rather than to pursue the question of a transition to the metallic phase, an expansion procedure will be used. We keep terms in V_{ani} through second order only. This means that we should find φ_{2i} and u_{2i} to first order in V_{ani} and φ_{0i} and u_{0i} to second order. If φ_{0i} is normalized to 1, then each single-particle wave function should be multiplied by $N_1^{-\frac{1}{2}}$, where

$$
\begin{aligned}
N_1 & = \int \varphi_{0i}^2(1)\, \mathrm{d}^3 r_1 + \int \varphi_{2i}^2(1)\, \mathrm{d}^3 r_1 \\
& = 1 + \int \varphi_{2i}^2(1)\, \mathrm{d}^3 r_1 .
\end{aligned}
\tag{20}
$$

Also, to maintain the proper normalization of the two-particle Green's function, the correlation function should be divided by N_2, where

$$
\begin{aligned}
N_2 = 1 + 2 \int & [\chi_{ij}^{02}(1,2)\, \varphi_{0i}^2(1)\, \varphi_{0j}(2)\, \varphi_{2j}(2) \\
& + \chi_{ij}^{20}(1,2)\, \varphi_{0j}^2(2)\, \varphi_{0i}(1)\, \varphi_{2i}(1) \\
& + \chi_{ij}^{00}(1,2)\, \varphi_{0i}^2(1)\, \varphi_{2j}^2(2)]\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 ,
\end{aligned}
\tag{21}
$$

where we have used

$$
\int \chi_{ij}^{00}(1,2)\, \varphi_{0i}^2(1)\, \varphi_{0j}^2(2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 = 1 .
$$

The single-particle potential is given to the appropriate order in V_{ani} by

$$
\begin{aligned}
u_{0i}(1) = {} & \sum_j{}' \int V^{00}\, \chi_{ij}^{00}\, \varphi_{0j}^2\, N_2^{-1}\, \mathrm{d}^3 r_2 \\
& + 2 \sum_j{}' \int V^{00}\, \chi_{ij}^{02}\, \varphi_{0j}\, \varphi_{2j}\, \mathrm{d}^3 r_2 \\
& + 2 \sum_j{}' \int V^{02}\, \chi_{ij}^{00}\, \varphi_{0j}\, \varphi_{2j}\, \mathrm{d}^3 r_2 \\
& + \sum_j{}' \int V^{00}\, \chi_{ij}^{00}\, \varphi_{2j}^2\, \mathrm{d}^3 r_2 \\
& + \sum_j{}' \int V^{02}\, \chi_{ij}^{02}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 \\
& + \tfrac{7}{8} \sum_j{}' \int V^{20}\, \chi_{ij}^{20}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 \\
& + \tfrac{7}{8} \sum_j{}' \int V^{22}\, \chi_{ij}^{22}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2
\end{aligned}
\tag{22}
$$

and

$$
\begin{aligned}
u_{2i}(1) = {} & \sum_j{}' \int V^{20}\, \chi_{ij}^{00}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 \\
& + \sum_j{}' \int V^{00}\, \chi_{ij}^{20}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 .
\end{aligned}
\tag{23}
$$

The expression for u_{0i} is correct to second order in V_{ani} while u_{2i} is first order. In these equations, corrections to first order in V_{ani} only are needed in $\chi_{ij}^{ll'}$. These are determined as follows: Eq. (18) is multiplied by $Y_0(\omega_1)\, Y_0(\omega_2)$ and integrated over ω_1 and ω_2 to give

$$
H_{ij}^{00}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} ,
$$

where H_{ij}^{00} is the operator $\{\ldots\}$ in eq. (4). Thus χ_{ij}^{00} is just the correlation function of EBNER and SUNG (1971a). Of course, φ_{0i} differs from the single-particle function when V_{ani} is not present, but the difference is second-order and we shall ignore it. By also multiplying $Y_2(\omega_1)\, Y_0(\omega_2)$, $Y_0(\omega_1)\, Y_2(\omega_2)$ and $Y_2(\omega_1)\, Y_2(\omega_2)$ into eq. (18) and integrating over ω_1 and ω_2, we obtain three equations for the anisotropic part of the correlation function,

$$
\begin{aligned}
H_{ij}^{00}\, \chi_{ij}^{20}\, \varphi_{0i}\, \varphi_{0j} + 6 B_I\, \chi_{ij}^{20}\, \varphi_{0i}\, \varphi_{0j} + 6 B_I\, \chi_{ij}^{00}\, \varphi_{2i}\, \varphi_{0j} & \\
+ H^{20}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{20}\, \varphi_{0i}\, \varphi_{0j} , &
\end{aligned}
\tag{24}
$$

$$
\begin{aligned}
H_{ij}^{00}\, \chi_{ij}^{02}\, \varphi_{0i}\, \varphi_{0j} + 6 B_I\, \chi_{ij}^{02}\, \varphi_{0i}\, \varphi_{0j} + 6 B_I\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{2j} & \\
+ H^{02}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{02}\, \varphi_{0i}\, \varphi_{0j} &
\end{aligned}
\tag{25}
$$

and

$$
\begin{aligned}
H_{ij}^{00}\, \chi_{ij}^{22}\, \varphi_{0i}\, \varphi_{0j} + 12 B_I\, \chi_{ij}^{22}\, \varphi_{0i}\, \varphi_{0j} & \\
+ H^{22}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{22}\, \varphi_{0i}\, \varphi_{0j} , &
\end{aligned}
\tag{26}
$$

where

$$
H^{02} = H^{20} = \frac{V^{20}}{4\pi}, \quad H^{22} = \frac{V^{22}}{4\pi} .
$$

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

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

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

and

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

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,

$$E = N_1^{-1} \int \varphi_i^*(1, \omega_1) \Big(- \frac{\nabla_1^{\,2}}{2m} + \frac{1}{2I} J_1^{\,2} + u_i(1, \omega_1) \Big) \varphi_i(1, \omega_1)\, \mathrm{d}^3 r_1\, \mathrm{d}\omega_1 \,. \qquad (30)$$

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 $\rho = \rho_{\text{t}} = 0.283$ Å and $\rho = \rho_{\text{e}} = 0.239$ 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, $\rho = \rho_{\text{e}}$ leads to very good agreement of theory and experiment for $V \lessapprox 15$ 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 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 $|\,\Delta E_{\text{a}}\,|$ 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.

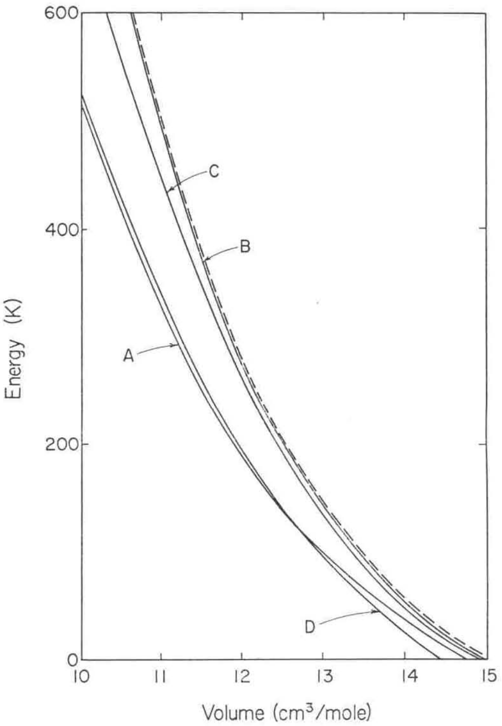

Fig. 2. Ground state energy E versus molar volume V.

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 $V \gtrapprox 11$ 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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