

## Ground-State Properties of Solid H<sub>2</sub> at High Pressures

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*A simple variational calculation, based on a Heitler-London wave function, is used to describe the high-pressure properties of solid hydrogen at 0 K. The system properties are expressed as a power series in  $\hbar$ , which is utilized to investigate the onset of classical behavior. The high-pressure results for the energy and the pressure-volume relation are in close agreement with a recent calculation which used the Domb-Salter approximation. Information is given on the pressure dependence of the two-body correlations in the solid.*

### 1. INTRODUCTION

There has been recent interest in the high-pressure properties of the quantum solids, especially the isotopes of hydrogen. This interest is partially motivated by efforts to produce a high-pressure metallic phase of hydrogen and also by the belief that the Jovian planets are composed mainly of solid hydrogen.<sup>1</sup>

It is speculated that, at sufficiently high pressures, the molecules of these solids become sufficiently localized so that approximations commonly used for heavy solids, such as the various harmonic approximations,<sup>2</sup> can be employed. Such calculations are known to be unacceptable for quantum solids at low pressures.<sup>3</sup>

Krumhansl and Wu<sup>4</sup> (KW) have calculated the pressure-volume relation for solid hydrogen using the cluster-expansion approximation developed by Nasanow.<sup>5</sup> In this theory the wave functions are assumed to be of the form

$$\psi(\bar{r}_1, \dots, \bar{r}_N) = \prod_{i=1}^N \phi(\bar{r}_i) \prod_{j < k}^N f(r_{jk}) \quad (1)$$

where the  $\phi(\bar{r}_i) \equiv \phi(\bar{r}_i - \bar{R}_i)$  are single-particle functions localized about their equilibrium lattice sites  $\bar{R}_i$ , and the  $f(r_{jk})$  are functions which introduce short-range correlations between pairs of molecules. Using an exp-6 interaction potential and suitably parameterized forms for  $f$  and  $\phi$ , they truncated the cluster expansion at second order and minimized the ground-state energy with respect to the

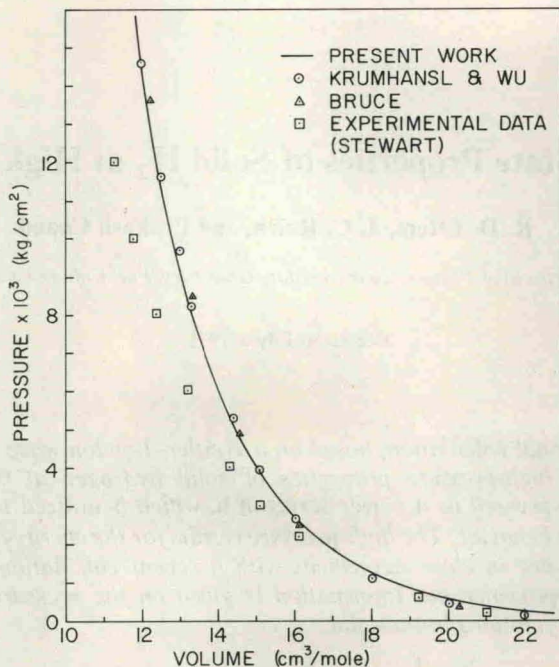


Fig. 1. The  $P$ - $V$  curve. The solid line represents the results of the present theory. The various dots represent the results of other theoretical calculations and the data of Stewart,<sup>6</sup> as indicated on the graph.

parameters. Their results, shown in Fig. 1, do not compare well with the experimental data of Stewart<sup>6</sup> at the higher pressures, although that data may be subject to further refinements. However, the theory itself may be a source of the difficulty since it is known to have certain deficiencies. Another possible source of error in their work is the use of a spherically symmetrical potential which, for  $\text{H}_2$ , may be a poor approximation. Bruce<sup>7</sup> has recently performed a calculation on  $\text{H}_2$  using a wave function of the form of Eq. (1) which avoids some theoretical difficulties in the cluster-expansion approximation. They use a Monte Carlo scheme much like that employed by Hansen and Levesque<sup>8</sup> for helium. Another approach to the problem, a self-consistent  $T$ -matrix approximation, has been used by Ebner and Sung.<sup>9</sup> Their calculated  $P$ - $V$  relation is virtually identical to the KW results.

The calculation described in this article is motivated by the possibility that, for increasing pressures, the overlap of the wave function between neighboring lattice sites becomes small and that the molecules become increasingly localized. This condition would lead ultimately to classical behavior and a simple description of high-pressure solid hydrogen. Some evidence of this possibility is found in the pressure dependence of tunneling processes in solid  $^3\text{He}$ .<sup>10</sup> The tunneling, which depends on the overlap between neighboring sites, is substantially reduced at high pressures. Under the conditions just outlined an expansion of the system

properties in powers of  $\hbar$  is a useful way to investigate the onset of classical behavior. A variational approach developed by Bernardes<sup>11</sup> is ideally suited for this investigation. A description of that theory is given in Section 2.

## 2. THEORY

The wave equation for a system of  $N$  interacting particles can be written in the form

$$\left[ -\lambda^2 \sum_i \nabla_i^2 + \left(\frac{1}{2}\varepsilon\right) \sum_{i,j} v(x_{ij}) \right] \psi = (E/\varepsilon)\psi \quad (2)$$

where  $\bar{x}_{ij} = \bar{r}_{ij}/\sigma$ , a dimensionless length. The potential is

$$V(x) = 4\varepsilon[x^{-12} - x^{-6}] \quad (3)$$

and  $\lambda^2 = (\hbar^2/2m\varepsilon\sigma^2)$ ,  $m$  being the particle mass. For  ${}^2\text{H}_2$ ,  $\varepsilon = 37$  K and  $\sigma = 2.93$  Å.<sup>12</sup> The variational wave function is

$$\psi(\bar{r}_1, \dots, \bar{r}_N) = \prod_{i=1}^N \phi(\bar{r}_i - \bar{R}_i) \quad (4)$$

For simplicity  $\phi(x)$  is chosen to be of the form

$$\phi(x) = (\pi/2a^3)^{1/2} [(\sin |\pi\sigma x/a|)/(|\pi\sigma x/a|)] \quad x \leq a/\sigma \quad (5)$$

$$\phi(x) = 0 \quad x > a/\sigma \quad (6)$$

where  $a$  is a variational parameter to be determined. These conditions are just a statement of the Heitler-London method, where each wave function is localized about its lattice site and is not allowed to overlap with wave functions of neighboring sites. Such an approximation is consistent with our original statement of the problem.

Using Eqs. (4)–(6), the expectation value of the Hamiltonian per particle becomes, in dimensionless units,

$$E = \langle H/N\varepsilon \rangle = E_{st} + \lambda^2 \alpha^{-2} + \sum_{n=1}^{\infty} \alpha^{2n} A_n \quad (7)$$

where  $\alpha \equiv a/\pi\sigma$ . For a close-packed lattice, the static intermolecular energy  $E_{st}$  is

$$E_{st} = \frac{1}{2}[C_{12}V^{-4} - 2C_6V^{-2}] \quad (8)$$

where  $C_6$  and  $C_{12}$  are lattice summation constants<sup>13</sup> and  $V$  is the volume in units of  $N\sigma^3$ .

$$A_1 = 10^2[5.9V^{-14/3} - 2.84V^{-8/3}]$$

$$A_2 = 10^3[36.7V^{-16/3} - 5.23V^{-10/3}]$$

$$A_3 = 10^4[184V^{-6} - 9.8V^{-4}]$$

Following Bernardes,<sup>11</sup> we truncate the series in Eq. (7) after the  $n = 3$  term and minimize  $E$  with respect to  $\alpha^2$ . Similarly, the pressure is determined from the expression  $P = -\partial E/\partial V$ . At high pressures, it is sufficient to keep terms only to order  $\hbar$  in the expressions for  $E$  and  $P$ . In this case only the  $n = 1$  term is kept in Eq. (7). The energy and pressure then become

$$E(V) = E_{st}(V) + 2\lambda A_1(V) \quad (9)$$

$$P(V) = 2[C_{12}V^{-5} - C_6V^{-3}] + 114\lambda V^{-10/3}f(V) \quad (10)$$

where  $f(V) = (1 - 0.27V^2)/(1 - 0.48V^2)^{1/2}$ . In Eq. (9)  $E_{st}$  can be interpreted as the classical contribution to the energy, and the second term is, to first order in  $\hbar$ , the zero-point energy. It is Eqs. (9) and (10) which are particularly useful in studying the onset of classical behavior at high pressures.

### 3. RESULTS

Figure 1 shows the pressure-volume relation for close-packed solid  $H_2$  at 0 K, from 22.65 to 11  $cm^3/mole$ . The solid line represents our calculation obtained by taking the volume derivative of Eq. (7), truncated after  $n = 3$ . Higher order terms were found to be negligible, except at the lowest pressures where the theory is not expected to be very accurate. The calculations are compared with other theories mentioned earlier<sup>4,7,9</sup> and with the experimental results of Stewart.<sup>6</sup> Our results coincide with those of KW<sup>4</sup> and others<sup>7,9</sup> for volumes  $V \gtrsim 17 cm^3/mole$ , but not with experimental data. It is interesting to note that our results agree surprisingly well with experiment in the regime  $V > 17 cm^3/mole$ . The extension of the calculations to very high pressures ( $\sim 2 \times 10^6 atm$ ) is shown in Fig. 2. For comparison, results obtained from a Domb-Salter approximate calculation<sup>14</sup> are displayed. The two different theoretical approaches give essentially identical results. The energies do not agree as well as the  $P$ - $V$  relations at the lower pressures ( $E \simeq -62 K$  at 22.65  $cm^3/mole$  compared with an experimental result of  $-92 K$ ). However, for all  $V < 13 cm^3/mole$  our calculated energies agree very closely with KW and the Domb-Salter approximation of Pollock *et al.*<sup>14</sup>

To investigate the onset of classical behavior, the pressure was calculated at small volumes using Eq. (10), which is quite accurate for volumes  $V < 13 cm^3/mole$ . The ratio of the second term in Eq. (10) to the total pressure gives the relative zero-point contribution to the pressure. The zero-point motion contributes less than 5% to the total pressure for volumes less than 3  $cm^3/mole$ . A similar condition obtains for the energy. Hence, below this volume the systems behavior is essentially classical. This regime corresponds to pressures above  $1.5 \times 10^7 atm$ .

### 4. DISCUSSION

This simple Heitler-London calculation, being an expansion in powers of  $\hbar$ , is well suited for investigating the high-pressure properties of hydrogen. It is clear that the system approaches classical behavior at high pressures, not only from the analysis of Eqs. (9) and (10), but also from the fact that the ratio of the

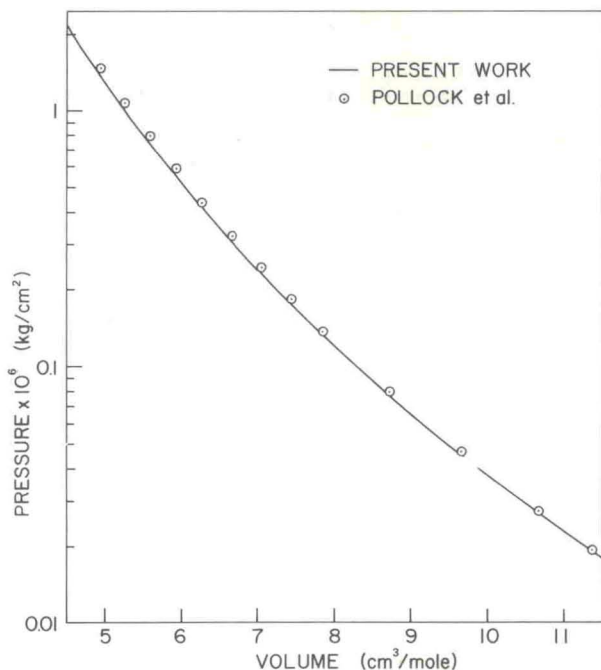


Fig. 2. The  $P$ - $V$  curve at high pressures. The solid line represents the results of the present theory. The dots represent the theoretical calculations of Pollock *et al.*<sup>14</sup>

calculated kinetic energy to the potential energy decreases monotonically as the pressure increases. The onset of classical behavior is easily recognized. The lack of theoretical agreement with experiment at higher pressures may well be due to the use of an inadequate interaction potential. This interpretation is particularly plausible since our calculation agrees so closely with other quite different theoretical approaches at high pressures. The success of the theory at low pressures is interesting.

Finally, an interpretation of the pressure dependence of the pair correlation function  $f(r)$  in Eq. (1) is possible in terms of this theory. The boundary condition  $\phi(x) = 0$  for  $x > a/\sigma$  can be interpreted as equivalent to a step-function form for  $f(r)$ . The pressure dependence of  $f(r)$  is then determined by the behavior of  $a$ . Our calculations show that  $a$  decreases by approximately a factor of two as the volume is reduced from 22 to 11 cm<sup>3</sup>/mole. The location of the step in  $f$  is shifted from  $x = 0.895$  to  $x = 0.83$  as the volume is decreased in this interval. In terms of Eq. (1) the particles become more localized as the pressure is increased, as evidenced by the narrowing of  $\phi(x)$ . In addition, as the pressure increases, the position of the step in  $f(r)$  is shifted further into the region containing the strong repulsive potential core. These results tend to support the notion that the shape of  $f(r)$  is fairly sensitive to changes in the volume.

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