

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