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Ground-State Properties of Solid H_2 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 ħ, 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.[1]

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,[2] can be employed. Such calculations are known to be unacceptable for quantum solids at low pressures.[3]

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

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

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 ϕ, they truncated the cluster expansion at second order and minimized the ground-state energy with respect to the

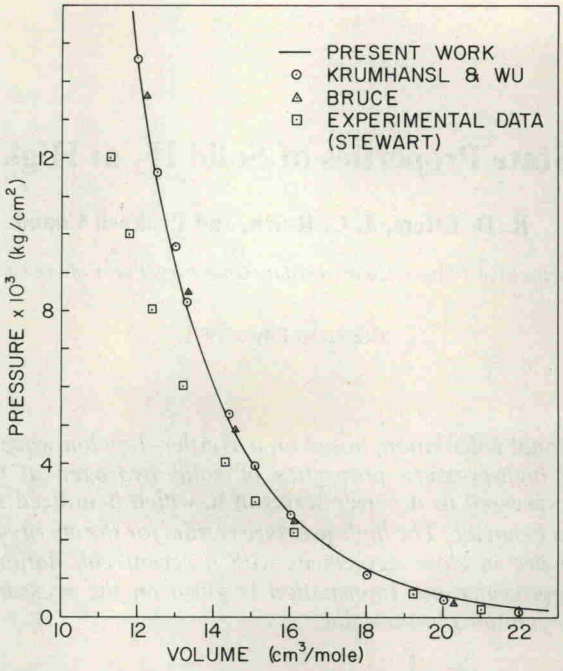

Fig. 1. The P–V curve. The solid line represents the results of the present theory. The various dots represent the results of other theoretical calculations and the data of Stewart,[6] as indicated on the graph.

parameters. Their results, shown in Fig. 1, do not compare well with the experimental data of Stewart[6] 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 H_2, may be a poor approximation. Bruce[7] has recently performed a calculation on 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[8] for helium. Another approach to the problem, a self-consistent T-matrix approximation, has been used by Ebner and Sung.[9] 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}He.[10] 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