Solid Hydrogen: Ground-State Energy, Pressure, and Compressibility

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The ground-state energy, the pressure, and the compressibility of solid molecular hydrogen is calculated by means of a modified Brueckner theory. The Bethe–Goldstone equation is solved to give the reaction matrix or an effective interaction in coordinate space; the ground-state energies for normal hydrogen and deuterium are calculated. Also, the pressure and the compressibility is estimated from the dependence of the ground-state energy on density or molar volume. Both hcp and fcc structures are considered. Theoretical results for the ground-state energy per particle are $-82 \text{ K}$ for solid hydrogen at a molar volume of $22 \text{ cm}^3/\text{mole}$ and $-135 \text{ K}$ for solid deuterium at a molar volume of $19 \text{ cm}^3/\text{mole}$. The corresponding experimental results are $-92$ and $-138 \text{ K}$, respectively. We obtain zero pressure for solid hydrogen at a molar volume of $22.45 \text{ cm}^3/\text{mole}$ and for solid deuterium at a molar volume of $19.2 \text{ cm}^3/\text{mole}$. The corresponding experimental results are $22.65$ and $19.56 \text{ cm}^3/\text{mole}$, respectively. Theoretical results for the compressibility at zero pressure are $5.3 \times 10^{-4} \text{ atm}^{-1}$ for solid hydrogen and $2.6 \times 10^{-4} \text{ atm}^{-1}$ for solid deuterium. The corresponding experimental results are $4.9 \times 10^{-4}$ and $3.0 \times 10^{-4} \text{ atm}^{-1}$, respectively. The agreement with experimental results is reasonably good since higher order cluster terms are not included in this first approximation.

1. INTRODUCTION

Solid hydrogen and deuterium are quantum solids or quantum crystals. The two-body potential has a very strong repulsion at small distances, and because of the relatively weak attractive part of the interaction and the small atomic mass, we get strong short-range correlations and a relatively large zero-point motion, although the attractive well in the intermolecular potential is much deeper than in the interatomic helium potential. The zero-point energy is comparable to the potential energy, and the root-mean-square deviation of a molecule from its equilibrium position at a lattice site is not small compared with the nearest-neighbor distance or the lattice constant.
Solid hydrogen should be a simple quantum solid, but experiments have shown two crystalline forms, i.e., the hexagonal close-packed (hcp) structure, and the cubic close-packed or face-centered cubic (fcc) structure. The normal structure is an hcp lattice,\textsuperscript{1-2} while the low-temperature modification is an fcc lattice.\textsuperscript{3-9} The energy difference between the two phases is, however, expected to be very small. We find the same phases for solid deuterium,\textsuperscript{10-14} where fcc deuterium is the low-temperature structure.

Calculations of properties of solid hydrogen and deuterium can give a comparison of two systems with different zero-point energy because of different atomic mass, but which are otherwise identical with the same two-body interaction between the molecules. In addition to comparison of theoretical results with experimental values, such calculations can also be a test of methods already worked out for solid helium.\textsuperscript{15} And properties of solid hydrogen are also of astrophysical interest, since the planets Jupiter and Saturn are expected to consist mainly of solid hydrogen under enormous pressure.\textsuperscript{16}

\section{2. GENERAL THEORY}

Standard many-body methods cannot be applied directly to quantum crystals because the usual form of the unperturbed Hamiltonian does not produce sufficient correlations in the unperturbed ground state. It is important for the convergence of a perturbation expansion that the solution for the unperturbed system contains the essential features of the actual system, and it is important to include the correlation effects in the wave function in a microscopic calculation. A cluster expansion should give rapid convergence since the localization of a particle in the crystal allows it to interact strongly only with particles nearby, particularly with the nearest neighbors. Multiple correlations are probably not important since simultaneous close approach of several particles is not very likely because of this localization.

It is thus clear that calculations of the ground-state energy of solid hydrogen must include the strong correlation effects. Strong short-range correlations can be treated by a modified Brueckner theory as already demonstrated for nuclear matter,\textsuperscript{17} liquid helium,\textsuperscript{18-20} or solid helium.\textsuperscript{15} Introducing a reaction matrix, we construct an analog to the Brueckner theory by including two-body correlations in a ladder approximation. It permits a pair of particles to interact by the softened reaction matrix instead of the almost hard-core two-body potential, moving in a self-consistently softened potential well formed by summing and averaging the reaction matrix over the remaining neighbors.

In translationally invariant systems, such as nuclear matter or liquid helium, the Brueckner theory or the ladder approximation is essentially a