GROUND STATE ENERGY OF SOLID MOLECULAR HYDROGEN AT HIGH PRESSURE

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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, sec-

ond, 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

from a given intermolecular potential. These calcula-
tions are fairly consistent with the older, classical cal-
culations and give theoretical pressures which are lar-
ger 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 calcula-
tion 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 inter-
molecular potential. There are several conventional
choices which are discussed in some detail by KRUM-
HANSL 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 empi-
rically 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),

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

with $\varepsilon_0 = 38.0$ K, $r_m = 3.339$ Å, $\alpha = 14.0$ and $r_{max}/r_m
= 0.20$; 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 concern-
ing the reliability of the potential in the core region is
probably not useful in the absence of more direct ex-
perimental information.

Another, and, we believe, the most important source
of the discrepancy between experimental and theoret-
ical 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 rota-
tional 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 in-
creasingly 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,
$\Delta E_a = \mathrm{O}\ (V_{ani}^2/B_I)$, 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
$V \lesssim 15$ cm^3. The purpose of this paper is to calculate
the energy change ΔE_a within the context of our quan-
tum 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 espe-
cially 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 quan-
tum mechanical rotators rather than as classical objects
which one can simply orient in certain directions with-
out 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-