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ABSTRACT

An equation of state for solid molecular hydrogen at 0°K is obtained using the self-consistent field method for calculating the electronic structure of the solid. Pressures up to 12.5 megabars are included in the calculation. Errors in the pressure are less than 5 kilobars in the low pressure region where experimental data are available. It is hoped they are less significant at higher pressures.

The author has made a number of calculations of 0°K equations of state of metals with simple crystal structures[1] (lithium, beryllium, aluminum, and iron) using the self-consistent-field approximation and a Green function band structure program[2] as the main analytical tool. The results of these calculations have been good: calculated lattice parameters at zero pressure are correct to a few percent, compressibilities to ten percent or so, and the agreement with the experimental equations of state is acceptable.

Recently there has been some interest in the equation of state of hydrogen because of a prediction that the metallic phase would be a superconductor with a high transition temperature,[3] and because of the interest in a suggested scheme for compressing and heating deuterium to a point where fusion is obtained.[4] Experimental data on the equation of state of hydrogen are available only to 20 kilobars,[5] so calculations which go beyond this point are of interest. There have already been a number of these,[6] but the differences between them are considerable. The present calculation agrees well with that of Ross[6] who used a method based on intermolecular potentials and with a similar calculation by Trubitsyn.[6] Our calculated pressures are substantially lower than those of Abrikosov, De Marcus, and Neece, Rogers and Hoover.[6]

Some problems arise in doing band structure calculations for molecular hydrogen which did not occur in the earlier calculations for lithium, etc. The first of these is that solid hydrogen is known to exist in several rather complicated crystal structures. At high pressures one may expect some sort of close-packed structure. There should not be much error in choosing a simple structure for the calculation rather than the more complicated (and still uncertain) one which actually occurs.

A second problem relates to a limitation of the Green function method for computing band structures. It is adapted only to "muffin-tin" potentials which are spherical and nonoverlapping. For the case of molecular hydrogen this means the muffin-tin spheres will have a radius of half the interatomic separation (which is 0.741Å in hydrogen) and will only occupy 1 or 2% of the volume of the crystal as against 68 or 74% in the simple metals. The source of the trouble is the small separation between the atoms in molecular hydrogen as compared with the size of a cell in the crystal. If this interatomic separation were zero the hydrogen molecules would become helium atoms and we would again have a tractable problem. The similarity between hydrogen molecules and helium atoms (the solids have similar volumes per molecule) suggests that the potential function of the two nuclei in the hydrogen molecule be expressed in a multipole expansion about their common center:

$$v(\underline{r}) = -\frac{e^2}{|\underline{r}-\underline{b}|} - \frac{e^2}{|\underline{r}+\underline{b}|} = \begin{cases} -\frac{2e^2}{r}\sum_0^{\infty}\left(\frac{b}{r}\right)^{2n} P_{2n}(\cos\theta) & r > b \\ \\ -\frac{2e^2}{a}\sum_0^{\infty}\left(\frac{r}{b}\right)^{2n} P_{2n}(\cos\theta) & r < b\ , \end{cases}$$

where

$$\cos\theta = \underline{r}\cdot\underline{b}/rb\ .$$

For the calculation of the equation of state we expect the wave function at large radii to be most important. This suggests that details in the potential function at small radii are of secondary importance, so we are led to drop all but the $n = 0$ term in the above expression for the nuclear potential:

$$v(r) \simeq \begin{cases} -\frac{2e^2}{r} & r > b \\ \\ -\frac{2e^2}{b} & r < b\ . \end{cases}$$

Since the approximate nuclear potential is spherical, the corresponding "pseudo-hydrogen molecule" will also be spherical. We may therefore choose a simple FCC lattice for the solid.

The next question which arises is how to choose the interatomic distance, 2b. For the free hydrogen molecule it is known to be 0.74Å and we could settle for using this number. In priciple b can be determined as part of the self-consistent field calculation, and this is what we do. The explicit dependence of the total energy on b is all contained in

$$E_b = e^2\left\{\frac{1}{2b} - \int_0^b \frac{2}{b}\,4\pi\rho(r)r^2dr - \int_a^c \frac{2}{r}\,4\pi\rho(r)r^2dr\right\}$$

(c is ∞ in the case of the free molecule and the Wigner-Seitz cell radius in the case of the solid)

where the first term in the brackets is the interaction energy of the two nuclei and the remaining terms are the interaction energy of the electrons with the nuclei in the spherical approximation. E_b is now to be minimized with respect to variations in b, taking into account only the explicit dependence on b. The easily obtained result is

$$\int_0^b 4\pi\rho(r)r^2dr = \frac{1}{4}\ ,$$

i.e., ¼ of an electron charge is inside the radius b and 1¾ units of charge are outside.

Finally it must be decided which of the several self-consistent-field schemes in common use for atomic and solid state calculations is to be used in this case. We have chosen a modification of the one proposed by Kohn and Sham which has worked well for us in the calculations for several metals mentioned above.[1] No justification for this is offered beyond our favorable experience in the past and the fact that the present results seem good so far as one can evaluate them.

The foregoing outlines the nature of the calculations insofar as they differ from others we have already done and described in reference 1. The results are given in the table and the figures.

TABLE

CALCULATED EQUATION OF STATE OF MOLECULAR HYDROGEN AND DISTANCES BETWEEN ATOMS IN THE HYDROGEN MOLECULE

R/a_0	V (cm^3/mole H_2)	P (kbar)	D/a_0
3.6	17.44	-4.37	1.275
3.4	14.69	-3.64	1.275
3.2	12.25	-0.01	1.273
3.0	10.09	+10.81	1.269
2.8	8.21	37.0	1.262
2.6	6.57	95.4	1.251
2.4	5.167	221.	1.234
2.2	3.980	489.	1.210
2.0	2.990	1064.	1.177
1.8	2.180	2333.	1.134
1.6	1.531	5273.	1.077
1.4	1.026	12551.	1.004

R is the radius of the Wigner-Seitz sphere containing one H_2 molecule. D(=2b) is the distance between nuclei in a molecule. The energy per molecule in atomic units (e^2/a_0) is approximately given by

$$E = 0.2488(3.2 - R/a_0)^2 \exp\,(1.267\,a_0/R - 1.241\,R/a_0).$$

The high pressure part of the equation of state is shown in Fig. 1 together with the corresponding calculations of Ross and of Neece, Rogers and Hoover. The contribution to the pressure from lattice vibrations is not included in these equations of state. Our pressures agree very well with Ross's and are substantially below those of Neece et al.

The low pressure calculations are shown in Fig. 2 -- again without any correction for lattice vibrations. A rough comparison with Stewart's[5] measured equations of state for hydrogen and deuterium is made by assuming that the lattice vibrations are harmonic and therefore that their contribution to the pressure is proportional to the inverse square root of the molecular mass. This permits one to subtract off the pressure due to lattice zero point oscillations. The remaining "static lattice" pressure is also plotted in Fig. 2.

We have not attempted to add corrections to our calculation of the pressure by an estimate of the contribution from the lattice vibration. The estimates given by Ross and Neece, Rodgers and

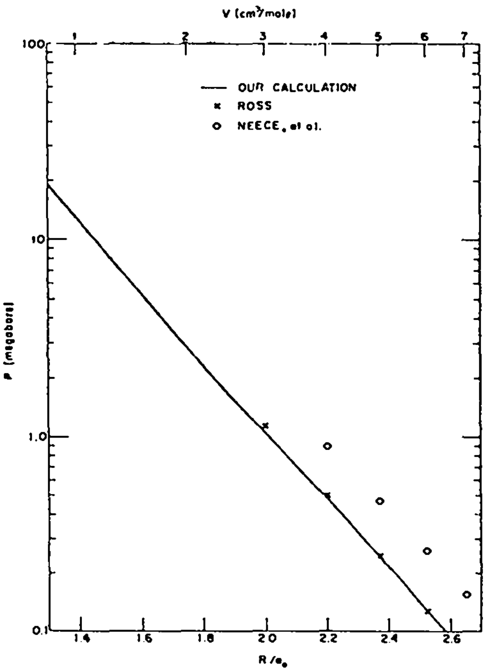

Fig. 1. Calculated equations of state of molecular hydrogen at 0°K without the contribution to the pressure of lattice vibtations. The pressure is in megabars. R is the radius of sphere whose volume is that of one molecule.

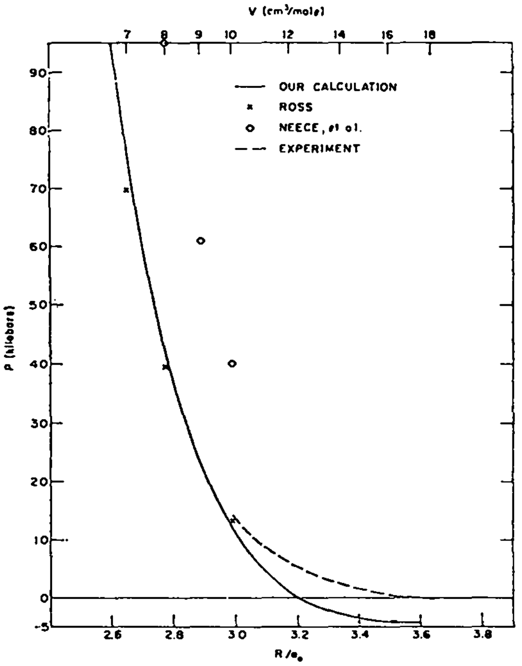

Fig. 2. Calculated equations of state of molecular hydrogen at 0°K without the contribution to the pressure of lattice vibrations. The experimental equation of state (based on Stewart's data for H_2 and D_2) has the pressure due to lattice vibrations subtracted out. The pressure is in kilobars.

Hoover are plotted in Fig. 3. Also the correction mentioned in the preceding paragraph based on the experimental data for hydrogen and deuterium is shown in this graph.

Returning to a consideration of the high pressure part of the calculations, it may be noted that the discrepancy between the equations of state of Ross and of Neece et al.[6] is somewhat puzzling. Both use the intermolecular potentials determined by Magnasco and Musso,[7] but Ross averages these over angle. One would expect this to result in a harder potential function and, in consequence, higher pressures in the equation of state; however Fig. 1 shows the two calculations are not in the expected relationship to each other.

Another question which arises in considering the high pressure region is how accurate is Magnasco and Musso's[7] calculation of the intermolecular potential. We don't know. Obviously a similar question may be asked in regard to our calculations.

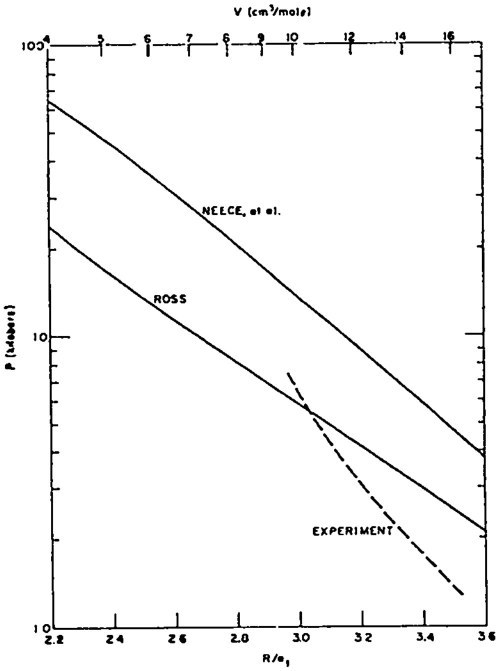

Fig. 3. Estimated contributions to the pressure of lattice vibrations. The curve labeled "experiment" is based on Stewart's data for H_2 and D_2 and assumes this contribution to the pressure is proportional to the inverse square root of the molecular mass; i.e. the lattice vibrations are harmonic.

We usually expect the electronic structure calculations to be better at high densities, but in this case the spherical approximation used for the nuclear potential creates an additional uncertainty. To get some idea of the magnitude of the error introduced by this approximation we used perturbation theory to estimate the correction due to the quadrupole term in the expansion of the potential of the nuclei:

$$v_2(r) = \begin{cases} -\dfrac{2e^2b^2}{r^3} P_2(\cos\theta) & r > b \\ -\dfrac{2e^2r^2}{b^3} P_2(\cos\theta) & r < b\,. \end{cases}$$

The contribution to the pressure ranged from about -50 kbar at the highest compression to about -0.1 kbar at the lowest. Probably this is a considerable underestimate, but it does suggest that the spherical approximation is not unreasonable.

The following points may be made in summary:

1. An equation of state of molecular hydrogen has been calculated for 0°K neglecting the effects of lattice vibrations.
2. The method used is similar to the one used by Wigner and Seitz[8] for calculating the cohesive energy of the alkali metals and is the same as that used by the author in previous successful calculations for lithium, beryllium, aluminum, and iron.[1]
3. Ordinarily these calculations are expected to be most reliable for high densities because they rely on the theory of the electron gas for the treatment of exchange and correlation. In practice they have been found to be acceptable at normal densities also.
4. In molecular hydrogen the main uncertainty is believed to be the additional approximation of replacing the potential of the two nuclei in a molecule by a spherical average about the common center.

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