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Exact-Exchange Crystal Hartree-Fock Calculations of Molecular and Metallic Hydrogen and Their Transitions*

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(Received 17 September 1974)

Hartree-Fock calculations using the exact-exchange operator are reported for molecular and metallic solid hydrogen. Both calculations used the same basis set and the same crystal formalism. The calculations indicate a transition to the metallic phase at a pressure of 2.1 Mbar, in agreement with recent experiments.

In recent years there has been a widespread interest in the possibility of producing metallic hydrogen in the laboratory[1] by means of a pressure-induced transition from the molecular phase. To determine the feasibility of such a process, it is important to have some estimate as to the pressure needed. Previous calculations[2-5] have produced estimates ranging from 0.25 to 20 Mbar, the lower pressure being relatively easy to reach in the laboratory, and the higher pressure out of reach at least statically.[6] Recent experimenters[7-8] achieving high pressures dynamically suggest that they may have detected the transition at pressures of 2.0 to 2.8 Mbar. In this Letter we present preliminary results which are obtained from calculations more rigorous than those previously performed, and which support the experimental evidence of a possible transition.

Theoretical estimates of the pressure required for the transition at zero temperature are obtained from the common tangent to the energy-volume curves for the two solid phases. Most of the previous estimates have been based on fairly similar equations of state for the metallic phase, but have used widely different and less reliable equations of state for the molecular phase. In fact, the metallic-phase equation of state recently obtained by Neece, Rogers, and Hoover[2] from the self-consistent calculation, using the Kohn-Sham local potential to approximate exchange and correlation effects, is not substantially different from the approximate cellular calculation by Wigner and Huntington[3] in 1935. The molecular-phase equation of state has been obtained by solving the Bethe-Goldstone equations using an approximate analytically fitted curve for the H_2-H_2 interaction potential.[5] Forms such as the Lennard-Jones 6-12 or 6-8 potentials were used, with parameters obtained either from experimental virial coefficients and viscosities for molecular hydrogen, or from variational calculations of the interaction of two H_2 molecules.[9] The molecular-phase equation of state varies sharply with the choice of parameters, with the result that estimates of the transition pressure based on slightly different H_2-H_2 pair potentials vary from 0.84 to 4.2 Mbar.[10] A main difficulty with all the previous work is that the metallic and molecular crystals are not treated in an internally consistent degree of approximation.

The calculations presented here are based on the techniques developed by Harris and Monkhorst[11] for the computation of Hartree-Fock wave functions and energies. In their method each valence Bloch orbital $|\vec{k}\rangle$ is expanded according to

$$|\vec{k}\rangle = \sum_m C_m(\vec{k})\,|k_m\rangle, \tag{1}$$

where the $|\vec{k}_m\rangle$ are basis Bloch functions with Bloch wave vector $\vec{k}$:

$$|\vec{k}_m\rangle = \exp(i\vec{k}\cdot\vec{r})\sum_{\mu}\sum_{n=1}^{d}\varphi_m(\vec{r}-\vec{R}_\mu-\vec{s}_n). \tag{2}$$

The sum over μ in Eq. (2) runs over all the lattice cells, $\vec{R}_\mu$ is the origin of cell μ, and $\vec{s}_n$ is the position relative to the cell origin of atom n. The φ_m are Slater-type atomic orbitals, and the coefficients $C_m(\vec{k})$ are determined, as functions of $\vec{k}$, by solution of the Hartree-Fock equations.

A key feature of the method of Harris and Monkhorst is the reduction of all the crystal integrals arising in the Hartree-Fock formalism to lattice sums. This reduction is accomplished by introducing Fourier representations for the integrals, and using convolution theorems and lattice-orthogonality relations. It then becomes possible to treat exchange exactly, and to avoid many of the problems encountered in approaches based on finite clusters of atoms. The method has been applied to cubic metallic hydrogen[12] and to lithium crystals.[13]

Calculations based on the above-described method were carried out for metallic hydrogen in a bcc lattice and for molecular hydrogen in a simple cubic lattice with one H_2 molecule per unit cell. The molecular-hydrogen crystal was constructed by placing one atomic nucleus at the origin of each unit cell, with the other in the principal diagonal at the position yielding a minimum Hartree-Fock energy. In this way the H-H distance in the molecular phase was optimized at each density. Both the metallic and molecular phases are treated by the same formalism and with the same orbital basis set, leading to Hartree-Fock results which should be of comparable quality.

It should be noted that at experimentally attainable pressures the structure of the molecular-hydrogen crystal is not simple cubic. Moreover, some calculations have indicated that the most stable structure for the metallic phase is not bcc.[14,15] However, it has been argued that these structure effects are not significant,[9] and we believe that they involve amounts of energy which are small relative to those of primary importance in the transition. Another potential limitation of our calculation is that it does not include the correlation energy. Calculations on hydrogen[12] indicate that the correlation energy is relatively insensitive to structure and denstiy, and so its omission for both phases should not have major effects. Finally, we note that our calculations apply at zero temperature. The effect of finite temperature on the transition pressure has been estimated to be small.[2]

In carrying out the calculations to be reported here, we found it necessary to use a different basis set than that used by Kumar, Harris, and Monkhorst[12] in their work on the metallic-hydrogen lattice. Their basis was restricted to $|\vec{k}_m\rangle$ with $\vec{k}$ values in the first Brillouin zone, and is unsuitable for the molecular crystal when it should have a Fermi surface greatly distorted from a spherical shape. Therefore, rather than using several different Slater-type orbitals φ_m, we used a single φ but $\vec{k}$ values in several zones. Functions of this type can be written as

$$|\vec{k}\rangle = \sum_{\vec{K}} C(\vec{k}+\vec{K}) \times \exp[i(\vec{k}+\vec{K})\cdot\vec{r}] \sum_{\mu} \sum_{n=1}^{d} \varphi(\vec{r}-\vec{R}_\mu-\vec{s}_n), \quad (3)$$

with $\vec{k}$ restricted to the first Brillouin zone and $\vec{K}$ a reciprocal-lattice vector. The contribution to $|\vec{k}\rangle$ from $\vec{K}=0$ corresponds to a function of the type used in the earlier work, while nonzero $\vec{K}$ allow for the p-type character necessary near the Brillouin-zone boundaries. The function φ, which we took as a Slater-type 1s orbital, is needed to account properly for the cusp in the wave function at each nucleus.

The basis used in this work then can be regarded as intermediate between a conventional plane-wave expansion

$$|\vec{k}\rangle = \sum_{\vec{K}} {}_{\vec{K}} C(\vec{k}+\vec{K}) \exp[i(\vec{k}+\vec{K})\cdot\vec{r}] \quad (4)$$

and the regular tight-binding expansion

$$|\vec{k}\rangle = \sum_{\vec{\mu}} \exp(i\vec{k}\cdot\vec{R}_\mu) \sum_{n=1}^{d} \varphi(\vec{r}-\vec{R}_\mu-\vec{s}_n). \quad (5)$$

The importance of the cusp and hence the slow convergence of the plane-wave expansion has been recently illustrated for metallic hydrogen.[15] Our expansion also has some computational advantages over the tight-binding expansion.[11] Details of the computational techniques will be reported in a forthcoming paper. Our techniques closely parallel those employed by Oddershede,

TABLE I. Total Hartree-Fock energies per atom E/Nd (in hartree), percent occupancy in the second Brillouin zone O_2, and molecular-hydrogen bond lengths for simple-cubic molecular- and bcc atomic-hydrogen crystals at compound lattice spacing a (in bohr).

	Molecular			Atomic	
a	E/Nd	H-H	O_2	E/Nd	O_2
2.4				−0.400	15.1
2.6				−0.430	15.1
3.0				−0.463	15.2
3.15	−0.478	1.610	8.10		
3.2	−0.486	1.580	5.86		
3.4	−0.505	1.458	4.93		
3.464				−0.475	15.3
3.8	−0.516	1.448	1.47	−0.470	15.5

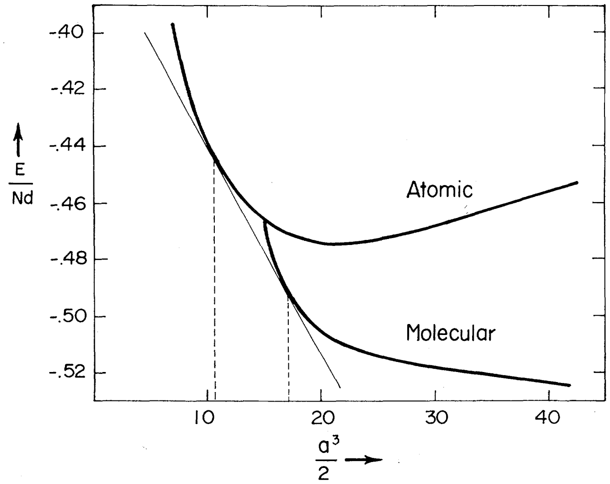

FIG. 1. Total Hartree-Fock energies per atom E/Nd (in hartree) for molecular- and atomic-hydrogen crystals versus volume per atom $a^3/2$ (in cubic bohr).

Kumar, and Monkhorst[16] for the plane-wave expansion.

Table I summarizes our results at several lattice spacings using seven $\vec{K}$ values (the 000 and 100 stars) and a single 1s Slater-type orbital. At each density the Slater exponent was optimized. These results are plotted in Fig. 1, which also shows the construction of the common tangent. The molecular curve does not continue beyond its junction with the metallic curve because the optimization of the H-H bond distance then makes the two curves identical.

In Table I are also presented data showing the percent occupancy (O_2) of the second Brillouin zone for the molecular-crystal wave function. These data indicate that prior to reaching the transition pressure the nature of the molecular crystal changes continuously from a typical insulator toward a more conducting phase, concurrently with a corresponding change in the intramolecular H-H distance.

We obtain a pressure of 2.1 Mbar for the transition. During the transition the density changes from 0.65 to 1.07 g/cm^3. This can be compared with the densities 1.08 to 1.30 g/cm^3 reported by Grigor'ev *et al.*[7] Our results are consistent with the experimenters' interpretation that they observed a transition. Further calculations using 19 $\vec{K}$ values (including the 110 star) should decrease O_2 and may slightly increase our estimate of the pressure at the transition.

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*Work supported in part by the Office of Aerospace Research, U. S. Air Force, under Grant No. AFOSR-71-1992, and in part by the National Science Foundation under Grant No. CP-31373X.

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