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STRUCTURE AND SCREENING IN MOLECULAR AND METALLIC
HYDROGEN AT HIGH PRESSURE*

(NASA-CR-164467) STRUCTURE AND SCREENING IN
MOLECULAR AND METALLIC HYDROGEN AT HIGH
PRESSURE (Cornell Univ., Ithaca, N. Y.)
32 p HC A03/MF A01

N81-25780

CSSL 20H

Unclas
27861

G3/72

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April 1981

MSC Report #4460

Abstract

A variational wavefunction proposed by Abrikosov is used to express the (spin-restricted) Hartree-Fock energy as reciprocal lattice sums for static lattice FCC monatomic hydrogen and diatomic Pa3 molecular hydrogen. In the monatomic phase the hydrogenic orbital range is found to closely parallel the inverse Thomas-Fermi wavevector; the corresponding energy E has a minimum of -0.929 Ryd/electron at $r_s = 1.67$. For the diatomic phase $E(r_s)$ is similar, but the constituent energies, screening, and bond length all reflect a qualitative change in the nature of the solid at $r_s = 2.8$. This change is interpreted in terms of a transition from protons as structural units (at high density) to weakly interacting molecules (at low density). Insensitivity of the total energy to a rapid fall in the bond length suggests association with the rotational transition, where the rigid molecular orientations characteristic of high pressures disappear and the molecules rotate freely at low pressure. The importance of phonons (neglected here) in a correct treatment of the total energy is emphasized, and the possible connection between the rotational transition and metallization of the diatomic phase is discussed. It is concluded that methods which sphericalize the Wigner-Seitz cell may overlook important structural properties (to which the total energy is relatively insensitive) for the diatomic phase.

I: Introduction

Hydrogen continues to attract attention among condensed matter physicists because it has the potential to be the simplest of all possible physically realizable metals. Because of its low nuclear mass and the metallic nature of the high density condensed phase, metallic hydrogen is expected to exhibit interesting electronic ordered states, for example, high temperature superconductivity.^{1,2} Indeed, precisely because dense hydrogen is a quantum system--one whose zero point energy is significant in comparison to the binding energy of the condensed phase itself--it may not be a solid at all, but rather a metallic liquid^{3,4} (and possibly the first known liquid superconductor⁵), with associated interesting two-component Fermi liquid effects at low temperatures.⁶ For our purposes we will assume the monatomic phase to be crystalline, in fact, face centered cubic (in accordance with the work of Straus and Ashcroft⁷). This assumption is reasonable since the energies associated with ordering are exceedingly small compared with the structural energies that we shall encounter.

The molecular solid observed for low temperatures and pressures exhibits interesting properties of its own, again associated with the low mass of the hydrogen atom.⁸ At low pressures the remarkable sphericity of para-hydrogen molecules and their small moment of inertia (a consequence of the compactness of a molecule) permits them to rotate freely. For para-hydrogen at higher pressures, where the enhanced electric quadrupole-quadrupole interaction between molecules locks them into orientational order, there are elementary excitations in the form of librations, i.e., quantum mechanical "zero point motion" associated with the (not always) small amplitude orientational oscillations of the hydrogen dumbbells about their crystalline orientations. (The characteristic temperature scale for these excitations

is somewhat lower for ortho-hydrogen.) In what follows we shall assume that the structure of ortho-hydrogen at low temperatures and pressures⁸ (the space group Pa3) is appropriate for both ortho- and para-hydrogen at high pressures.

The process of metallization of hydrogen may occur in two distinct ways:⁹ (i) As in the case of iodine,¹⁰ another covalently bonded diatomic solid, the application of pressure may continuously reduce the overall gap between valence and conduction bands to the extent that, without change in structure band overlap occurs, thereby giving rise to conduction. The basic diatomic order remains. (ii) The hydrogen molecules may be directly pressure-ionized and dissociated, the associated change in structure giving rise to a monatomic metallic phase. Part of the work to be described here is directed toward an understanding of the manner in which this dissociation occurs.

Many past estimates of the equations of state and the transition pressure from diatomic to monatomic hydrogen have relied on different calculational techniques for the two phases. Often, for example, the energy of the molecular phase has been taken from a superposition of pair potentials, while most recent treatments of metallic hydrogen have used perturbation theory about the uniform interacting electron gas.¹¹ There are, however, fundamental reasons for believing that a pair potential approach will lose validity at high pressures (when the energy of molecular interaction becomes comparable to the lattice binding energy),^{12,13} requiring a scheme better suited to the delocalized nature of the resulting electron wavefunctions.

We shall adopt below an "exact exchange" Hartree-Fock description of the condensed phases of hydrogen. There are, of course, more realistic formalisms which are on a firmer footing as regards the incorporation of

many-body (i.e., correlation) effects, chief among these the density-functional scheme.¹⁴ As usually implemented, these procedures include in an approximate local exchange-correlation potential the physical effects of electron indistinguishability. All such local approximations are enormously simpler computationally than the corresponding Hartree-Fock calculations, with their characteristic non-local exchange terms.

However, as yet no density-functional calculation has been applied to a system of full three-dimensional crystalline symmetry, i.e., it has been customary to replace the Wigner-Seitz cell of the crystal with a sphere of equal volume, and the periodic boundary conditions of the crystal with the Wigner-Seitz boundary condition.¹⁵ Although in terms of total energy this procedure typically gives rise to proportional shifts expected to be of the order of the difference between Madelung energies of different cubic structures ($0(10^{-4})$), a great deal of structural information is relinquished in such a description. This is of relatively little consequence for monatomic phases, but for molecular hydrogen at high pressures, as has been discussed by Chakravarty et al.,¹⁴ phonon energies are quite comparable both to the static energy differences between different crystal structures and to the solid binding energy per electron itself. It is therefore of interest to examine calculational schemes in which such small structural differences are retained. While we shall completely neglect the effect of lattice vibrations below, we will retain a complete description of the diatomic crystalline structure, with the hope of understanding the behavior of the structural and screening properties of the diatomic phase at high pressures.

Hartree-Fock (HF) theory for solids, as mentioned above, has been comparatively rarely implemented.^{16,17} It is useful to keep in mind a number of limitations of the Hartree-Fock approach: (i) The correlation energy (by definition) is omitted. Insofar as we shall be concerned with structural

details, and the density dependence of the correlation energy is believed to be weak, we shall not be concerned about this problem; (ii) Hartree-Fock calculations for the band structures of metals typically give rise to bandwidths (i.e., the energy difference between the bottom of the valence band and the Fermi level) excessively large in comparison to either competing calculational methods or to experiment. For a total structural energy calculation, such as we perform below, however, the energy per electron generally is not unsatisfactory. (iii) Spin-restricted Hartree-Fock, in which each electron level has twofold spin-degeneracy, leads to physical curiosities in the extreme low-density limit of a crystal. Instead of reproducing properties of an isolated atom, spin-restricted H-F typically gives rise to neutral or even partially charged pseudo-atoms which, even if neutral, attract each other at long distances.¹⁸ As noted by Stanton,¹⁸ this is essentially because the entity associated with a pseudo-atom is a fraction of an electron pair, not a single electron: it is not surprising that the high on-site correlation energy (the repulsive energy associated with an electron pair on a pseudo-atom) makes the binding energy of a pseudo-atom anomalously small. We shall return to this point below in a discussion of the results for metallic (monatomic) hydrogen.

II: Abrikosov Variational Wavefunction

We will adopt a wavefunction proposed by Abrikosov¹⁹ as a reasonable choice for a unified description of both molecular and metallic hydrogen at high pressure. It is

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{R}\vec{b}} \phi(\vec{r}-\vec{R}-\vec{b}) \quad (1)$$

with

$$\phi(\vec{r}) = \sqrt{\frac{\lambda^3}{\pi}} \exp(-\lambda r) \quad (2)$$

where we have chosen a (lattice + basis) description of the crystal structure of interest, with $\{\vec{R}\}$ the underlying Bravais lattice and $\{\vec{b}\}$ the set of basis vectors within a conventional unit cell. The subscript \vec{k} is intended to indicate the delocalized nature of this wavefunction: it is explicitly of Bloch form. By the use of a variational parameter λ , we have allowed for the possibility that in a condensed environment the shape of a hydrogen wavefunction may differ from that of an isolated atom. In the molecular phase the protons are grouped in pairs centered at the sites of the Bravais lattice and both λ and the molecular inter-proton spacing $2D$ (which enters straightforwardly in the specification of the Pa3 lattice) will be such variational parameters.

A few remarks about the form of (1) are appropriate. In the standard tight binding method²⁰ one constructs the wavefunction by superposing linear combinations of localized atomic wavefunctions, i.e.,

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}, \vec{b}} e^{i\vec{k} \cdot (\vec{R} + \vec{b})} \phi_{\vec{k}}(\vec{r} - \vec{R} - \vec{b}) \quad (3)$$

where

$$\phi_{\vec{k}}(\vec{r}) = \sum_n a_n(\vec{k}) \psi_n(\vec{r}) \quad (4)$$

and the $\psi_n(\vec{r})$ satisfy the Schrödinger equation for an isolated atom; one hopes that relatively few n are needed in (4). Our choice (1) differs from (3) in that (i) we are using only one atomic orbital, (ii) the choice of phase is site-independent; this will mean important simplifications later in the evaluation of, for example, the kinetic energy.

Point (i) is not a serious approximation if one is specifically interested in the electronic ground state. The choice of phase (point (ii)) allows for delocalization of conduction electrons while preserving the essential atomic-like nature of the wavefunctions near the proton sites. We will see that this choice will mean that free electron behavior will emerge naturally in the limit of large densities. In connection with the choice of phase it is also useful to observe that for the molecular solid the scale of significant variation of the wavefunction (1) is set by the molecular inter-proton spacing $2D$, while the scale of k is such that $k \ll k_F$ where k_F is the Fermi wavevector. For low pressures $2k_F D \sim 0.15 \ll 1$ so that the chosen variational function will tend to preferentially deposit charge between the protons in the same molecule, i.e., there is relatively little of the "antibonding" orbital mixed in, and (1) should be satisfactory for a variational calculation.

In particular, it should be noted that since $|\psi_{\vec{k}}(\underline{r})|^2$ is independent of the Bloch wavevector \vec{k} , we are restricted to the description of a system with a spherical Fermi surface. It is known from the structural expansion method, for example, that effects originating from departures from sphericity of the Fermi surface first occur in fourth order in perturbation theory about the homogeneous interacting electron gas, the perturbation being the electron-ion interaction.¹¹ This therefore suggests that, at least at high pressures, the assumed absence of a dependence of the energy on the direction of \vec{k} will also be a satisfactory approximation. For possible cubic phases of (monatomic) metallic hydrogen this assumption is quite well justified;²¹⁻²³ for the insulating molecular phase, where one might imagine proceeding via a tight-binding calculation, this approximation is probably poor at quite low density.

III: Hartree-Fock Constituent Energies

As noted, in what follows we shall neglect the kinetic energy of the ions (i.e., phonons) within the framework of the Born-Oppenheimer (adiabatic) approximation.²⁴

For our purposes a description in momentum space is convenient. With $Z = 1$ and wavefunctions (1) our Hartree-Fock states are specified by the Bloch wavevector \vec{k} and the spin. For a crystal of N cells and volume Ω the wavefunction becomes

$$\psi_{\vec{k}}(\vec{r}) = \frac{N n_b}{\Omega} \sum_{\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \phi_{1s}(\vec{G}) s^*(\vec{G}) \quad (5)$$

and the crystal potential (pure Coulomb for hydrogen) is

$$V(\vec{r}) = -e^2 \frac{N n_b}{\Omega} \sum_{\vec{G}} \frac{4\pi}{G^2} e^{i\vec{G}\cdot\vec{r}} s^*(\vec{G}), \quad (6)$$

where n_b is the number of sites in the basis, and for reciprocal lattice vector \vec{G} , s is the normalized basis structure factor

$$s(\vec{G}) \equiv \frac{1}{n_b} \sum_{\vec{b}} e^{i\vec{G}\cdot\vec{b}}. \quad (7)$$

The constituent Hartree-Fock energies are kinetic ($\langle K.E. \rangle$), electron-proton ($\langle V_{e-p} \rangle$), electron-electron ($\langle E_{e-e} \rangle$) and exchange ($\langle E_{ex} \rangle$). Per electron, these are, respectively,

$$\langle K.E. \rangle = \frac{3}{5} \epsilon_f + \frac{\hbar^2}{2m} \sum_{\vec{G}} G^2 |s(\vec{G})|^2 |\phi(\vec{G})|^2 / [\sum_{\vec{G}} |s(\vec{G})|^2 |\phi(\vec{G})|^2]. \quad (8)$$

$$\langle V_{e-p} \rangle = - \frac{N_{ion}}{\Omega} e^2 \sum_{\vec{G} \neq 0} \frac{4\pi}{G^2} s^*(\vec{G}) N_{\vec{G}}, \quad (9)$$

$$\langle E_{e-e} \rangle = \frac{e^2}{2} \frac{N_{ion}}{\Omega} \sum_{\vec{G} \neq 0} \frac{4\pi}{G^2} |N_{\vec{G}}|^2, \quad (10)$$

and

$$\langle E_{ex} \rangle = - \frac{e^2 k_F}{8\pi} \sum_{\vec{G} \neq 0} |N_{\vec{G}}|^2 f_A(G/k_F), \quad (11)$$

where in the above

$$N_{\vec{G}} = \frac{\sum_{\vec{G}'} \phi^*(\vec{G}+\vec{G}') \phi(\vec{G}') s(\vec{G}+\vec{G}') s^*(\vec{G}')}{\sum_{\vec{G}'} |\phi(\vec{G}')|^2 |s(\vec{G}')|^2}, \quad (12)$$

is the normalized G th Fourier component of the electron density, ϵ_F is the Fermi energy and k_F the Fermi wavevector, and $N_{ion} = N n_b$. Here

$$\frac{k_F}{8\pi\Omega} f_A(G/k_F) = \frac{1}{(2\pi)^6} \int d\vec{k} \int d\vec{q} \frac{4\pi}{(\vec{k}+\vec{q}+\vec{G})^2} \quad (13)$$

with both integrations extending over a spherical Fermi surface. Explicitly

$$f_A(x) = \left\{ \left(\frac{8}{5x} - 2x \right) \ln \left| \frac{2+x}{2-x} \right| + \frac{22}{5} + \frac{x^2}{5} + x^2 \left(\frac{x^2}{20} - 1 \right) \ln \left| \frac{4}{x^2} - 1 \right| \right\}. \quad (14)$$

This function was first evaluated by Abrikosov.¹⁹

The total energy also includes the Madelung energy E_{Mad} , i.e., the energy of a lattice of point positive ions (embedded in a uniform background of compensating negative charge) interacting via the Coulomb potential. The total energy per electron (neglecting phonons) may thus be written

$$E_{\text{tot}} = \left(\frac{e^2}{2a_0}\right) \left[\frac{3}{5} \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2} - \frac{3}{2\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \right] + E_{e1}(\vec{G} \neq 0) + E_{\text{Mad}}, \quad (15)$$

where $E_{e1}(\vec{G} \neq 0)$, the electronic energy, is the sum of terms (7)-(11) except that we have rewritten the $\vec{G} = 0$ contributions to the kinetic and exchange energies in terms of the familiar dimensionless density parameter r_s defined by

$$\frac{4\pi}{3} n r_s^3 = \frac{1}{na_0^3} \quad (16)$$

where n is the electron number density and a_0 is the Bohr radius. We then recognize the terms in brackets above as the kinetic and exchange energies of a uniform interacting electron gas; the $\vec{G} = 0$ Hartree-Fock energy could be supplemented by an estimate of the correlation energy, e.g., the Nozières-Pines interpolation formula.²⁹ No $\vec{G} = 0$ terms appear in the electrostatic energies because the system as a whole is neutral.

For purposes of computation it is convenient to back-transform into real space the simple k-space sums appearing in the kinetic energy. This is expected to be beneficial since our orbital $\phi(\vec{r})$ decays exponentially for large distance, so the real space sums we generate should converge well, at least at low densities where the system is most non-uniform. We find

$$\begin{aligned} \langle KE \rangle_{\vec{G} \neq 0} &= \frac{\hbar^2}{2m} \lambda^2 \frac{\left[1 + \frac{1}{n_b} \sum_{\vec{R} \neq 0} \sum_{\vec{b}\vec{b}'} e^{-X}(1 + X - X^2/3) \right]}{\left[1 + \frac{1}{n_b} \sum_{\vec{R} \neq 0} \sum_{\vec{b}\vec{b}'} e^{-X}(1 + X + X^2/3) \right]} \\ &= \frac{e^2}{2a_0} (\lambda a_0)^2 D_1/D_2. \end{aligned} \quad (17)$$

where $X = \lambda |\vec{R} + \vec{b} - \vec{b}'|$. We find, furthermore, that

$$N_{\vec{G}} = \frac{1}{N_{\text{nor}}} \frac{1}{g'} \frac{1}{[z^2 + (\vec{g} + \vec{g}')^2]^2} \frac{1}{[z^2 + g'^2]^2} s^*(\vec{G}') s(\vec{G} + \vec{G}') \quad (18)$$

where the normalizing constant is

$$N_{\text{nor}} = \frac{(2\pi)^3}{64\pi} \left(\frac{2\pi}{\lambda a}\right)^5 \frac{D_2}{n_b}, \quad \left(z = \frac{\lambda a}{2\pi}, \quad g = \frac{Ga}{2\pi}\right). \quad (19)$$

Note that for $\vec{G} = \frac{2\pi}{a} (i, j, k)$, $\vec{g} = (i, j, k)$. Taken together the total energy for hydrogen is

$$\begin{aligned} E_{\text{tot}} &= E_{\text{Mad}} + [E_{e1}(\vec{G}=0)] + \{E_{e1}(\vec{G} \neq 0)\} \\ &= \alpha_M / r_s + \left[\frac{3}{5} \gamma^2 / r_s^2 - \frac{3}{2\pi} \gamma / r_s \right] + \\ &+ \left\{ (\lambda a_0)^2 D_1 / D_2 - \frac{3}{2\pi^2} \frac{1}{r_s} \beta^2 \sum_{\vec{G} \neq 0} s^*(\vec{G}) N_{\vec{G}} \frac{1}{g^2} + \frac{3}{8\pi^2} \frac{\beta^2}{r_s} \sum_{\vec{G} \neq 0} |N_{\vec{G}}|^2 \frac{1}{g^2} \right. \\ &\left. - \frac{\gamma}{4\pi r_s} \sum_{\vec{G} \neq 0} |N_{\vec{G}}|^2 f_A(G/k_F) \right\}; \quad (20) \end{aligned}$$

with

$$\gamma = \left(\frac{9\pi}{4}\right)^{1/3}, \quad \beta = \left(\frac{4\pi}{3} n_b\right)^{1/3}. \quad (21)$$

We have used the general form of the Madelung energy

$$E_{\text{Mad}} = \alpha_M Z^{2/3} / r_s. \quad (22)$$

In the spirit of the structural expansion mentioned above, we may now identify the "band structure energy." It is that portion of the total energy due to non-uniformity of the electronic system. To all orders in the electron-ion interaction in this model, it is the term in { } above.

IV: Computational Details

Equation (20) is the basis for a Hartree-Fock calculation of the zero temperature equation of state of both monatomic and molecular (diatomic) hydrogen, results of which are presented below. Inspection of Eqs. (20) and (18) indicate that the inhomogeneous ($\vec{G} \neq 0$) contributions to the energy involve a sixfold summation over the reciprocal lattice indices (i,j,k) and (i',j',k') . It is thus imperative to exploit such symmetries as may be present to facilitate evaluation of the sums. Further details are given in Appendix A.

A unit cell of the Pa3 structure, believed to be appropriate to solid diatomic hydrogen at low temperatures and high pressures for both the ortho and para phases^{25,26} is shown in Figure 1. It is most simply described as a simple cubic conventional cell (of side a) with an eight-point basis, with ions at the points

$$\begin{aligned}
 \vec{b}_{1,2} &= \pm ar \\
 \vec{b}_{3,4} &= a[(0, \frac{1}{2}, \frac{1}{2}) \pm r(1, -1, 1)] \\
 \vec{b}_{5,6} &= a[(\frac{1}{2}, 0, \frac{1}{2}) \pm r(1, 1, -1)] \\
 \vec{b}_{7,8} &= a[(\frac{1}{2}, \frac{1}{2}, 0) \pm r(-1, 1, 1)]
 \end{aligned}
 \tag{23}$$

where $r = D/(\sqrt{3}a)$ and $2D$ is the "bond length" of a given molecule. (The structure is FCC with molecules at each site, each oriented along a different body diagonal.) This is a highly unsymmetrical structure; its normalized basis structure factor for a simple cubic reciprocal lattice

vector $G = \frac{2\pi}{a} (i, j, k)$ is

$$S(i, j, k) = 2[\cos\alpha(i + j + k) + (-1)^{i+j}\cos\alpha(-i + j + k) + (-1)^{j+k}\cos\alpha(i - j + k) + (-1)^{i+k}\cos\alpha(i + j - k)] \quad (24)$$

where $\alpha = \frac{2\pi D}{\sqrt{3}a}$. For $D/a = \sqrt{3}/4$ the ions are equally spaced along the body diagonals, and the structure becomes simple cubic with a lattice constant $a/2$. The Madelung energy per electron for this structure may be computed using the usual Ewald expression

$$E_M = \frac{e^2}{2a_0} \frac{Z^{2/3}}{r_s} \left[3 \sum_{\vec{g} \neq 0} \frac{1}{g^2} |s(\vec{G})|^2 e^{-g^2/P^2} + \frac{1}{n_b} \sum'_{\vec{R}\vec{b}\vec{b}'} \frac{\text{erfc}(\frac{P}{2}|\vec{x}|)}{|\vec{x}|} - \left(\frac{3}{P^2} + \frac{P}{\sqrt{\pi}} \right) \right] \quad (25)$$

where P is the free parameter resulting from the Ewald process (i.e., E_M should be numerically independent of P for P of order 1), erfc is the complementary error function, $g = Ga/(2\pi)$, and the prime indicates omission of the $\vec{R} = 0, \vec{b} = \vec{b}'$ term, i.e.,

$$\sum'_{\vec{R}\vec{b}\vec{b}'} = \sum_{\vec{R} \neq 0} \sum_{\vec{b} \neq \vec{b}'} + \sum_{\vec{R} = 0} \sum_{\vec{b} \neq \vec{b}'} + n_b \sum_{\vec{R} \neq 0}$$

The Madelung constant α_M for the Pa3 structure, as a function of the parameter D/a , is displayed in Figure 2; also shown for comparison is the Madelung constant for a "rotationally averaged Pa3" structure, discussed in Appendix B. The latter, denoted $\langle \text{Pa3} \rangle$, results from taking the orientation of the molecules on the underlying FCC sites to be random. The

remarkable insensitivity of the Madelung energy (indeed, the total energy) to the orientation of the molecules for small values of Q/a will be discussed below. Further details are given in Appendix A.

V: Metallic Hydrogen

The total static Hartree-Fock energy in Ryd/electron for FCC monatomic hydrogen using the Abrikosov wavefunction is shown as a function of the electron density parameter r_s in Figure 3. Also displayed in this figure are the constituent energies--the non-uniform parts of the kinetic, electron-proton, electron-electron and exchange energies. For comparison a curve showing the homogeneous interacting electron gas Hartree-Fock terms and the Wigner-Seitz sphere electron-proton energy (i.e., the analog of the Madelung energy), is also displayed. Perhaps the most striking feature of the H-F curve is how little it departs from this simple estimate: the value of r_s at the minimum is essentially unchanged by inclusion of the non-uniform terms (the "band structure energy"). It is also noteworthy that the two terms in principle hardest to compute--the electron-electron and exchange energies--are very small (and their sum even more so) over most of the region of interest. An identical calculation using the Abrikosov wavefunction for FCC monatomic hydrogen was performed, but over a limited range of r_s , by Ross and McMahan.²⁷ We will be interested, however, in a discussion of screening over a large density range. At very low density (large r_s) we find²⁸

$$\lim_{r_s \rightarrow \infty} E_{el}^{tot} = [(\lambda a_0)^2 - 2\lambda a_0] + \left(\frac{5}{8} - \frac{5}{16}\right) \lambda a_0 \quad (26)$$

where the terms are, respectively, the kinetic, electron-proton,

electron-electron, and exchange energies. The minimum, for $\lambda a_0 = 27/32$, gives a Hartree-Fock energy

$$\lim_{r_s \rightarrow \infty} E_{\min}^{\text{H-F}} = - \left(\frac{27}{32} \right)^2 = -0.7119 \text{ Ryd/electron} \quad (27)$$

to which the total energy in Figure 3 tends asymptotically (and rather quickly). As mentioned above, the fact that this value is not that of an isolated hydrogen atom reflects the restricted Hartree-Fock substitution of a pseudo-atom (an equal mixture of spin-up and spin-down states) for the genuine spin-polarized atom, and the total absence of correlation energy. As is typical of variational calculations, the energy approaches its asymptotic variational minimum faster than do its variational parameters, here only λa_0 .

The inclusion of the correlation energy in the electron gas portion of the energy via, for example, the Nozières-Pines interpolation formula,²⁹ will barely bind FCC metallic hydrogen; the Hartree-Fock minimum energy, at $r_s = 1.67$ and $\lambda a_0 = 1.24$, is -0.929 Ryd/electron: the inclusion of this correlation estimate brings the total energy to -1.028 Ryd/electron. The H-F energy thus compares very well with other recent H-F calculations for metallic hydrogen,³⁰⁻³² for example, that of Tua and Mahan,³¹ who found (using a similar basis of functions but with three variational parameters) a H-F energy of -0.9327 Ryd/electron. In addition, Harris et al.³⁰ found a minimizing value of -0.931 Ryd/electron with $\lambda a_0 = 1.25$, using a more complicated wavefunction. Ross and McMahan²⁷ naturally found results identical to ours in the density range where comparison can be made.

Of considerable interest is the density dependence of the wavefunction decay parameter λ , shown in Figure 4; the original result of Abrikosov,¹⁹

and the Thomas-Fermi prediction

$$k_{TF} a_0 = \left(\frac{12}{\pi}\right)^{1/3} \frac{1}{\sqrt{r_s}} \quad (28)$$

are also displayed for comparison. We may interpret this figure as an indication of the metallic nature of the monatomic solid as follows. If we consider the response of the electrons in metallic hydrogen to the fields of the protons, then in the Thomas-Fermi model of metallic screening (valid as $r_s \rightarrow 0$) we would expect the induced electron charge density to be

$$\rho_{ind}^{TF}(\vec{r}) = -\frac{Qk_{TF}^2}{4\pi r} e^{-k_{TF}r}. \quad (29)$$

On the other hand, around an isolated hydrogen atom the charge density is

$$\rho^H(\vec{r}) = -e \frac{\lambda^3}{\pi} e^{-2\lambda r} \quad (30)$$

with $\lambda = 1/a_0$. In a condensed metallic phase we would expect λ and k_{TF} to scale similarly as a function of the density r_s . What is remarkable, however, is the range of density over which the H-F and Thomas-Fermi screening parameters actually do track one another; the charge density in this model of monatomic hydrogen bears little resemblance to that of an isolated atom, and we conclude that the system is genuinely metallic. In this context Abrikosov's original calculation is inappropriate for densities of physical interest.³³

VI: Pa3 Molecular Hydrogen

In Figure 5 are shown the curves for Pa3 molecular hydrogen analogous to those in Figure 3 for the monatomic phase. Here, once again, we display a comparison curve, consisting of the interacting electron gas energy and

the minimized Madelung energy for the $\langle Pa3 \rangle$ structure, Eq. B5. While there is a superficial resemblance to their metallic counterparts, all the constituent energies show a remarkable transition at $r_s \approx 2.8$, although the total energy is quite insensitive to these rather precipitous changes. The density dependence of λa_0 (Figure 6) again closely follows the Thomas-Fermi wavevector, as expected for the spherical Fermi surface resulting from the use of wavefunction (1). Changes in λa_0 near $r_s = 2.8$ are relatively slight, but a marked flattening-out of $\lambda(r_s)$ beyond $r_s = 2.8$ is to be noted.

The density dependence of the interproton spacing (here D/a , i.e., the ratio of half the molecular bond length to the lattice constant of the conventional simple cubic cell) is shown in Figure 7, and it is clear that the abrupt drop in D/a for $r_s = 2.6-3.0$ is the origin of the pronounced changes in the constituent energies in Figure 5. Shown in the same figure are (i) the curves expected if the molecular bond length is frozen at its zero pressure value, (ii) the results of the recent density functional calculation of Chakravarty et al.,³⁴ (iii) the results of Liberman,³⁵ who used a modified density functional procedure with a sphericalized potential, and (iv) the results of Ramaker, Kumar and Harris³⁶ for simple cubic oriented molecular hydrogen.

The computed dependence of D/a on density may be understood in terms of a qualitative change in the nature of the solid molecular phase around $r_s = 2.8$. For extremely high densities (small r_s) Figure 2 shows that to minimize the Madelung energy, D/a should asymptotically approach a constant value ≈ 0.27 , as we observe in Figure 7. At extremely low densities on the other hand ($r_s \rightarrow \infty$), one should recover in an exact treatment a

lattice of non-interacting hydrogen molecules with fixed $2D/a_0 = 1.401$. For Pa3 structure this would imply $D/a \sim 0.217/r_s$.

The static Hartree-Fock calculation clearly does rather poorly in giving the expected quantitative behavior for low density. However, the rather sudden change in behavior does clearly reflect a transition from a solid whose essential structural units are "locked into" the unit cell as a whole (so that all intracellular distances scale together, corresponding to $D/a = \text{constant}$) to one whose structural units are the molecules themselves, with fixed bond length (i.e., $D/a = \text{const}/r_2$). The roughly flat dependence of λ on r_s beyond $r_s \approx 2.8$ in Figure 6 is also characteristic of weakly interacting molecules. This qualitative change is present, in an attenuated form (at a much smaller value of r_s) in simple second-order structural expansion results.³⁷

The calculations of Liberman³⁵ and Chakravarty et al.³⁴ use the Wigner-Seitz method of sphericalizing the crystalline cell containing one molecule and, as such, discard detailed information about the lattice to which the total energy is relatively insensitive (though structural parameters like D/a may depend sensitively on the approximation). For this reason, neither of these calculations exhibit any feature which may be identified as the qualitative change we observe. The calculation of Ramaker et al.³⁶ does keep a crystalline cell and predicts (at a much higher density) a rapid plunge of D/a , but it is for a structure which has not been observed for hydrogen.

It is reasonable to associate the 'transition' at $r_s \approx 2.8$ with the "rotational transition"³⁸ marking the onset of free rotation of the hydrogen molecules about their centers of mass (ignoring, as usual, the distinction between para- and ortho-hydrogen) from the hindered angular oscillation or libration characteristic of higher pressures. It is clear that the closer

the two protons of a given molecule approach the more nearly spherical is the associated charge cloud, so the less important are the configurations of other such molecules in the same (or other) unit cells. Hence merely on the basis of energetics (the insensitivity of the total energy, Figure 5, to variation in D/a beyond $r_s \approx 2.9$) and proximity (the rapid reduction of the bond length shown in Figure 7 around $r_s = 2.8$), any tendency toward free rotation will be markedly increased beyond $r_s \approx 2.8$.

The scaling together of intracellular dimensions below $r_s \approx 2.8$ is typical of metallic systems, where it is the volume-dependent electron gas contributions and the interactions of individual ions with the electron gas which stabilize the system. In a molecular insulating solid the essential entities (the molecules) are neutral and it is fluctuating dipole or higher multipolar interactions which stabilize the solid. Simple arguments of Mott and others^{39,40} indicate that for a system with long-range Coulomb interactions a metal-insulator transition will occur; the system will be metallic for an average number density n if

$$n^{1/3} a_0 = \left(\frac{3}{4\pi} \right)^{1/3} \frac{1}{(r_s/a_0)} \gtrsim 0.2, \quad (31)$$

for which the transition density is $r_s \approx 3.1$. Using the simple cubic monatomic hydrogen lattice as a model for such a transition, Rose, Shore and Sander⁴¹ do indeed find a metal-insulator transition (from a paramagnetic metal for higher density to a ferromagnetic insulator at low density) at $r_s = 2.84$. The precise relevance of results for the monatomic phase to the diatomic phase is unclear, but it should be remembered that both systems are described by the same Hamiltonian, with an instability toward molecular pairing as a structural symmetry breaking. It is believed that as a function

of increasing pressure the diatomic phase will first become conducting by (indirect) band overlap,⁴² and only at higher pressure³⁴ will the diatomic order disappear. The actual onset of free rotation in (para) hydrogen may also be assisted by a Peierls distortion.

In this context it is important to note that for molecular hydrogen the inclusion of lattice dynamics is crucial to obtain a quantitative understanding of the equation of state for low pressures. This problem occurs for the monatomic case as well, where the preference of static structural expansion calculations for anisotropic planar structures is no longer present when a careful self-consistent phonon calculation is made.⁷ It may be understood qualitatively by observing that we expect phonon energies per electron in the condensed phase to scale roughly as the ionic plasma frequency

$$\frac{1}{2} \hbar \omega_{\text{phonon}} \approx \frac{1}{2} \hbar \omega_{\text{plasma}}^{\text{ion}} = \sqrt{\frac{3m_e}{M_{\text{proton}}}} \frac{1}{r_s^{3/2}} \quad (\text{Ryd}) \quad (32)$$

for m and M the electron and proton masses, respectively. This quantity ranges from about 0.04 Ryd at $r_s = 1$ to 0.005 Ryd at $r_s = 4$. For comparison, the zero pressure binding energy per electron for solid molecular hydrogen is only about 0.0006 Ryd. The importance of a unified treatment of phonons together with the electronic system has been stressed by Chakravarty et al.³⁴ For the molecular phase they used a Wigner-Seitz approximation; within the W-S sphere around a given molecule they sphericalized the ionic potential by smearing the protons out on a shell of radius D , reintroducing deviations from spherical symmetry of the total potential within the spherical cell by perturbation theory. They found good agreement for molecular hydrogen at low density for the binding energy, interproton spacing and

optic mode ("stretch") frequency. The phonon problem manifests itself, however, in the fact that the computed equation of state $E(r_s)$ showed an overall shallow minimum at $r_s = 2.1$, even when an estimate of the effects of phonons was included; the experimental $P = 0$ density for diatomic hydrogen corresponds to $r_s = 3.10$.

We may gain a qualitative feeling for the importance of phonons in the present calculations of the molecular phase by examining Figure 8, which shows (for fixed overall density $r_s = 2.8$) the dependence of the second order structural expansion total energy for the Pa3 and rotationally averaged $\langle \text{Pa3} \rangle$ structures (see Appendix B for a brief description of the second order structural expansion and the rotationally averaged $\langle \text{Pa3} \rangle$ structure). Although the detailed values of D/a and energy are not reliable, we note that (i) the Pa3 curve is extraordinarily flat over a very large range of D/a out to the simple cubic value $D/a = \sqrt{3}/4$ (using Hubbard-Geldart-Vosko screening--see Appendix B); (ii) the rotationally averaged $\langle \text{Pa3} \rangle$ curve falls below the Pa3 curve, indicating a possible preference for a lattice of free rotators. Moreover, both the splitting between the two curves and the "flatness" of the Pa3 curve are of the order of a typical phonon energy, indicating that only the inclusion of phonons can specify reliably the density-dependence of the molecular inter-proton spacing, the onset of the putative rotational solid, and ultimately the low-pressure molecular equation of state.

VII: Summary and Conclusions

The main emphasis here has been on the Pa3 molecular hydrogen structure. For this case screening is found to be quite metallic-like below $r_s \approx 2.8$;

for larger r_s both the screening parameter and the molecular 'bond length' cease to depend strongly on density, suggesting a transition to a solid of weakly interacting molecules. The detailed nature of this transition has yet to be established but a rotational transition and a metal-insulator transition at $r_s \approx 2.8$ are possible candidates. In making the connection, it is important to include the effect of phonons.

Our principal conclusion is that cellular methods which discard information about the details of the lattice may do very well when used to compute total energies, at the expense, however, of possibly missing important structural changes to which the total energy is relatively insensitive. We have confirmed once more that it is the difficulty of obtaining a reliable first principles molecular equation of state which remains the primary obstacle to the understanding of hydrogen at high pressure.

Acknowledgments

Conversations with Drs. Sudip Chakravarty and Jim Rose during early stages of this work are gratefully acknowledged. This work was supported by NASA under Grant NSG-7487.

Appendix A: Computational Details

In the FCC metallic phase ($\alpha_M = -1.7917472304$) the only variational parameter is the quantity λ characterizing the shape of the hydrogen wavefunction. In practice for each value of r_s eight values of λa_0 straddling the minimum (as a function of λa_0) were scanned, a polynomial was fit to the resulting energy values, and the appropriate zero of the derivative was used as the physically relevant value of λa_0 . The energy was then evaluated using the curve fit.

The computational problem for the Pa3 molecular hydrogen phase is of a different order of magnitude than for the monatomic phase; not only are there two variational parameters, but the lattice itself is of a symmetry low enough that systematic exploitation of symmetry is difficult. In order to scan a reasonable range of λ and D/a in permissible computer time for each value of r_s , five values of λa_0 and eight of D/a were selected to encompass the energy minimum. The resulting table of numbers (from k-space summations extending only far out enough to reflect the essential dependence on the variational parameters) was interpolated using a bicubic spline method, and the minimum found by a two-dimensional Newton-like method. The electronic energy was then re-evaluated at the corresponding values of λa_0 and D/a , summing out as far as possible in k-space to improve the accuracy of the total energies.

For several large values of r_s , where the total energy is a more rapidly varying function of the parameters D/a and λa_0 , computer runs with a mesh about twice as fine were made to give more reliable values for the structural parameters. Even though we feel the variational parameters to be accurate (within the limitations of the model), the absolute energies

for the molecular phase still contain small uncertainties that make comparison of the equations of state of the molecular and metallic hydrogen difficult, especially if the intent is to extract, for example, the transition pressure from one phase to the other. Indeed, only the availability of the Floating Point Systems Array Processor (and its associated Cornell Fortran compiler) made the Pa3 calculation feasible at all in its present form.

Fluctuations evident in the computed points are due to the sensitive dependence of the structural energy on the parameter D/a , and associated uncertainty in the output of the fitting and minimization programs. For several values of large r_s finer-grid computer runs, indicated by triangles, were made. As usual for variational calculations, 'noise' of order δ in the variational parameters emerges as noise in the energy of order δ^2 . The error bars in Figure 6, for example, are indicative of the worst variation in results from normal-length computer runs straddling the minimum in parameter space in different ways.

Appendix B: The Structural Expansion and the Rotationally Averaged $\langle Pa3 \rangle$ Structure

Within the structural expansion formalism one begins with a lattice of positive ions in the presence of a uniform compensating negative background and, in the same volume, a uniform interacting electron gas of identical overall charge density, together with its uniform compensating positive background (so that each system is separately neutral). One then introduces the electron-ion interaction using perturbation theory.¹¹ To lowest order in the electron-ion interaction one finds

$$E_{\text{tot}}^{(2)} = E_{e1}^{(0)}(r_s) + E_{\text{Mad}}(\{\vec{R}, \vec{b}\}, r_s) + E_{\text{BS}}^{(2)}(\{\vec{R}, \vec{b}\}, r_s) \quad (\text{B.1})$$

+

where $E_{e1}^{(0)}$ is the energy of the uniform interacting electron gas at the appropriate density, E_{Mad} is the Madelung energy, given by

$$E_{\text{Mad}} = \frac{Z^2 e^2}{2\Omega} \sum_{\vec{q} \neq 0} [\rho_{\vec{q}}^{\text{ion}} \rho_{-\vec{q}}^{\text{ion}} - N_{\text{ion}}] \frac{4\pi}{q^2} \quad (\text{B.2})$$

(where $\rho_{\vec{q}}^{\text{ion}}$ is the q -th Fourier component of the ion density), and the "second order band structure energy" $E_{\text{BS}}^{(2)}$ is

$$E_{\text{BS}}^{(2)} = \frac{1}{2} \left(\frac{N_{\text{ion}} Z}{\Omega} \right) \sum_{\vec{q} \neq 0} \left(\frac{q^2}{4\pi e^2} \right) \left[\frac{v_{ei}(\vec{q})}{Z} \right]^2 \left[\frac{1}{\epsilon(\vec{q})} - 1 \right] \frac{\rho_{\vec{q}}^{\text{ion}} \rho_{-\vec{q}}^{\text{ion}}}{N_{\text{ion}}^2} \quad (\text{B.3})$$

where v_{ei} is the electron-ion interaction potential (or pseudopotential) with $\epsilon(q)$ the dielectric function of the uniform interacting electron gas. For our calculations we used the Hubbard dielectric function as modified by Geldart and Vosko,⁴³ and the bare Coulomb potential appropriate to hydrogen.

In both expressions above the quantity of interest is the combination $\rho_{\vec{q}}^{\text{ion}} \rho_{-\vec{q}}^{\text{ion}}$. In the context of an FCC lattice of freely rotating hydrogen molecules it is useful to consider an FCC lattice for which the molecular bond orientation is a random function of position. One must distinguish between the contribution to $\rho_{\vec{q}}^{\text{ion}} \rho_{-\vec{q}}^{\text{ion}}$ from the two protons associated with a given FCC site (which are perfectly correlated in the molecule there) and those associated with other (randomly oriented) molecules. We find

$$\langle \rho_{\vec{k}} \rho_{-\vec{k}} \rangle = 2N \left(1 + \frac{\sin 2kD}{2kD} \right) + N(N \delta_{\vec{k}, \vec{G}} - 1) \frac{4 \sin^2 kD}{k^2 D^2} \quad (\text{B4})$$

where the \vec{G} are the reciprocal lattice vectors for the real space FCC lattice; the expression above readily divides into discrete reciprocal lattice contributions and a continuous part, which will give rise to integrals in the Madelung and band structure energies. Here N is the number of FCC sites.

Provided the "charged spherical shells" resulting from the rotational averaging process do not overlap (for the FCC case this is value for $0 < D/a < \sqrt{2}/4$) the Madelung energy can then be written

$$E_M(\langle Pa3 \rangle) = \left[\frac{e^2}{2a_0} \right] \frac{2^{2/3}}{r_s/a_0} \left[\alpha_{\text{FCC}} + \frac{1}{4z} + z^2 \right] \quad (\text{B5})$$

where α_{FCC} is the Madelung constant of the FCC structure and $z = \left(\frac{D}{a} \right) \left(\frac{16\pi}{3} \right)^{1/3}$.

The band structure energy, to second order, becomes

$$E_{\text{BS}}^{(2)}(\langle Pa3 \rangle) = \frac{2N}{\Omega} \frac{e^2}{2} \sum_{\vec{G} \neq 0} \frac{4}{G^2} \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{\sin GD}{G^2 D^2} \right)^2 + e^2 \int \frac{d\vec{k}}{(2\pi)^3} \frac{4\pi}{k^2} \left[\frac{1}{\epsilon(\vec{k})} - 1 \right] \left[1 + \frac{\sin 2kD}{2kD} - \frac{2 \sin^2 kD}{k^2 D^2} \right] \quad (\text{B6})$$

These expressions were used in the evaluation of the $\langle Pa3 \rangle$ curves (Figures 2 and 8).

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Figure Captions

- Fig. 1. The α -N₂ or Pa3 structure assumed for the calculation of diatomically ordered dense hydrogen.
- Fig. 2. The Madelung constant as a function of interproton spacing (D) (as a fraction of conventional cubic cell dimension a). Full line: Pa3 structure. Dotted line: rotationally averaged Pa3 (see text).
- Fig. 3. The total static Hartree-Fock energy (per electron) for monatomic hydrogen obtained with the Abrikosov trial state (1) (lower curve). The component parts of the energy are discussed in the text.
- Fig. 4. Density dependence of the variational orbital range parameter λ in the Abrikosov state (1) for FCC monatomic hydrogen (solid curve). The dashed line is the corresponding range in Thomas-Fermi linear screening model. The dotted curve is Abrikosov's original calculation. The numerical details are found in Appendix A.
- Fig. 5. The total static Hartree-Fock energy (per electron) for diatomically ordered hydrogen, minimized with respect to D/a and λ . The component parts of the energy and their rapid changes near $r_s = 2.8$ are discussed in the text. Note that the total energy is relatively featureless at $r_s \sim 2.8$.
- Fig. 6. Density dependence of the variational orbital range parameter λ for diatomic hydrogen (solid line). Again the dashed line gives the linear-screening result in the Thomas-Fermi approximation (see Fig. 4).

Fig. 7. Minimizing values of D/a for the diatomically ordered phase of hydrogen (solid line and points). Also shown is the curve expected if the interproton spacing is held constant at its zero pressure value ($D = (P = 0)$ value), the results of Chakravarty et al. (Ref. 14), Liberman (Ref. 35), and Ramaker et al. (Ref. 17).

Fig. 8. Second order structural expansion energies (at $r_s = 2.8$) for a Pa3 structure (solid line) and rotationally averaged Pa3 structure (dashed line). Note the extreme insensitivity to D/a (see text).