PHYSICAL REVIEW B VOLUME 18, NUMBER 9 1 NOVEMBER 1978

Ground state of metallic hydrogen

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(Received 19 June 1978)

A proposed liquid state of metallic hydrogen at zero temperature is explored, and a variational upper bound to the ground-state energy is calculated. It is shown that the possibility that metallic hydrogen is a liquid around the metastable point ($r_s = 1.64$) cannot be ruled out. This conclusion crucially hinges on the contribution to the energy arising from the third order in the electron-proton interaction, which is shown here to be more significant in the liquid phase than in crystals.

I. INTRODUCTION

An interesting possibility of a zero-temperature liquid ground state of metallic hydrogen has been recently explored in a calculation[1] that makes use of a Jastrow-Slater many-particle variational wave function[2,3] to calculate the ground-state energies of both solid and liquid phases. The symmetric part of the wave function is treated by the Monte Carlo technique and exchange is neglected in both liquid and solid phases. It is found that the differences in the energies of the liquid and the solid phases varies from 0.1% at $r_s = 1.6$ to about 3% at $r_s = 0.8$ [here $4\pi/3(r_s a_0)^3 = 1/n$ and n is proton or electron density]. From a rough estimate of the energies it is argued that the solid phase is energetically more favorable throughout the entire range of densities considered. However, the calculation is based on a model of pair interactions between protons and therefore contains only terms generated to second order in the electron-proton interaction. The contribution coming from the third order in the electron-proton interaction is known to be significant in the calculation of the band-structure energy[4,5] in the solid. In view of the small energy difference between the solid and the liquid phases it is therefore necessary to estimate the third-order term for the liquid as well. Furthermore, since in the liquid certain configurations will permit three protons to come closer together than they would in a solid, we might also expect that the contribution from the term third order in the electron-proton interaction may be relatively more important in the liquid phase.

In this paper we shall first show that a simple one-parameter variational wave function, when combined with the hypernetted-chain (HNC) integral equation,[2] can reproduce the energies calculated in Ref. 1 (with a six-parameter variational wave function and the Monte Carlo technique) to within 0.025%–4.2%, and therefore provides a very reasonable upper bound. Precise agreement is not in fact necessary in order to provide variational answers to the following questions: (a) How much does the third-order term contribute to the ground-state energy of the liquid? (b) What are the corrections in the energy of the liquid state attributable to long-wavelength phonons? (c) Is it possible to lower the energy of the liquid by permitting partial alignment of the spins of the protons?

The calculation described below is a judicious combination of variational and perturbative methods, and is intended to suggest that for certain densities the possibility of a liquid metallic phase of hydrogen at zero temperature cannot be ruled out. The conclusion hinges on the fact that the third-order term is significant and is perhaps more so in the liquid.

II. FORMULATION

In a sense, hydrogen is the simplest metal; its Hamiltonian is known exactly: For N protons, N electrons, and volume Ω we write

$$H = H_e + H_p + H_{ep}$$

$$= \left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla^2_{\vec{r}_i} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right) + \left(-\frac{\hbar^2}{2m_p} \sum_{i=1}^{N} \nabla^2_{\vec{R}_i} + \sum_{i<j} \frac{e^2}{|\vec{R}_i - \vec{R}_j|} \right) - \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{R}_j|} . \tag{2.1}$$

Here we have denoted the proton coordinates by $\{\vec{R}_i\}$ and the electron coordinates by $\{\vec{r}_i\}$. A major simplification takes place[6] when we realize that there are two widely different time scales involved in the problem, allowing us to remove electronic degrees of freedom by assuming that at any instant we can consider the electrons to be in the ground state corresponding to the instantaneous proton configuration. This Born-Oppenheimer adiabatic approximation reformulates the problem in terms of an effective Hamiltonian of protons. The price we pay is that the indirect interaction between the protons, now mediated by the electrons, is no longer a simple Coulombic pair interaction, but contains many-body forces.[7] With electron coordinates now integrated out, the total Hamiltonian for the protons becomes[8]

$$H_p = E_{eg} + T_p + V_{pp} + E_b^{(2)}(\{\vec{R}_l\}) + E_b^{(3)}(\{\vec{R}_l\}) + \cdots , \tag{2.2}$$

where E_{eg}, which is the *exact* ground-state energy of the *interacting* electrons in a uniform positive background appears as a constant energy, and simply drops out of the calculation. In Eq. (2.2) T_p and V_{pp} are the parts of the original Hamiltonian of the protons and $E_b^{(n)}(\{\vec{R}_l\})$, which are functions of the proton coordinates, are the electron-mediated interactions between protons that are generated by adiabatic perturbation theory. *Provided Eq. (2.2) converges*, the procedure is exact within the adiabatic approximation. Most important, note that to this point we have not made any assumptions regarding the positions of the ions; the discussion holds for liquids and crystals, whether static or dynamic. The precise form of $E_b^{(n)}(\{\vec{R}_l\})$ can easily be written[8]

$$E_b^{(2)}(\{R_l\}) = \tfrac{1}{2}\Omega \sum_{\vec{k}_1}{}' V(\vec{k}_1) V(-\vec{k}_1) \chi^{(1)}(\vec{k}_1) , \tag{2.3}$$

$$E_b^{(3)}(\{R_l\}) = \tfrac{1}{3}\Omega \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3}{}' V(\vec{k}_1) V(\vec{k}_2) V(\vec{k}_3) \times \chi^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_3) \delta_{\vec{k}_1 + \vec{k}_2 + \vec{k}_3, 0} , \tag{2.4}$$

and similarly for the nth-order term. Here,

$$V(\vec{k}) = \sum_{\vec{R}_l} e^{i\vec{k}\cdot\vec{R}_l} \frac{4\pi e^2}{k^2} \tag{2.4'}$$

and

$$\chi^{(1)}(\vec{k}) = \frac{k^2}{4\pi e^2}\left(\frac{1}{\epsilon(k)} - 1\right) \tag{2.5}$$

is the exact first-order static response of the interacting electron gas to an external potential. Similarly, $\chi^{(n)}(\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_{n+1})$ is the exact nth order response. In other words, if we know the nth-order response function of the interacting electron gas exactly, we would also know exactly these extra many-body interactions between protons, and we can proceed to diagonalize the proton Hamiltonian.

The interesting point to note is that the rewriting of the original Hamiltonian in the form given in Eq. (2.2) splits off a large volume-dependent term (order 1 Ry) that does not depend on whether the protons form a liquid or a solid, and therefore simply drops out of the *difference* in energies between the liquid and the solid phases, which is the important quantity in examining the phase transitions between the two. The uncertainties in the electron-gas response functions $\chi^{(n)}(\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_{n+1})$ will surely affect each of the terms $E_b^{(n)}(\{\vec{R}_l\})$, but, once again, they will not influence too greatly the *difference* in energies. Thus this particular reformulation, Eq. (2.2), should be a reliable starting point to calculate the energy difference between liquid and solid phases.

For $\chi^{(1)}(k)$ we shall choose the Hubbard-Geldart-Vosko[9] (HGV) form for the dielectric function $\epsilon(k)$ which is known to be of sufficient accuracy at least for $r_s < 2$. For $\chi_2(\vec{k}_1, \vec{k}_2, \vec{k}_3)$ we shall make use of the *form* used by Brovman, Kagan and Holas,[5] in which the one-body interactions are screened by the HGV dielectric function. This approximation for $\chi^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_3)$ has been used extensively, and is believed to be reasonably accurate. The Hamiltonian can now explicitly be written[10] if we neglect $E_B^{(n)}(\{\vec{R}_l\})$ for $n \geq 4$:

$$H = E_\Omega - \frac{\hbar^2}{2m_p} \sum_{i=1}^{N} \nabla^2_{\vec{R}_i} + \sum_{i<j} \phi^{(2)}(R_{ij}) + \sum_{i<j<k} \phi^{(3)}(R_{ij}, R_{jk}, R_{ik}) , \tag{2.6}$$

where

$$E_\Omega = E_{eg} - \frac{N}{2n\kappa} + \frac{N}{2(2\pi)^3} \int_{(\text{all } \vec{k})} d\vec{k}\, \frac{4\pi e^2}{k^2} \left(\frac{1}{\epsilon(k)} - 1\right) \tag{2.7}$$

is a large volume-dependent term that is convenient to separate out. In Eq. (2.7) n is the number density (N/Ω) and κ is the compressibility of the uniform interacting electron gas neutralized by a uniform positive background at the same density. Note that the terms $E_b^{(2)}(\{\vec{R}_l\})$ and V_{pp} have been combined to give

$$\phi^{(2)}(R_{ij}) = \frac{1}{(2\pi)^3} \int d\vec{k}\, \frac{4\pi e^2}{k^2} \frac{1}{\epsilon(k)} e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} , \tag{2.8}$$

an effective *linear-response* pair potential. Finally, the third-order term[11] is given by

$$\phi^{(3)}(R_{ij}, R_{jl}, R_{il}) = -\frac{1}{(2\pi)^6} \int d\vec{k}_1 \int d\vec{k}_2 \times e^{i\vec{k}_1\cdot\vec{R}_i + \vec{k}_2\cdot\vec{R}_j - i(\vec{k}_1 + \vec{k}_2)\cdot\vec{R}_l} \times \tilde{\Lambda}(\vec{k}_1, \vec{k}_2, -\vec{k}_1 - \vec{k}_2) . \tag{2.9}$$

Here $\tilde{\Lambda}$ is

$$\tilde{\Lambda}(\vec{k}_1,\vec{k}_2,\vec{k}_3)=\frac{(4\pi e^2)^3}{k_1^2k_2^2k_3^2\epsilon(k_1)\epsilon(k_2)\epsilon(k_3)}\Lambda(\vec{k}_1,\vec{k}_2,\vec{k}_3)\,, \tag{2.10}$$

with

$$\Lambda(\vec{k}_1,\vec{k}_2,\vec{k}_3)=\left(\frac{2m^2}{\pi^2\hbar^4}\right)\left(\frac{k_R^2}{k_1k_2k_3}\right)\left(\sum_{i=1}^{3}\cos\theta_i\ln\left|\frac{2k_F+k_i}{2k_F-k_i}\right| - 2\Theta(k_F-k_R)\Delta\tan^{-1}\Delta A - [1-\Theta(k_F-k_R)]\times\Delta\ln\left|\frac{1-\Delta A}{1+\Delta A}\right|\right), \tag{2.11}$$

where $\Theta(x)=1$ for $x\geqslant 0$ and 0 for $x<0$. The remaining parameters are given below:

$$A=\frac{k_1k_2k_3}{(2k_F)^3}\left(1-\frac{1}{2}\frac{k_1^2+k_2^2+k_3^2}{(2k_F)^2}\right)^{-1}\,, \tag{2.12}$$

$$\Delta=|k_F^2-q_R^2|^{1/2}/q_R\,,$$

$$q_R=\frac{k_1k_2k_3}{2[k_1^2k_2^2-(\vec{k}_1\cdot\vec{k}_2)^2]^{1/2}}\,, \tag{2.13}$$

$$\cos\theta_1=-\vec{k}_2\cdot\vec{k}_3/k_2k_3\,, \tag{2.14}$$

$$\cos\theta_2=-\vec{k}_3\cdot\vec{k}_1/k_3k_1\,, \tag{2.15}$$

and

$$\cos\theta_3=-\vec{k}_2\cdot\vec{k}_1/k_2k_1\,. \tag{2.16}$$

If we take $\epsilon(k)$ to be the random-phase approximation (RPA) dielectric function, then $\tilde{\Lambda}$ would be precisely the RPA approximation for the three-tailed diagram.

As mentioned earlier, the dielectric function $\epsilon(k)$ is taken to be of the HGV form and is explicitly given as

$$\epsilon(\eta)=1+\frac{\alpha F(\eta)/\eta^2}{1-\alpha F(\eta)/(2\eta^2+g)}\,, \tag{2.17}$$

where

$$F(\eta)=1+[(1-\eta^2)/2\eta]\ln|(1+\eta)/(1-\eta)|\,, \tag{2.18}$$

$$\alpha=(r_s/2\pi)(4/9\pi)^{1/3}\,, \tag{2.19}$$

$$g=1/[1+0.031(4/9\pi)^{1/3}\pi r_s/2]\,, \tag{2.20}$$

and $\eta=k/2k_F$.

Finally, we obtain

$$H=E_\Omega+H^{(2)}+\sum_{i<j<k}\phi^{(3)}(R_{ij},R_{jk},R_{ik})\,, \tag{2.21}$$

where E_Ω is a constant volume-dependent term and we have split off the $\phi^{(3)}$ term from $H^{(2)}$ given by

$$H^{(2)}=-\frac{\hbar^2}{2m_p}\sum_{i=1}^{N}\nabla_i^2+\sum_{i<j}\phi^{(2)}(R_{ij})\,. \tag{2.22}$$

In Ref. 1, H was approximated by $E_\Omega+H^{(2)}$. We proceed from this point and shall first attempt to diagonalize $H^{(2)}$ as well as possible with a one parameter-variational function that, as we shall see, will give an error of no more than 4% when compared to the calculation of Ref. 1 employing six variational parameters. An optimum wave function obtained in this way will be used to calculate the variational bound for the contribution from $\phi^{(3)}$.

III. CALCULATIONAL TECHNIQUE

In this section we shall outline the method used in calculating the ground-state energy of the Fermi liquid corresponding to the Hamiltonian given in Eq. (2.6). A Jastrow-Slater variational wave function[2,3]

$$\Psi(1,2,\ldots,N)=D\Psi_0^B \tag{3.1}$$

will be used to calculate an upper bound to the ground-state energy. In Eq. (3.1) D is a Slater determinant made out of plane waves and Ψ_0^B is a symmetric correlating factor designed to take care of the strong interparticle interactions. It is responsible for a large part of the energy. A subsequent Wu-Feenberg expansion[2,3] then uses an *exact* transformation to recast the problem into a calculation of two distinct parts. Thus we shall set

$$E=E_B+E_{\rm ex}\,, \tag{3.2}$$

where $E_{\rm ex}$ is the exchange contribution and E_B is the eigenvalue of a symmetric ground state corresponding to the Hamiltonian. Then

$$H(\{\vec{R}_l\})\Psi_0^B=E_B\Psi_0^B\,, \tag{3.3}$$

where Ψ_0^B in Eq. (3.1) is chosen to be the eigenfunction of Eq. (3.3). The calculation of E_B therefore does *not* involve the antisymmetric factor and results in a considerably simplified problem. A knowledge of this Ψ_0^B is then utilized to calculate

$$E_{\rm ex}=\frac{\hbar^2}{2m}\sum_{l=1}^{N}(\Psi_0^B)^2\nabla_l D^*\cdot\nabla_l D\,d\vec{r}_1\cdots d\vec{r}_N \times\left[\int(\Psi_0^B)^2\,d\vec{r}\cdots d\vec{r}_N\right]^{-1}\,, \tag{3.4}$$

which may be calculated by a statistical cluster expansion of the type

$$E_{\mathrm{ex}} = E_F^{01} + E_F^{02} + E_F^{03} + \cdots \ , \tag{3.5}$$

where E_F^{0n} involves n-particle exchange. These terms are easily calculated (at least up to the third order) as we shall see below. The entire procedure is meaningful when E_B is much greater than E_{ex} and the series in E_{ex} converges rapidly. We shall see later that the first condition is very well satisfied, E_B being several orders of magnitude larger than E_{ex}. However, the second is only moderately well satisfied, each term dropping by a factor of $\frac{1}{3}-\frac{1}{5}$ of the previous term.

So far we have implictly assumed a paramagnetic ground state, each level being doubly occupied in the Slater determinant. However, it is easy to extend the result to a departure from double occupancy.[2,3,12] The resulting form for E_{ex} is then

$$E_{\mathrm{ex}}(x) = E_F^{01}(x) + E^{02}(x) + E^{03}(x) + \cdots \ , \tag{3.6}$$

where x is the spin-imbalance order parameter defined by

$$x = (N_+ - N_-)/N \ . \tag{3.7}$$

Here N_+ (N_-) are the numbers of up (down) spins and N is the total number of spins. A nonzero value of x will signify a magnetically ordered phase. Clearly $x=1$ will represent a ferromagnetically ordered phase. Notice that E_0^B does not depend on x. We shall try to determine whether $E_{\mathrm{ex}}(x)$ possesses a minimum $E_{\mathrm{ex}}^m(x_m)$ per particle at a nonzero value of x. It will turn out that the energy difference $\Delta E(x) = E_{\mathrm{ex}}(x=0) - E_{\mathrm{ex}}^m(x_m)$ per particle is small, only ~10^{-5} Ry. (It is worth noting that this is not small on the scale of a superconducting pairing energy.)

IV. VARIATIONAL METHOD

From the variational point of view, E_B in Eq. (3.2) is conveniently split into three parts,

$$E_B = E_B^{(2)} + E_B^{(3)} + \Delta_B^{\mathrm{ph}} \ . \tag{4.1}$$

The first term, $E_B^{(2)}$, is calculated by variationally optimizing the Hamiltonian $H^{(2)}(\{\vec{R}_l\})$ with the many-body Jastrow wave function given by

$$\Psi_0^B = \prod_{i<j} e^{-u(r_{ij})/2} \ , \tag{4.2}$$

where

$$u(r) = (b/r)^3 e^{-(r/b)^3} \ . \tag{4.3}$$

This wave function is a simplified one-parameter form for that used in Ref. 1. The energy functional is minimized with respect to the parameter b at every value of r_s, and the resulting wave function is then used to calculate the expectation value of $\phi^{(3)}(\{\vec{R}_l\})$. The $E_B^{(3)}$ obtained in this first-order perturbation is also a variational bound. The $u(r)$ expressed in Eq. (4.3) is short ranged and does not include the contribution due to the long-wavelength phonons. This is done perturbatively with the help of the Chester-Reatto wave function.[13] The relevant formulas are summarized below:

$$\begin{aligned}\frac{E_B^{(2)}}{N} &= \frac{1}{\pi}\left(\frac{m_e}{m_p}\right)\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{r_s^2}\int_0^\infty dx\, g_B^0(x)\left(\frac{b_F}{x}\right)^3 e^{-(x/b_F)^3}\left[3\left(\frac{x}{b_F}\right)^6 + 2\left(\frac{x}{b_F}\right)^3 + 2\right] + \frac{8}{3\pi^2}\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}\int_0^\infty dx\, x^2 v_0(x) g_B^0(x) \\ &= T_B^{(2)}/N + P_B^{(2)}/N \ ,\end{aligned} \tag{4.4}$$

where all distances are scaled with respect to the inverse Fermi wave vector, $1/k_F$, including the variational parameter b $(b = b_F/k_F)$. In Eq. (4.4), r_s denotes the average interparticle distance scaled by the Bohr radius and $g_B^0(x) \equiv g_B^0(r)$, $(r = x/k_F)$ is the pair correlation function defined as[2,3]

$$g_B^0(r_{12}) = \frac{N(N-1)}{n^2}\int (\Psi_0^B)^2 d\vec{r}_3 \cdots d\vec{r}_N \times\left[\int (\Psi_0^B)^2 d\vec{r}_1 \cdots d\vec{r}_N\right]^{-1} \tag{4.5}$$

Note that Ψ_0^B is defined in Eqs. (4.2) and (4.3). The corresponding static-structure factor $S_0^B(k)$ is defined by the Fourier transform[2,3]

$$S_B^0(k) = 1 + n\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}[g_B^0(r) - 1] \ . \tag{4.6}$$

Finally, with the distance and the wave vector scaled,

$$v_0(x) = \int_0^\infty dy\, \frac{\sin xy}{xy}\,\frac{1}{\epsilon(y)} = \frac{\pi}{2e^2 k_F}\,\phi^{(2)}(x) \tag{4.7}$$

is the screened interaction and $\epsilon(y)$ is the HGV dielectric function. Once again, all wave vectors are scaled by $k_F(|k| = yk_F)$. For $g_B^0(r)$ we shall use the HNC approximation,[2,3] which is known to be satisfactory for Bose fluids and has been tested for a variety of interaction potentials.[2,3] In this approximation $g_B^0(r)$ is the solution of the nonlinear integral equations relating the direct correlation function $c(r)$ to $g_B^0(r)$:

$$g_B^0(r) - 1 = c(r) + n\int d\vec{r}'\, c(|\vec{r} - \vec{r}'|)[g_B^0(r') - 1] \ , \tag{4.8}$$

$$c(r)=g_B^0(r)-1-\ln g_B^0(r)+u(r)\,. \tag{4.9}$$

The procedure is to solve Eqs. (4.8) and (4.9) for a given value of the variational parameter b by a standard numerical procedure and to use the resulting $g_B^0(r)$ in Eq. (4.4) to calculate the energy. This process is repeated for a number of different values of b to find the optimum $g_B^0(r)$, $u(r)$, and the minimum in energy at a given density or r_s. We then proceed to calculate the contribution due to $\phi^{(3)}(\{\vec{R}\})$. Thus

$$\begin{aligned} E_B^{(3)} &= \frac{\langle\Psi_0^B|H^3(\{\vec{R}_l\})|\Psi_0^B\rangle}{\langle\Psi_0^B|\Psi_0^B\rangle} \\ &= -\frac{e^6}{\pi^3}\int d\vec{k}\int d\vec{q}\,\frac{1}{q^2\epsilon(q)}\,\frac{1}{k^2\epsilon(k)} \\ &\qquad\times\frac{1}{(\vec{q}-\vec{k})^2\epsilon(\vec{q}-\vec{k})}\,S_B^0(\vec{k},\vec{q},-\vec{k}-\vec{q}) \\ &\qquad\times\Lambda(\vec{k},\vec{q},-\vec{k}-\vec{q})\,, \end{aligned} \tag{4.10}$$

where

$$S_B^0(\vec{k},\vec{q},-\vec{k}-\vec{q})=\langle\Psi_0^B|\rho_{\vec{k}}\rho_{\vec{q}}\rho_{-\vec{k}-\vec{q}}|\Psi_0^B\rangle/\langle\Psi_0^B|\Psi_0^B\rangle \tag{4.11}$$

and

$$\rho_{\vec{k}}=\sum_{i=1}^{N}e^{-i\vec{k}\cdot\vec{r}_i}\,,\quad \vec{k}\neq 0\,. \tag{4.12}$$

A distinct feature[11] of the response function of $\Lambda(\vec{k},\vec{q},-\vec{k}-\vec{q})$ is its singular behavior when $\vec{k}+\vec{q}=0$, i.e.,

$$\Lambda(\vec{k},-\vec{k},0)\sim\ln|k_F^2-\tfrac{1}{4}k^2|\,. \tag{4.13}$$

This singularity is stronger here than in the second-order response, where only the derivative has a logarithmic singularity. This amplification is due to the confluence of the usual second-order Kohn anomaly, which is always present in the third-order response, and the intrinsic singularity of the third order response. It is clear that the integral in Eq. (4.10) can only be defined if this singularity is canceled by other terms present in the integrand. To this effect we prove rigorously in the Appendix the following result: $\lim_{k\to 0}S_B(\vec{k},\vec{l},-\vec{k}-\vec{l})\to\alpha k$ if $\lim_{k\to 0}S_B(k)\to\alpha k$. Similar results hold when $l\to 0$ and $|\vec{k}+\vec{l}|\to 0$.

Thus it is necessary that $S(k)$ vanish at least linearly with k in the limit of small k. Furthermore, any approximation for the three-particle-structure factor must be such as to preserve this property. One such approximation is the convolution approximation[2,3] for the three-particle-structure factor, an approximation that has been extensively tested for soft-core potentials[14] and in many other situations.[14] Thus we set

$$S_B(\vec{k},\vec{q},-\vec{k}-\vec{q})\sim S_B(k)S_B(q)S_B(\vec{k}+\vec{q})\,, \tag{4.14}$$

which clearly has the required property that it vanishes when any of the three arguments vanishes. As is made clear in the Appendix, this is simply because of the fact that the convolution approximation satisfies all of the normalization conditions to be required of the probability-distribution functions. However, as is well known,[2,3] the short-range wave function in Eq. (4.3) does *not* lead to a $S_B(k)$ that vanishes as $k\to 0$. This needs to be corrected for the presence, expected physically, of long-range phonons before we can evaluate the third-order energy given by Eqs. (4.10) and (4.14). The procedure is almost standard.[15] The Chester and Reatto wave function is long ranged and has the form

$$e^{-U_{Lr}(r)/2}=\exp\frac{3m_p c}{\hbar k_F}\left(\frac{1}{x^2+x_0^2}\right), \tag{4.15}$$

where we have scaled the distance by k_F, i.e., $r=x/k_F$ and x_0 is a variational cutoff parameter. Here c is the velocity of sound in this hypothetical Boson system and can be obtained from the energy $E_B^{(2)}/N$:

$$c(r_s)=\frac{c_{BS}}{\sqrt{3}}\left[r_s\left(\frac{4}{9\pi}\right)^{1/3}\left(\frac{r_s^2}{2}\,\frac{d^2E_B^{(2)}}{dr_s^2}-r_s\,\frac{dE_B^{(2)}}{dr_s}\right)^{1/2}\right], \tag{4.16}$$

where $c_{BS}=(v_F/\sqrt{3})(m_e/m_p)^{1/2}$ and $v_F=\hbar k_F/m_e$. The choice of such a long-range wave function leads to a sequence of changes, given next. The structure factor $S_B^0(k)$ calculated with the short-ranged (LR) wave function is modified to $S_B(k)$, given by

$$S_B(k)=S_B^0(k)/[1+nS_B^0(k)U_{LR}(k)]\,, \tag{4.17}$$

where LR is long ranged and the corresponding correction in the pair-correlation function is

$$\delta g(r)=g_B^0(r)(e^{-\Gamma(r)}-1)\,, \tag{4.18}$$

where

$$g_B(r)=g_B^0(r)+\delta g(r)\,, \tag{4.19}$$

and $U_{LR}(k)$ is the Fourier transform of U_{LR}. Finally,

$$\Gamma(r)=\frac{1}{(2\pi)^3}\int e^{i\vec{k}\cdot\vec{r}}\,\frac{S_B^0(k)^2U_{LR}(k)}{1+nU_L(k)S_B^0(k)}\,d\vec{k}\,. \tag{4.20}$$

The correction to the energy is then

$$\frac{\Delta E_B^{\mathrm{ph}}}{N} = \frac{\hbar^2 n}{8m_p}\int d\vec{r}\, g_B^0(r)\nabla^2 U_{LR}(r) + \frac{\hbar^2 n}{8m_p}\int d\vec{r}\,\delta g(r)\nabla^2[U(r)+U_{LR}(r)] + \tfrac{1}{2}\rho\int v(r)\,\delta g(r)\,d\vec{r}\,. \tag{4.21}$$

Finally, Eq. (4.10) can be rewritten to obtain the third-order contribution to the energy,

$$\frac{E_B^{(3)}}{N} = -\frac{8e^6}{\pi}\int_0^\infty dk\,\frac{S_B(k)}{\epsilon(k)}\int_0^\infty dq\,\frac{S_B(q)}{\epsilon(q)}\int_0^\pi \sin\theta\, d\theta\,\frac{1}{(\vec{q}+\vec{k})^2}\,\frac{1}{\epsilon(\vec{k}+\vec{q})^2}\,S_B(\vec{k}+\vec{q})\Lambda(\vec{k},\vec{q},-\vec{k}-\vec{q})\,, \tag{4.22}$$

where θ is the angle between the vectors $\vec{k}$ and $\vec{q}$. Thus $E_B^{(3)}/N$ can now be calculated numerically if $S_B(q)$ is known.

V. EXCHANGE CONTRIBUTIONS

As mentioned earlier, the Wu-Feenberg expansion is used to obtain the exchange contributions to the energy. The total energy per particle is

$$E(x)/N = E_{\mathrm{ex}}/N = [E_B^{(2)} + E_B^{(3)} + \Delta E_B^{\mathrm{ph}}]/N + E_{\mathrm{ex}}(x)/N\,, \tag{5.1}$$

where $E_{\mathrm{ex}}(x)/N$ is the exchange energy of the fermions (protons in this case). In Eq. (5.1) the energy up to third order in exchange is given by

$$E_{\mathrm{ex}}/N = E_{01}^F(n,x)/N + E_{02}^F(n,x)/N + E_{03}^F(n,x)/N + \cdots\,, \tag{5.2}$$

where

$$\frac{E_{01}^F(n,x)}{N} = \tfrac{3}{10}e_F[(1+x)^{5/3}+(1-x)^{5/3}]\,, \tag{5.3}$$

$$\frac{E_{02}^F(n,x)}{N} = 12\,e_F\left((1+x)^{8/3}\int_0^1 (y^4-\tfrac{3}{2}y^5+\tfrac{1}{2}y^7)[S(2k_F^+y)-1]\,dy + (1-x)^{8/3}\int_0^1 (y^4-\tfrac{3}{2}y^5+\tfrac{1}{2}y^7)[S(2k_F^-y)-1]\,dy\right), \tag{5.4}$$

and

$$\frac{E_{03}^F(n,x)}{N} = -\frac{e_F}{2}\left(\frac{3}{8\pi}\right)^3\left((1+x)^{11/3}\int_{y_i<1} y_{12}^2 S(k_F^+y_{12})[S(k_F^+y_{23})-1][S(k_F^+y_{13})-1]\,d\vec{y}_1\,d\vec{y}_2\,d\vec{y}_3 + (1-x)^{11/3}\int_{y_i<1} y_{12}^2 S(k_F^-y_{12})[S(k_F^-y_{23})-1][S(k_F^-y_{13})-1]\,d\vec{y}_1\,d\vec{y}_2\,d\vec{y}_3\right). \tag{5.5}$$

Note that $e_F = \hbar^2k_F^2/2m_p$, $k_F^\pm = k_F(1\pm x)^{1/3}$, and $x = (N_+ - N_-)/N$. As mentioned earlier, our intention is to compute the ground-state energy as a function of x. The term E_{03}^F is calculated by making the quadratic approximation described in Refs. 2 and 12.

VI. RESULTS

In Fig. 1 we show the dimensionless potential function $v_0(x)$ [Eq. (4.7)] for some typical values of r_s. In Fig. 2 we show the corresponding pair-correlation functions $g_B(r)$. The actual fermion pair-correlation function can be obtained from these by the Wu-Feenberg expansion,[2,3] fermion corrections being small in this case. The reason why we have not displayed them is because they are not explicitly required in the method of calculating the Wu-Feenberg series used here. The structure factor $S_B(k)$ corresponding to $g_B(r)$ is shown in Fig. 3 for a few typical values of r_s. It is clear from these plots that there is a considerable amount of short-range order in liquid metallic hydrogen as compared to, say, liquid helium. One should also note that the interaction potential exhibits a strong density dependence.

Table I compares our results for $E_B^{(2)}$ [Eq. (4.4)] with the calculation in Ref. 1. It is clear that our one-parameter variational wave function gives a reasonably good upper bound. Also shown in Table I is the detailed decomposition of $E_B^{(2)}$ into kinetic and potential energies. We should emphasize that precise agreement between our one-parameter variational results with the six-parameter Monte Carlo results,[1] is not necessary since we are simply interested in an *upper bound* for the contribu-

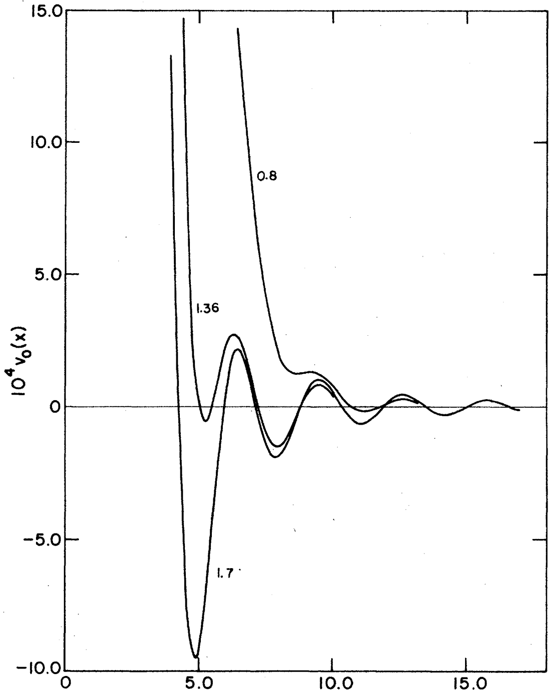

FIG. 1. $v_0(r)$ for some typical values of r_s.

tion arising from the three-body forces. These are given in Table I along with the volume-dependent terms. In calculating E_Ω and E_{eg} we have made use of the Nozières and Pines interpolation[16] formula for the correlation energy of electron gas, which is consistent with our choice of HGV dielectric function. From Table I one can also see that $\Delta E_B^{\rm ph}/N$ [Eq. (4.21)] makes a negligible contribution to the total energy. The main effect of the long-range phonons is to produce an $S_B(k)$ that vanishes in the limit of small k, which, in turn, allows us to calculate $E_B^{(3)}/N$ [Eq. (4.22)]. As noted above, the integral is ill conditioned if $S_B(k)$ approaches a nonzero value as k goes to zero.

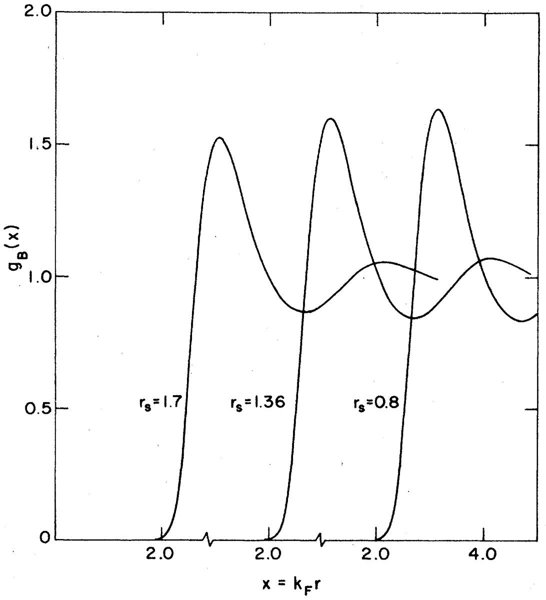

FIG. 2. $g_B(r)$ for some typical values of r_s.

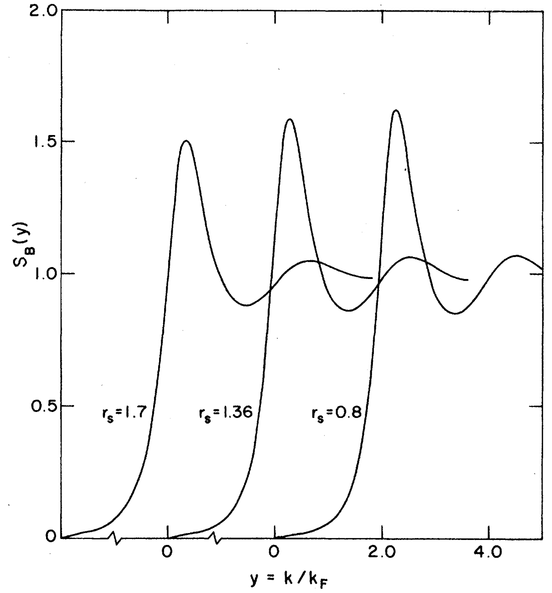

FIG. 3. $S_B(k)$ for some typical values of r_s.

In Table II we have shown the exchange corrections. It is seen that a partially spin-aligned state of protons is in fact favored throughout the entire range of densities considered. As mentioned earlier we should be cautious about this conclusion, since E_{03}^F has been calculated with the help of the conventional[2,10,12] quadratic approximation, and thus may be quite inaccurate, especially for larger values of the order parameter x. In view of the fact that this term is considerably smaller than the rest and that one needs a complicated numerical procedure to calculate accurately, we have not examined it using a more elaborate computational method. We do not believe that the results will change qualitatively. Since the quadratic approximation is good in the neighborhood of $x=0$, the fact that the energy is lowered for nonzero values of x can be established although the exact value of x may be inaccurate. It is also worth remembering that the convergence of Wu-Feenberg series is not rigorously established.

The total energy for the liquid is compared in Table III, with the static energies for the solid phase obtained by Hammerberg and Ashcroft.[4] Note that the static energies do not contain the vibrational zero-point energy, which in the case of

TABLE I. Boson part E_B of the ground-state energy. $E_B^{(2)}(\mathrm{MC})$ is the Monte Carlo results of Ref. 1. All energies are expressed in Ry.

r_s	b_F	$T_B^{(2)}/N$	$P_B^{(2)}/N$	$E_B^{(2)}/N$	$E_B^{(2)}(\mathrm{MC})/N$	$\Delta E_B/N$	$E_B^{(3)}/N$	E_Ω/N
0.50	5.35	0.074 06	2.762 68	2.836 74		−0.001 58	−0.014 42	0.540 62
0.80	5.55	0.031 95	0.762 54	0.794 49	0.7943	−0.000 54	−0.021 20	−0.861 88
1.20	5.50	0.013 86	0.199 86	0.213 72	0.2079	−0.000 21	−0.029 44	−1.103 53
1.30	5.435	0.011 43	0.146 16	0.157 59				
1.36	5.40	0.010 26	0.121 04	0.131 30	0.1262	−0.000 16	−0.032 58	−1.100 50
1.40	5.37	0.009 54	0.106 65	0.116 19				
1.45	5.315	0.008 65	0.090 95	0.099 60				
1.488					0.0847			
1.50	5.28	0.007 94	0.077 26	0.085 20		−0.000 12	−0.035 28	−1.083 94
1.55	5.225	0.007 23	0.065 43	0.072 66				
1.60	5.175	0.006 61	0.055 10	0.061 71	0.0592	−0.000 11	−0.037 18	−1.067 90
1.70	5.05	0.005 49	0.038 24	0.043 73		−0.000 09	−0.039 08	−1.049 88
1.80	4.9	0.004 52	0.025 31	0.029 83		−0.000 08	−0.041 00	−1.030 74

hydrogen[16] could easily be of the order of 0.01 Ry. The contribution of the third-order term in the liquid is more significant than in the solid. For example, at $r_s = 1.6$, the third-order energy in the liquid is −0.0372 Ry, as opposed to −0.0322 Ry as calculated by Hammerberg and Ashcroft. The corresponding comparison at $r_s = 1.36$ yields −0.0326 Ry for liquid as opposed to −0.0281 Ry for the solid.[17] Finally, the liquid-state energies calculated in this paper are a variational upper bound, and the exact energy is expected to be lower. Thus one cannot in principle exclude the existence of a liquid ground state of metallic hydrogen, though it is certainly not established as a preferred ground state.

VII. CONCLUSION

We have investigated the possibility for a liquid ground state of metallic hydrogen at zero temperature. We conclude that the possibility of a liquid phase near the metastable zero pressure point cannot be ruled out. We have found that the third-order terms in the liquid are significantly *lower* than the corresponding ones in the solid, and a careful estimate of these terms in the solid phase, which also incorporates the dynamics of the protons, is essential to determine the liquid-solid transition (if any). We have also found that the contribution to the ground-state energy due to the long-range phonons is neglible, although their presence is necessary. An interesting part of our calculation is that the energy of this proton-electron liquid can be lowered by a partial spin alignment of the protons.

ACKNOWLEDGMENTS

We would like to thank Dr. P. Bhattacharya and Professor G. V. Chester for interesting discussions. This work was supported by NASA, under Grant No. NGR 33-010-188.

TABLE II. Exchange contribution to the ground-state energy. All energies are expressed in Ry.

r_s	x	$E_{\mathrm{ex}}(x)/N$
0.50	0.589	0.002 63
0.80	0.579	0.001 02
1.20	0.582	0.000 45
1.30	0.585	0.000 39
1.36	0.587	0.000 35
1.40	0.588	0.000 33
1.45	0.591	0.000 31
1.50	0.593	0.000 29
1.55	0.595	0.000 27
1.60	0.598	0.000 26
1.70	0.603	0.000 23
1.80	0.607	0.000 21

TABLE III. Comparisons of the ground-state energies of the liquid $[E(x)/N]$ and the solid phases $[E^s(\mathrm{HA})/N$: Hammerberg and Ashcroft, (Ref. 4)]. All energies are expressed in Ry. sc: simple cubic; bcc: body-centered cubic; face-centered cubic.

r_s	$E^s(\mathrm{HA})/N$			$E(x)/N$
	sc	fcc	bcc	
0.50				3.363 99
0.80				−0.088 11
1.00	−0.711 88	−0.71929	−0.718 19	
1.20	−0.937 96	−0.940 19	−0.939 02	−0.919 01
1.25	−0.968 42	−0.969 61	−0.968 43	
1.30	−0.992 17	−0.992 42	−0.991 22	
1.36				−1.001 59
1.50	−1.041 04	−1.038 18	−1.036 93	−1.033 85
1.60	−1.047 59	−1.043 45	−1.042 22	−1.043 22
1.65	−1.048 03	−1.043 38	−1.042 09	
1.70				−1.045 09
1.80				−1.041 78

APPENDIX

We shall prove that the limiting value of $S_B(\vec{k}, \vec{q}, -\vec{k}-\vec{q})$ as any one of the wave vectors approaches zero from above, vanishes, provided the static-structure factor $S_B(k)$ vanishes in the same limit. Strictly speaking, this result should be considered as a limiting value, defining the function by continuity at the origin and requiring the definition to hold in the thermodynamic limit.

First note that[2]

$$S_B(\vec{k}, \vec{q}, -\vec{k}-\vec{q}) = \frac{\langle \Psi_0^B | \rho_{\vec{k}} \rho_{\vec{q}} \rho_{-\vec{k}-\vec{q}} | \Psi_0^B \rangle}{N \langle \Psi_0^B | \Psi_0^B \rangle}$$

$$= 2 + S(k) + S(q) + S(|\vec{k}+\vec{q}|)$$

$$+ \frac{1}{N} \int e^{i\vec{k}\cdot\vec{r}_1 + \vec{q}\cdot\vec{r}_2 - i(\vec{k}+\vec{q})\cdot\vec{r}_3}$$

$$\times P(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3 , \tag{A1}$$

where the three-particle-distribution function $P(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is

$$P(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{N(N-1)(N-2)}{n^3}$$

$$\times \int (\Psi_0^B)^2\, d\vec{r}_4 \cdots d\vec{r}_N$$

$$\times \left[\int (\Psi_0^B)^2\, d\vec{r}_1 \cdots d\vec{r}_N \right]^{-1} . \tag{A2}$$

Since $S_B(\vec{k}, \vec{q}, -\vec{k}-\vec{q})$ is invariant with respect to the interchange of its arguments. it is sufficient to prove the result when any one of the wave vectors tends to zero, say $k \to 0^+$. The following cluster decomposition[2] of $P(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is exact as long as one does not specify $\delta P(\vec{r}_1, \vec{r}_2, \vec{r}_3)$:

$$P(\vec{r}_1, \vec{r}_2, \vec{r}_3) = n^3 [1 + h(r_{12}) + h(r_{13}) + h(r_{23})$$

$$+ h(r_{12}) h(r_{23}) + h(r_{23}) h(r_{31})$$

$$+ h(r_{31}) h(r_{32})] + \delta P(\vec{r}_1, \vec{r}_2, \vec{r}_3) , \tag{A3}$$

where $h(r) = g_B(r) - 1$. Then one can easily prove from the normalization of the probability-distribution functions that[2]

$$\delta P(\vec{r}_1, \vec{r}_2, \vec{r}_3)\, d\vec{r}_3 = -n^3 \int h(r_{13}) h(r_{23})\, d\vec{r}_3 . \tag{A4}$$

Now one can easily evaluate the right-hand side of Eq. (A1) for $k \to 0^+$ and obtain the stated result.

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[7] It is worthwhile to expand on what we mean by many-body forces. For example, $E_b^{(3)}(\{\vec{R}_l\})$ will contain a pair as well as a three-body interaction, similarly for the higher-order terms. For computational purpose there is no need to make this decomposition.

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