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ON THE GROUND STATE OF METALLIC HYDROGEN

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ABSTRACT

A proposed liquid ground 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 the 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.

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1. INTRODUCTION

An interesting possibility of a zero temperature liquid ground state of metallic hydrogen has been recently explored in a calculation[1] which makes use of a Jastrow-Slater many particle variational wavefunction[2,3] to calculate the ground state energies of both solid and liquid phases. The symmetric part of the wavefunction is treated by the Monte-Carlo technique; exchange is neglected in the solid and approximated in the liquid by the Wu-Feenberg expansion[2,3] 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 $4\pi/3(r_s a_o)^3 = 1/n$ and n is proton or electron density). The solid phase seems to be 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 wavefunction when combined with the Hypernetted Chain (HNC) integral equation[2] can reproduce the energies calculated in Ref. 1 with a 6-parameter variational wavefunction and the Monte-Carlo technique to within 0.025 - 4.2% and therefore provides a very reasonable upperbound. However, precise agreement is not 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 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.

2. FORMULATION

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

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

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

$$- \sum_{i,j}\frac{e^2}{|\vec{r}_i-\vec{R}_j|} \quad . \tag{2.1}$$

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]

$$H_p = E_{eg} + T_p + V_{pp} + E_b^{(2)}(\{\vec{R}_\ell\}) + E_b^{(3)}(\{\vec{R}_\ell\}) + \ldots \tag{2.2}$$

where E_{eg}, which is the <u>exact</u> ground state energy of the <u>interacting</u> 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 $E_b^{(n)}(\{\vec{R}_\ell\})$ which are functions of the proton coordinates are the electron mediated interactions between protons which are generated by adiabatic perturbation theory. <u>Provided Eq. (2.2) converges</u>, the procedure is exact within the adiabatic approximation. Most importantly, 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 $E_b^{(n)}(\{R_\ell\})$ can easily be written down[8]

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

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

and similarly for the <u>n</u>th order term. Here,

$$V(\vec{k}) = -\sum_\ell e^{i\vec{k}\cdot\vec{R}_\ell}\ \frac{4\pi e^2}{k^2}\ , \tag{2.4}$$

and

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

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 otherwords 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) which 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 interesting 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 $E_b^{(n)}(\{R_\ell\})$ 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 reasonable 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 down [10] if we neglect $E_B^{(n)}(\{\vec{R}_\ell\})$ for $n \geq 4$:

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

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, which is convenient to separate out. In (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 $E_b^{(2)}(\{\vec{R}_\ell\})$ 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 <u>linear-response</u> pair potential. Finally the third order term[11] is given by,

$$\phi^{(3)}(R_{ij}, R_{j\ell}, R_{i\ell}) = - \frac{1}{(2\pi)^6} \int dk_1 \int dk_2 e^{i\vec{k}_1\cdot\vec{R}_i + \vec{k}_2\cdot\vec{R}_j - i(\vec{k}_1+\vec{k}_2)\cdot\vec{R}_\ell} \; \tilde{\Lambda}(\vec{k}_1, \vec{k}_2, -\vec{k}_1 - \vec{k}_2) \tag{2.9}$$

Here $\tilde{\Lambda}$ is:

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

$$\Lambda(\vec{k}_1, \vec{k}_2, \vec{k}_3) = \left(\frac{2m^2}{3\pi^2\hbar^4}\right)\left(\frac{k_R^2}{k_1 k_2 k_3}\right)\Bigg[\sum_{i=1}^{3} \cos\theta_i \, \ln\left|\frac{2k_F + k_i}{2k_F - k_i}\right| - 2\theta(k_F - k_R) \tan^{-1}\Delta A$$
$$- \left\{1 - \theta(k_F - k_R)\right\} \ln \left|\frac{1-\Delta A}{1+\Delta A}\right| \Bigg] , \tag{2.11}$$

where $\theta(x) = 1$ for $x \geq 0$ and zero for $x < 0$. The remaining parameters are given below,

$$A = \frac{k_1 k_2 k_3}{(2k_F)^3} \left[1 - \tfrac{1}{2} \frac{k_1^2 + k_2^2 + k_3^2}{(2k_F)^2} \right]^{-1} . \tag{2.12}$$

$$\Delta = \left|\frac{k_F^2 - q_R^2}{q_R^2}\right|^{\frac{1}{2}} ,$$

$$q_R = \frac{k_1 k_2 k_3}{2\left[k_1^2 k_2^2 - (\vec{k}_1 \cdot \vec{k}_2)^2\right]^{\frac{1}{2}}} , \tag{2.13}$$

$$\cos\theta_1 = -\frac{\vec{k}_2 \cdot \vec{k}_3}{k_2 k_3} , \tag{2.14}$$

$$\cos\theta_2 = -\frac{\vec{k}_3 \cdot \vec{k}_1}{k_3 k_1} , \tag{2.15}$$

and

$$\cos\theta_3 = -\frac{\vec{k}_2 \cdot \vec{k}_1}{k_2 k_1} . \tag{2.16}$$

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

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

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

where

$$F(\eta) = 1 + \frac{(1-\eta^2)}{2\eta} \ln\left|\frac{1+n}{1-n}\right| , \tag{2.18}$$

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

$$g = \frac{1}{\left(1 + 0.031 \left(\frac{4}{9\pi}\right)^{1/3} \frac{\pi r_s}{2}\right)} \tag{2.20}$$

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 which, as we shall see, will give an error of no more than 4% when compared to the calculation of Ref. 1 employing 6 variational parameters. An optimum wavefunction obtained in this way will be used to calculate the variational bound for the contribution from $\phi^{(3)}$.

3. 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 wavefunction[2,3]

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

will be used to calculate an upperbound to the ground state energy. In Eq. (3.1) D is a Slater determinant made out of plane waves and $\underline{\Psi}_o^B$ is a symmetric correlating factor designed to take care of the strong inter-particle interactions. It is responsible for a large part of the energy. A subsequent Wu-Feenberg expansion[2,3] then uses an <u>exact</u> transformation to recast the problem into the calculation of two distinct parts. Thus we shall set

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

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

$$H(\{R_\ell\})\,\underline{\Psi}_o^B = E_B\underline{\Psi}_o^B \tag{3.3}$$

where $\underline{\psi}_o^B$ in Eq. (3.1) is chosen to be the eigenfunction of (3.3). The calculation of E_B therefore does <u>not</u> involve the antisymmetric factor and results in a considerably simplified problem. A knowledge of this $\underline{\psi}_o^B$ is then utilized to calculate,

$$E_{ex} = \frac{\hbar^2}{2m} \sum_{\ell=1}^{N} \frac{\int \underline{\psi}_o^{B^2} \nabla_\ell D^* \cdot \nabla_\ell D \, d\vec{r}_1 \ldots d\vec{r}_N}{\int \underline{\psi}_o^{B^2} \, d\vec{r}_1 \ldots d\vec{r}_N} \tag{3.4}$$

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

$$E_{ex} = E_F^{01} + E_F^{02} + E_F^{03} + \ldots \tag{3.5}$$

where $E_F^{(0n)}$ involves n-particle exchange. These terms are easily calculated (at least up to the 3rd 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 1/3 to 1/5 of the previous term.

So far we have implicitly 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 $E_{ex}(x)$ is then

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

where x is the spin imbalance order parameter defined by,

$$x = \frac{N_+ - N_-}{N} \tag{3.7}$$

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Here $N_+(N_-)$ are the numbers of up (down) spins and N is the total number of spins. A non zero value of x will signify a magnetically ordered phase Clearly $x = 1$ will represent a ferromagnetically ordered phase. Notice that E_o^B does not depend on x. We shall try to determine whether $E_{ex}(x)$ possesses a minimum $E_{ex}^m(xm)$ at a non-zero value of x. It will turn out that the energy difference $\Delta E(x) = E_{ex}(x=0) - E_{ex}^m(xm)$ per particle is small, only $\sim 2 \times 10^{-5}$Ry. (It is worth noting that this is not small on the scale of a superconducting pairing energy.)

4. VARIATIONAL METHOD

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

$$E_B = E_B^{(2)} + E_B^{(3)} + \Delta E_B^{Ph} . \tag{4.1}$$

The first term, $E_B^{(2)}$, is calculated by variationally optimizing the Hamiltonian $H^{(2)}(\{R_\ell\})$ with the many-body Jastrow wavefunction given by,

$$\Psi_o^B = \prod_{i<j} e^{-\frac{1}{2}u(r_{ij})} \tag{4.2}$$

where,

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

This wave function is a simplified one-parameter form for that used in Ref. 7. The energy functional is minimized with respect to the parameter b at every value of r_s, the resulting wavefunction is then used to calculate the expectation value of $\phi^{(3)}(\{\vec{R}_\ell\})$. 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 Chester-Reatto wavefunction[13]. The relevant formulae are summarized below:

$$E_B^{(2)}/N = \frac{1}{\pi}\left(\frac{m_e}{m_p}\right)\left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2} \int_0^\infty dx g_B^o(x)\left(\frac{b_F}{x}\right)^3 e^{-(x/b_F)^3}\left\{3\left(\frac{x}{b_F}\right)^6 + 2\left(\frac{x}{b_F}\right)^3 + 2\right\}$$

$$+ \frac{8}{(3\pi^2)} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \int_0^\infty dx\, x^2 v_o(x) g_B^o(x) \quad . \tag{4.4}$$

$$= T_B^{(2)}/N + P_B^{(2)}/N$$

where all distances are scaled with respect to the inverse Fermi wavevector, $1/k_F$, 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 $g_B^o(x) \equiv g_B^o(r)$, ($r = x/k_F$) is the pair correlation function defined as:[2,3]

$$g_B^o(r_{12}) = \frac{N(N-1)}{n^2} \quad \frac{\int (\psi_o^B)^2 d\vec{r}_3 \ldots d\vec{r}_N}{\int \psi_o^{B^2} d\vec{r}_1 \ldots d\vec{r}_N} \quad . \tag{4.5}$$

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

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

Finally with the distance and the wavevector scaled,

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

is the screened interaction and $\epsilon(y)$ is the HGV dielectric function. Once again all wavevectors are scaled by k_F($|k| = yk_F$). For $g_B^o(r)$ we shall use the

Hypernetted Chain 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 $g_B^o(r)$ is the solution of the non-linear integral equation relating the direct correlation function $c(r)$ to $g_B^o(r)$:

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

$$c(r) = g_B^o(r) - 1 - \log g_B^o(r) + u(r) \tag{4.9}$$

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 $g_B^o(r)$ in Eq. (4.4) to calculate the energy. This process is repeated for a number of different values of b to find the optimum $g_B^o(r)$, $u(r)$ and the minimum in energy at a given density or r_s. We then proceed to calculate the contribution due to $\phi^{(3)}(\{\vec{R}_\ell\})$. Thus

$$E_B^{(3)} = \frac{\langle \underline{\psi}_o^B|\ H^3(\{R_\ell\})\ |\underline{\psi}_o^B\rangle}{\langle \underline{\psi}_o^B|\underline{\psi}_o^B\rangle}$$

$$= -\frac{e^6}{\pi^3}\int d\vec{k}\int d\vec{q}\ \frac{1}{q^2\varepsilon(q)}\ \frac{1}{k^2\varepsilon(k)}\ \frac{1}{(\vec{q}+\vec{k})^2\varepsilon(\vec{q}+\vec{k})}\ S_B^o(\vec{k},\vec{q},-\vec{k}-\vec{q})\Lambda(\vec{k},\vec{q},-\vec{k}-\vec{q}) \tag{4.10}$$

where,

$$S_B^o(\vec{k},\vec{q},-\vec{k}-\vec{q}) = \frac{\langle \underline{\psi}_o^B|\rho_{\vec{k}}\rho_{\vec{q}}\rho_{-\vec{k}-\vec{q}}|\underline{\psi}_o^B\rangle}{\langle \underline{\psi}_o^B|\underline{\psi}_o^B\rangle} \tag{4.11}$$

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.,

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

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 cancelled by other terms present in the integrand. To this effect we prove rigorously in the Appendix the following result: $\lim_{k\to 0} S_B(\vec{k},\vec{\ell},-\vec{k}-\vec{\ell}) \to \alpha k$ if $\lim_{k\to 0} S_B(k) \to \alpha k$. Similar results hold when $\ell \to 0$ and $|\vec{k}+\vec{\ell}| \to 0$.

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 vanaishes. As is made clear in the appendix this is simply because of the fact that the convolution approximation satisfies all the normalization conditions to be required of the probability distribution functions. However, as is well known[2,3], the short range wavefunction written down in Eq. (4.3) does <u>not</u> lead to a $S_B(k)$ which 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 Eq. (4.10) and (4.14). The procedure is almost standard[15]. The Chester and Reatto wavefunction is long ranged and has the form

$$e^{-\frac{1}{2}U_{Lr}(r)} = e^{-\frac{3m_p c}{\hbar k_F}\frac{1}{(x^2+x_o^2)}} \tag{4.15}$$

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

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

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

$$S_B(k) = \frac{S_B^o(k)}{1 + n\cdot S_B^o(k)\ U_{LR}(k)} \tag{4.17}$$

and the corresponding correction in the pair correlation function is

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

where

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

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

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

The correction to the energy is then

$$\frac{\Delta E_B^{Ph}}{N} = \frac{\hbar^2\rho}{8m} \int d\vec{r} \; g_B^0(r) \; \nabla^2 U_{LR}(r) + \frac{\hbar^2\rho}{8m} \int d\vec{r} \delta g(r) \; \nabla^2 [U(r) + U_{LR}(r)]$$

$$+ \tfrac{1}{2}\rho \int v(r) \; \delta g(r) d\vec{r} \tag{4.21}$$

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

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

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.

5. 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

$$E(x)/N = E_B/N + E_{ex}/N$$

$$= (E_B^{(2)} + E_B^{(3)} + \Delta E_B^{Ph})/N + E_{ex}(x)/N \tag{5.1}$$

where, $E_{ex}(x)/N$ 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:

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

where

$$E^F_{01}(n,x)/N = \frac{3}{10}\, e_F\left[(1+x)^{5/3}+(1-x)^{5/3}\right] \tag{5.3}$$

$$E^F_{02}(n,x)/N = 12e_F\Big\{(1+x)^{8/3}\int_0^1 (y^4 - \tfrac{3}{2}\, y^5 + \tfrac{1}{2}y^7)\,[S(2k_F^+y)-1]dy$$

$$+ (1-x)^{8/3}\int_0^1 (y^4 - \tfrac{3}{2}\, y^5 + \tfrac{1}{2}y^7)\,[S(2k_F^-y)-1]dy \tag{5.4}$$

and

$$E^F_{03}(n,x)/N = -\frac{e_F}{2}\left(\frac{3}{8\pi}\right)^3\Big\{(1+x)^{11/3}\int_{y_1<1} y_{12}^2 S(k_F^+y_{12})\,[S(k_F^+y_{23})-1]\,[S(k_F^+y_{13})-1]d\vec{y}_1 d\vec{y}_2 d\vec{y}_3$$

$$+ (1-x)^{11/3}\int_{y_1<1} y_{12}^2 S(k_F^-y_{12})\,[S(k_F^-y_{23})-1]\,[S(u_F^-y_{13})-1]d\vec{y}_1 d\vec{y}_2 d\vec{y}_3\Big\} \tag{5.5}$$

Note that $e_F = \frac{\hbar^2 k_F^2}{2m_p}$, $k_F^{\pm} = k_F(1 \pm x)^{1/3}$ 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^F_{03} is calculated by making the quadratic approximation described in Refs. 2 and 12.

6. RESULTS

In Fig. 1 we show the dimensionless potential function $v_o(x)$, 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 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 1 compares our results for $E_B^{(2)}$, Eq. (4.4), with the calculation in Ref. 1. It is clear that our one parameter variational wavefunction gives

a reasonably good upperbound. Also shown in the table is the detailed decomposition of $E_B^{(2)}$ into kinetic and potential energies. We should emphasize that precise agreement between our 1-parameter variational results with the 6-parameter Monte Carlo results, Ref. 1, is not necessary since we are simply interested in an upperbound for the contribution arising from the three body forces. These are given in Table 1 along with the volume dependent terms. In calculating E_Ω and E_{eg} we have made use of the Nozieres and Pines interpolation[16] formula for the correlation energy of electron gas which is consistent with our choice of HGV dielectric function. From Table 1 one can also see that $\Delta E_B^{Ph}/N$, Eq. (4.21), makes a negligible contribution to the total energy. The main effect of the long range phonons is to produce an $S_B(k)$ which 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 non zero value as k goes to zero.

In Table 2 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 = o, the fact that the energy is lowered for non zero 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, Table 3, with the static energies the solid phase obtained by Hammerberg and Ashcroft[4]. Note that the static

hydrogen[16] could easily be of the order of 0.01Ry. 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 -0.0372Ry as opposed to -0.0322 calculated by Hammerberg and Ashcroft. The corresponding comparison at $r_s = 1.36$, yields -0.0326Ry for liquid as opposed to -0.0281 for the solid[17]. Finally, the liquid state energies calculated in this paper are a variational upperbound 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.

7. 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 out 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 negligible though their presence is necessary. An interesting part of our calculation is the fact that the energy of this proton-electron liquid can be lowered by a partial spin alignment of the protons.

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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 vector 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 true in the thermodynamic limit.

First note that[2],

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

$$= -2+S(k)+S(q)+S(|\vec{k}+\vec{q}|)+ \frac{1}{N} \int e^{i\vec{k}\cdot\vec{r}_1+i\vec{q}\cdot\vec{r}_2-i(\vec{k}+\vec{q})\cdot\vec{r}_3} P(\vec{r}_1,\vec{r}_2,\vec{r}_3) \, d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \qquad \text{(A1)}$$

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

$$P(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \frac{N(N-1)(N-2)}{n^3} \frac{\int \Psi_o^{B^2} d\vec{r}_4 \ldots d\vec{r}_N}{\int \Psi_o^{B^2} d\vec{r}_1 \ldots d\vec{r}_N} \quad . \qquad \text{(A2)}$$

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 wavevectors tend 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 $\delta P(\vec{r}_1,\vec{r}_2,\vec{r}_3)$:

$$P(\vec{r}_1,\vec{r}_2,\vec{r}_3) = n^3[1+h(r_{12})+h(r_{13})+h(r_{23})+h(r_{12})h(r_{23})+h(r_{23})h(r_{31}) +h(r_{31})h(r_{32})] + \delta P(\vec{r}_1,\vec{r}_2,\vec{r}_3) \qquad \text{(A3)}$$

where, $h(r) = g_B(r) - 1$.

Then one can easily prove from the normalization of the probability distribution functions that[2]

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

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 $E_b^{(3)}(\{\vec{R}_\ell\})$ 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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FIGURE CAPTIONS

Figure 1 $v_o(r)$ for some typical values of r_s

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

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

TABLE CAPTIONS

Table 1 Boson part, E_B, of the ground state energy. $E_B^{(2)}$ (MC) is the Monte-Carlo results of Ref. 1. All energies are expressed in units of Rydbergs.

Table 2 Exchange contribution to the ground state energy. All energies are expressed in units of Rydbergs.

Table 3 Comparisons of the ground state energies of the liquid (E(x)/N) and the solid phases (E^S(HA)/N: Hammerberg and Ashcroft, Ref. 4). All energies are expressed in units of Rydbergs. SC: Simple cubic; BCC: Body centered cubic; FCC: Face centered cubic.

TABLE 1

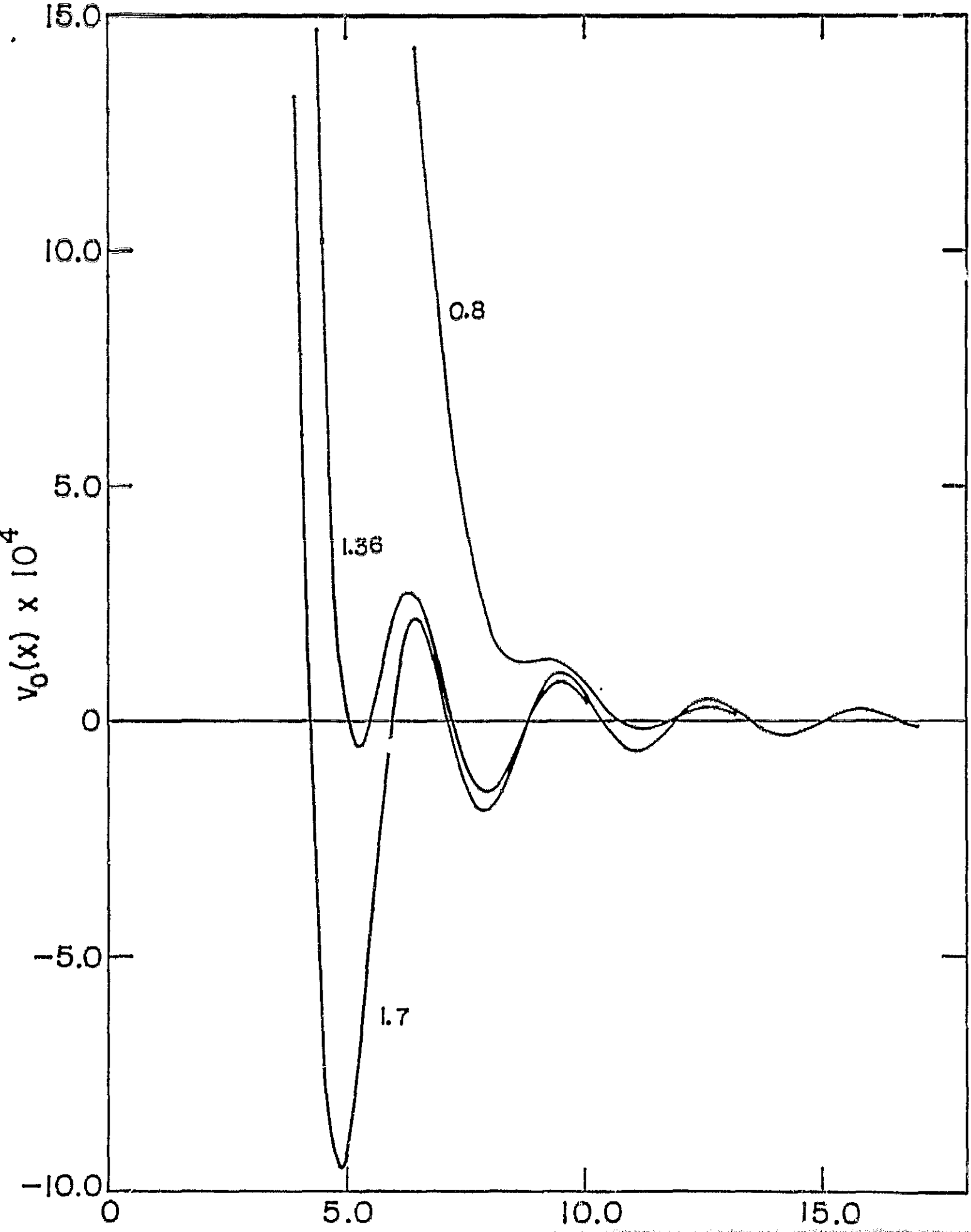
r_s	b_F	$T_B^{(2)}/N$	$P_B^{(2)}/N$	$E_B^{(2)}/N$	$E_B^{(2)}(MC)/N$	$\Delta E_B^{Ph}/N$	$E_B^{(3)}/N$	E_Ω/N
0.50	5.35	0.07406	2.76268	2.83674		-0.00158	-0.01442	0.54062
0.80	5.55	0.03195	0.76254	0.79449	0.7943	-0.00054	-0.02120	-0.86188
1.20	5.50	0.01386	0.19986	0.21372	0.2079	-0.00021	-0.02944	-1.10353
1.30	5.435	0.01143	0.14616	0.15759				
1.36	5.40	0.01026	0.12104	0.13130	0.1262	-0.00016	-0.03258	-1.10050
1.40	5.37	0.00954	0.10665	0.11619				
1.45	5.315	0.00865	0.09095	0.09960				
1.488					0.0847			
1.50	5.28	0.00794	0.07726	0.08520		-0.00012	-0.03528	-1.08394
1.55	5.225	0.00723	0.06543	0.07266				
1.60	5.175	0.00661	0.05510	0.06171	0.0592	-0.00011	-0.03718	-1.06790
1.70	5.05	0.00549	0.03824	0.04373		-0.00009	-0.03908	-1.04988
1.80	4.9	0.00452	0.02531	0.02983		-0.00008	-0.04100	-1.03074

TABLE 2

r_s	X	$E_{ex}(x)/N$
0.50	0.589	0.00263
0.80	0.579	0.00102
1.20	0.582	0.00045
1.30	0.585	0.00039
1.36	0.587	0.00035
1.40	0.588	0.00033
1.45	0.591	0.00031
1.50	0.593	0.00029
1.55	0.595	0.00027
1.60	0.598	0.00026
1.70	0.603	0.00023
1.80	0.607	0.00021

TABLE 3

r_s	$E^g(HA)/N$			$E(\infty)/N$
	SC	FCC	BCC	
0.50				3.36399
0.80				-0.08811
1.00	-0.71188	-0.71929	-0.71819	
1.20	-0.93796	-0.94019	-0.93902	-0.91901
1.25	-0.96842	-0.96961	-0.96843	
1.30	-0.99217	-0.99242	-0.99122	
1.36				-1.00159
1.50	-1.04104	-1.03818	-1.03693	-1.03385
1.60	-1.04759	-1.04345	-1.04222	-1.04322
1.65	-1.04803	-1.04338	-1.04209	
1.70				-1.04509
1.80				-1.04178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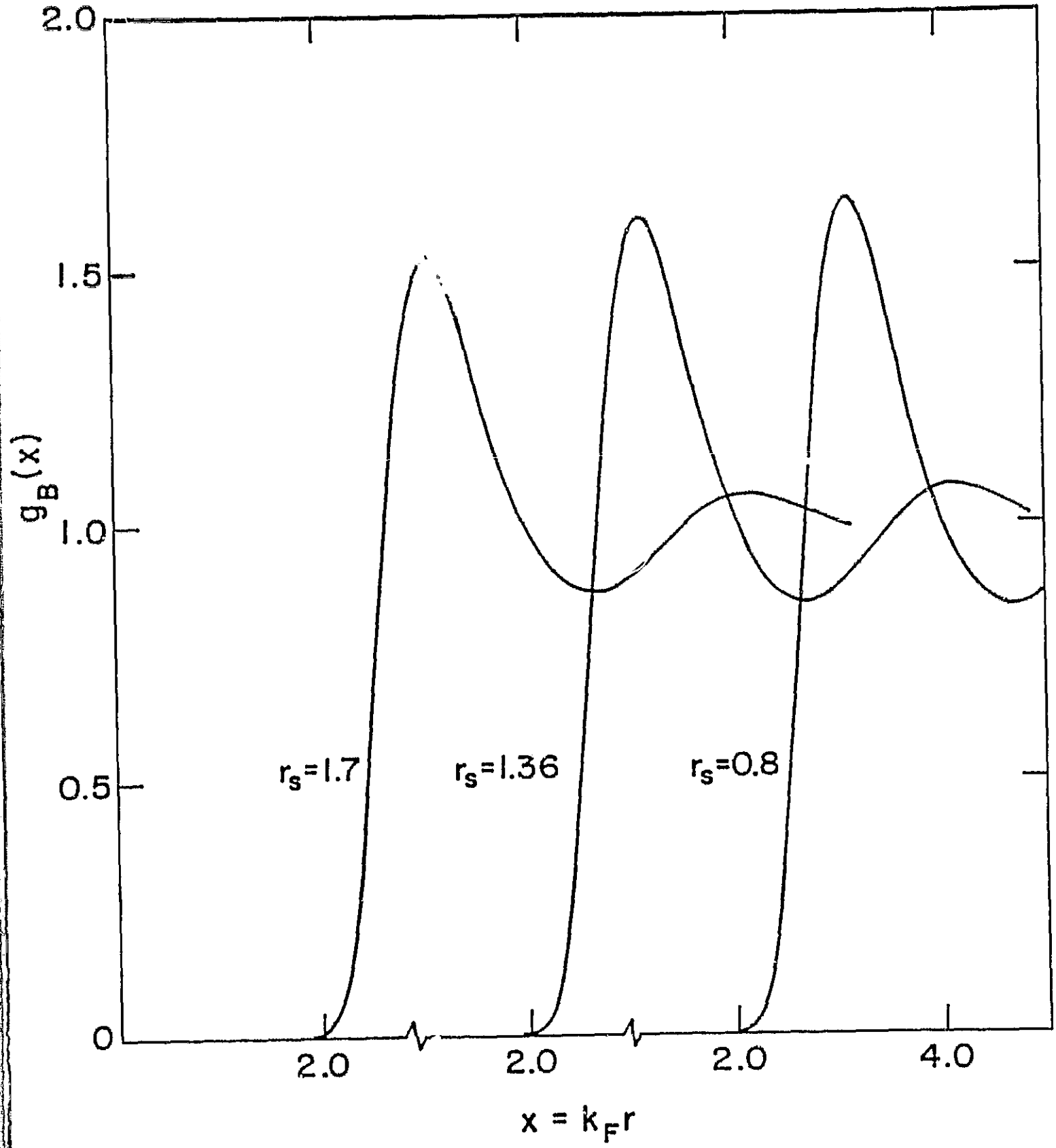
10.0
5.0
0
-5.0
-10.0
0
5.0
10.0
15.0
$v_0(x) \times 10^4$
0.8
1.36
1.7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1.5
1.0
0.5
0
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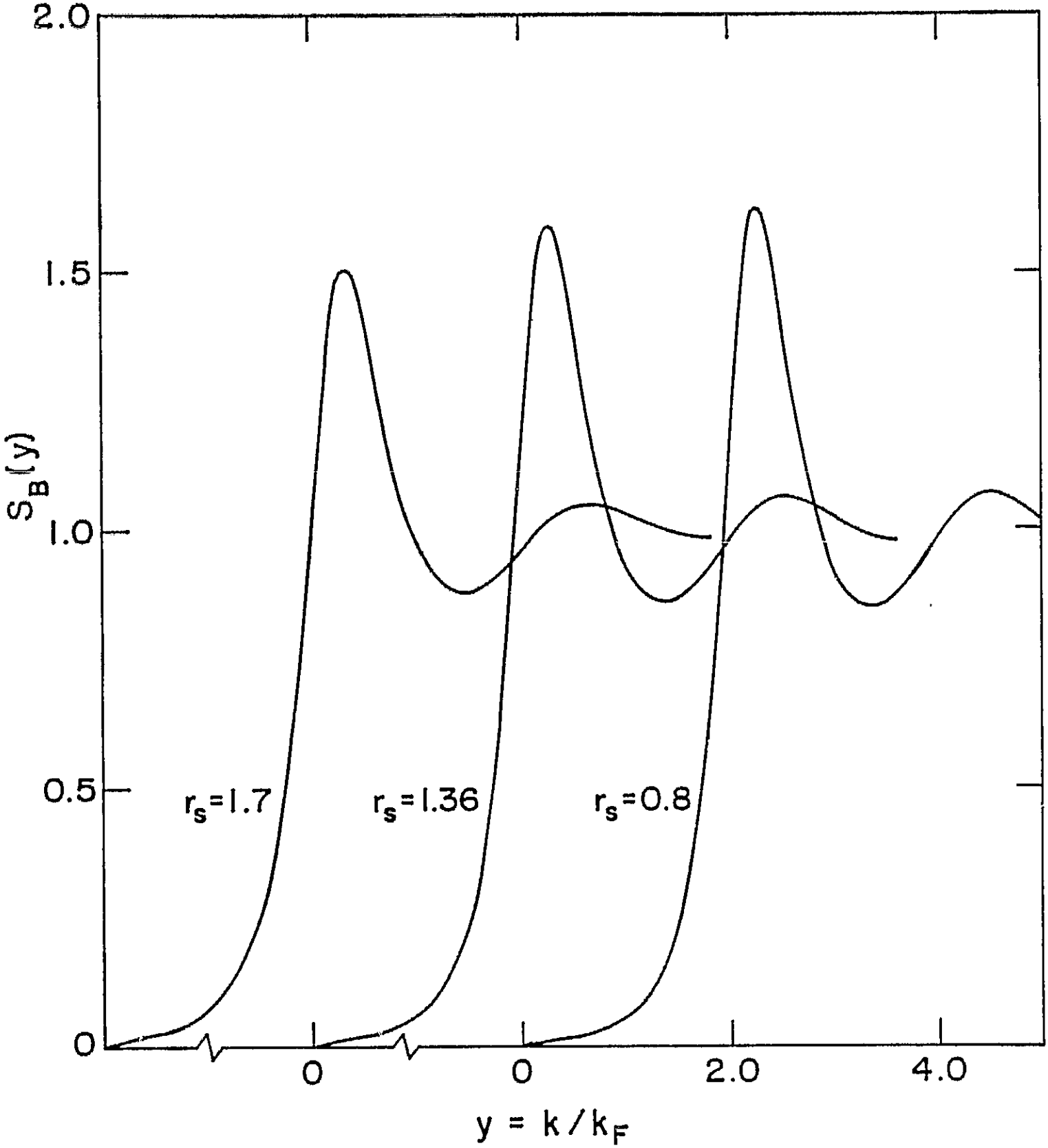
r_s=1.7
r_s=1.36
r_s=0.8
2.0
2.0
2.0
4.0
$x = k_F r$


2.0
1.5
1.0
0.5
0
$S_B(y)$
r_s=1.7
r_s=1.36
r_s=0.8
0
0
2.0
4.0
$y = k/k_F$