Theory of superconductivity based on direct electron-phonon coupling. I

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A perturbation theory is used to compute the leading terms in the difference between low-lying energy levels of metallic hydrogen. Energy levels are found which are lower than the normal state, provided that the nuclear mass is large enough, and these levels are assumed to be superconducting. The description of the superconductivity does not agree with that given by current models. The origin of the lower-energy states is a direct coupling between electrons and longitudinal long-wavelength bare phonons.

I. INTRODUCTION

Superconductivity represents a particularly difficult problem in solid-state theory because it involves the dynamics of both electrons and nuclei, and is driven by an exceptionally small energy difference from the normal state. Since the early work of Frohlich,[1] electron-phonon interaction has played a dominant role in the theory with the possible exception of the recently discovered heavy fermion superconductors. Current theory revolves around the electron-pairing model of Bardeen, Cooper, and Schrieffer[2] (BCS), where the phonons act only as intermediaries in coupling electrons. In contrast, the analysis given here is concerned with a new type of wave function and a new type of interaction which is based on direct coupling of electrons to phonons.[3] Only the case of metallic hydrogen[4] (or more correctly, a pseudometallic hydrogen with arbitrary nuclear mass) is examined, but it is believed that the interaction is general, and may lead either to a new class of superconductors, or to a modification of BCS theory. The question of whether the new interaction competes with the electron pairing or replaces it has been deferred to a later calculation. Predictions for T_c in metallic hydrogen based on current theory vary from several hundred degrees[5] to a few hundredths[6] depending on the density, lattice symmetry, and the approximations used. Values obtained here at the computed equilibrium density range from 0 to 50 K depending on the mass.

The calculation to be presented is a full many-body treatment as opposed to screened, one-particle approximations. No use is made of effective fields or dielectric constants nor is use made of the adiabatic approximation. However, only the ground state is examined. It is well known that the many-body theory can be formulated in two ways depending on whether the Hamiltonian is used in n-body configuration space or second quantized and used with the formalism of Green's functions. While the latter is now the common approach, it is useful here to use the former. A Rayleigh-Schrödinger-type perturbation expansion is made using the complete set of functions formed from Slater determinants of plane waves and bare-phonon functions.[7] The expansion leads to energy levels which depend only on fixed parameters of the system. The virtue of this approach is that no attempt is made to compute accurate expressions for the energy of a given state, but only to calculate accurate expressions for the energy difference between a pair of states. The only fundamental problems facing the calculation are questions of convergence, which are similar to those involved in other many-body calculations, and the effect of degeneracy. A basic disadvantage of the method is that the ground state is not obtained in an absolute sense, but only by comparison with other energy levels. However, this disadvantage is balanced by the relative simplicity of following energy levels in perturbation theory as opposed to following the ground state itself, as attempted in most other methods.

The new electron-phonon interaction can be interpreted as a screening by electrons of the zero-point motion of the nuclei, arising from coupling to virtual phonons and described by second-order perturbation theory. The important part of the interaction is that coming from the interaction with long-wavelength longitudinal phonons. Energy levels are found which lie below the normal state provided the nuclear mass is sufficiently heavy. If the low levels are assumed to be superconducting states, then within the accuracy provided by leading terms in the computation, the new interaction does not lead to superconductivity in ordinary metallic hydrogen but tritium would be a strong superconductor. However, the importance of the calculation is in the demonstration that direct electron-phonon coupling cannot be ignored *a priori* as a cause of superconductivity.

II. OUTLINE OF THE PERTURBATION CALCULATION

A. Perturbation approach

Because of the small observed energy difference between the normal and superconducting states, an attempt to establish a theory of superconductivity through *ad hoc* energy calculations is not likely to succeed, as was pointed out by Bardeen and Schrieffer.[8] This difficulty is overcome in the present analysis by the choice of the perturbation theory, which is developed in the configuration space of N electrons and N nuclei, and designed to compute sta-

tionary energy-level differences.[9] The unperturbed Hamiltonian consists of the kinetic energy of electrons and the harmonic vibrations of nuclei in a uniform background charge. Each unperturbed wave function is the product of a Slater determinant with a configuration of $3N$ oscillator functions. The wave functions are denoted by $k\kappa$ where k indicates a particular set of wave vectors $\mathbf{k}$ which form the Slater determinant (with spin implied), and κ denotes a set of phonon wave vectors $\boldsymbol{\kappa}$ (with polarizations implied). Since a well-defined complete set of wave functions is demanded, the phonons considered are bare phonons.

The perturbation series leads to an expansion in terms of two parameters: the Wigner-Seitz parameter r_s and the ratio m/M of electron to nuclear mass.[10] It is assumed that the leading terms in the energy difference between two low-lying states can be computed by subtracting the leading terms in a pair of perturbation expansions. No special accuracy is required of the individual energies, it is only necessary that the leading terms in each series are highly accurate. The perturbation expansion can be broken up into two series, one which applies for a fixed lattice, the other giving the effects of lattice dynamics. It is found that the series for the lattice dynamics must be carried to a higher order in the perturbation expansion than the fixed-lattice series.

In the parameter expansion for the fixed lattice the first two terms are the familiar kinetic and exchange energies of an electron gas, proportional to r_s^{-2} and r_s^{-1}, respectively. The next terms in the fixed-lattice expansion are the electron-gas correlation energy, $0(\text{const}, \ln r_s)$, plus a constant term arising from the periodic potential. The fixed lattice also introduces another large term of order r_s^{-1}, but this term is the same for all states. The series for the lattice dynamics starts with a term for the zero-point motion, which is the same for both states, assuming that the two states investigated are both taken to have no phonons. Thus, the first relevant contribution of the nuclear displacements is obtained in the second-order perturbation energy. It can be shown that in the limit of wave functions only slightly different from the normal state, the second-order electron-phonon energy can introduce a small Coulomb-like term, and therefore this energy should be considered together with the free-electron exchange energy, i.e., second-order terms in the second series can give expressions similar to first-order terms in the first series. As a practical matter, the perturbation expansion for the lattice dynamics is broken off with second order, since starting with third order the terms begin to proliferate, and since divergences begin to appear of the type which arise in second order for the electron-electron interaction. Presumably, such divergence can be removed by summing a suitable sub-series from third order to infinity following the well-known treatment of the electron-electron interaction that leads to the correlation energy.[11,12]

Since the perturbation series for the lattice dynamics is cut off at second order, consistency demands that the series for the fixed lattice must be cut off at first order, and, consequently, the energy difference between two energy levels is examined in the approximation

$$\Delta E = \Delta\epsilon_k + \Delta E_k^{\text{ex}} + \Delta E_{k\kappa}^{(2)\text{e-ph}} , \tag{1}$$

where ϵ_k is the unperturbed electron energy, i.e., the kinetic energy of the plane waves, E^{ex} is the free-electron exchange energy, and $E^{(2)\text{e-ph}}$ the second-order electron-phonon energy. The energy difference is computed with reference to the (spherical) normal state, defined as the state arising from an electronic Fermi sphere of wave vectors.[13] In summary, Eq. (1) corresponds to the first two terms for the fixed lattice and the lowest-order contribution of the lattice dynamics. It must be assumed that the series converges rapidly enough near the equilibrium density so that these terms give a good approximation for the total energy difference.

B. Degeneracy

The perturbed states will be labeled by $k\kappa$ corresponding to the unperturbed configurations. More correctly, in all but the normal state (which is nondegenerate) degenerate perturbation theory should be used, with the perturbed state labeled by a linear combination of degenerate unperturbed states. The present approximation corresponds to replacing the linear combination with the single configuration at its center. The approximation is based on the following arguments. (1) In the perturbation theory for a large many-body system exact degeneracy plays a much smaller role than in a molecular system, due to the large amount of near degeneracy and the fact that sums are replaced by integrals. (2) Degeneracy (nonaccidental) exists only for two unperturbed states with the same phonon configuration. For the energy of the term of principal interest, i.e., the electron-phonon interaction, matrix elements between degenerate states do not appear. It is possible that degeneracy will become more important as the expansion is carried further, and it offers one possibility for introducing Cooper pairs.

C. Change in ground-state symmetry

Since the individual energy levels rather than the ground-state wave function itself are followed in the perturbation theory, a discontinuous change in the wave function, or, for example, a change in symmetry of the ground state with the application of a magnetic field, occurs in a way which is simple to calculate. The perturbation does not appreciably change the wave functions for the levels, but rather it produces a crossover of energy levels, leaving a new unperturbed function as the new approximation for the ground-state wave function.

III. CALCULATION OF THE ELECTRON-PHONON ENERGY

For small values of m/r_sM the second-order electron-phonon energy in Rydbergs is given by[9]

$$E_{k\kappa}^{(2)\text{e-ph}} = -\frac{N}{\sqrt{3}\pi^4}\left[\frac{9\pi}{4}\right]^{2/3}\frac{1}{r_s}\left[\frac{r_s m}{M}\right]^{1/2}\sum_s \int d\mathbf{p}\int d\mathbf{p}'\, n(\mathbf{p})[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}',s) , \tag{2}$$

where N is the number of electrons, $n(\mathbf{p})$ $[=n_k(\mathbf{p})]$ is the average occupation of one-electron states given by the unperturbed wave function for each spin near a point in p space, and $\mathbf{p}=\mathbf{k}/k_F$ is a reduced wave vector, with k_F the Fermi radius. $F(\mathbf{p},\mathbf{p}',s)$ is given by

$$F(\mathbf{p},\mathbf{p}',s)=\frac{\frac{\omega(01)}{\omega(\kappa s)}\,|\,[(\mathbf{p}'-\mathbf{p})/|\,\mathbf{p}'-\mathbf{p}\,|\,]\cdot\mathbf{v}(\kappa,s)\,|^2}{|\,\mathbf{p}'-\mathbf{p}\,|^2[(p')^2-p^2+2\sqrt{3}(4/9\pi)^{2/3}(r_s m/M)^{1/2}\omega(\kappa,s)/\omega(01)]}\ , \tag{3}$$

where $\omega(\kappa s)$ is the phonon frequency for wave vector κ and polarization s, $\mathbf{v}(\kappa,s)$ is the polarization vector, and s is summed over 1,2,3, with 1 the nearly longitudinal mode. The phonon vector is given by

$$\kappa=k_F(\mathbf{p}'-\mathbf{p})-\mathbf{K}\ , \tag{4}$$

with $\mathbf{K}$ the reciprocal-lattice vector which for each value of $\mathbf{p}'-\mathbf{p}$ puts κ in the first Brillouin zone. The expression (2) is observed to be a function $(1/r_s)f(r_s m/M)$, which is to be evaluated for $r_s m/M \ll 1$, since $r_s \gtrsim 1$ and $m/r_s M \ll 1$.

Each Slater determinant specifies a distribution $n(\mathbf{p})$ and leads to a perturbed state of the system. Only states having distributions $n(\mathbf{p})$ with spherical symmetry are considered, and the state which arises from a Fermi sphere, $n(\mathbf{p})=1$ for $p<1$ and $n(\mathbf{p})=0$ for $p>1$ [labeled $n_0(\mathbf{p})$] serves as the normal or reference state. If p_2 is the maximum value of p for which $n(\mathbf{p})$ is nonvanishing and p_1 the smallest value of p for nonvanishing $1-n(\mathbf{p})$, then

$$\int d\mathbf{p}\int d\mathbf{p}'\,n(\mathbf{p})[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}',s) = \int_0^{p_2} d\mathbf{p}\int_{p_1}^{\infty} d\mathbf{p}'\,n(\mathbf{p})[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}'s) \tag{5}$$

and one can write

$$\int_0^{p_2} d\mathbf{p}\int_{p_1}^{\infty} d\mathbf{p}' = \int_0^{p_1} d\mathbf{p}\int_{p_1}^{\infty} d\mathbf{p}' + \int_{p_1}^{p_2} d\mathbf{p}\int_{p_2}^{\infty} d\mathbf{p}' + \int_{p_1}^{p_2} d\mathbf{p}\int_{p_1}^{p_2} d\mathbf{p}'\ . \tag{6}$$

In the first two terms on the right in (6) $p'>p$, while the third term describes a region of overlap, which vanishes for the normal state. Anticipating the form to be assumed for the superconducting ground state, one may concentrate on the overlap region of the integral. This follows because for this wave function it will be found (Appendix A) that the terms for $p'>p$ are nearly the same as for the normal-state wave function, and, therefore, these terms represent an energy of the normal state.

For all low-lying states, p_2 will be only slightly greater than unity and p_1 only slightly less than unity. Consider the integral over the angular part of $\mathbf{p}'$ in Eq. (5) under these conditions, where

$$\int_{p_1}^{p_2} d\mathbf{p}' = \int_{p_1}^{p_2} dp'(p')^2\int_0^{2\pi} d\phi\int_{-1}^{1} d(\cos\theta) \tag{7}$$

with θ the angle between $\mathbf{p}$ and $\mathbf{p}'$. The integral over $\cos\theta$ can be written as

$$\int_{-1}^{1} d(\cos\theta)F(\mathbf{p},\mathbf{p}',s)=\int_{-1}^{1} d(\cos\theta)F(\mathbf{p},\mathbf{p}',s) \quad \text{with } p'\approx 1 \text{ and } p\approx 1\ , \tag{8}$$

which is dominated by the factor $|\,\mathbf{p}'-\mathbf{p}\,|^{-2}=[(p')^2+p^2-2pp'\cos\theta]^{-1}$ in expression (3) for F. It is easily shown that

$$\lim_{p\to 1}\lim_{p'\to 1}\frac{pp'}{[(p')^2+p^2-2pp'\cos\theta]\ln[\,|p'-p|/(p'+p)]}=-\delta(1-\cos\theta)\ , \tag{9}$$

where $\delta(1-\cos\theta)$ is a Dirac delta function for the range of $\cos\theta$, and therefore as a reasonably good approximation $pp'|\,\mathbf{p}'-\mathbf{p}\,|^{-2}$ can be replaced by $-\ln[\,|p'-p|/(p'+p)]\delta(1-\cos\theta)$ in (8). But for p and p' nearly equal to unity and $\cos\theta=1$, it follows that $\mathbf{p}'\to\mathbf{p}$ and $\kappa=k_F(\mathbf{p}'-\mathbf{p})\to 0$ in Eq. (4). Therefore, the integral (8) approximately vanishes for the modes that become transverse as $\kappa\to 0$, and

$$pp'\int_{-1}^{1} d(\cos\theta)F(\mathbf{p},\mathbf{p}',1)\approx -\frac{\ln|\,(p'-p)/(p'+p)\,|}{(p')^2-p^2+2\sqrt{3}(4/9\pi)^{2/3}(r_s m/M)^{1/2}}\ . \tag{10}$$

The integral over ϕ and the integral over the angles of $\mathbf{p}$ multiply this result by a factor of $8\pi^2$, and

$$E_{k\kappa}^{(2)\text{e-ph}}\approx\frac{N8}{\sqrt{3}\pi^2}\left[\frac{9\pi}{4}\right]^{2/3}\frac{1}{r_s}\left[\frac{r_s m}{M}\right]^{1/2}\int_{p_1}^{p_2} dp\,p\int_{p_1}^{p_2} dp'\,p'\frac{n(p)[1-n(p')]\ln|\,(p'-p)/(p'+p)\,|}{(p')^2-p^2+\zeta}+\text{ terms for } p'>p\ , \tag{11}$$

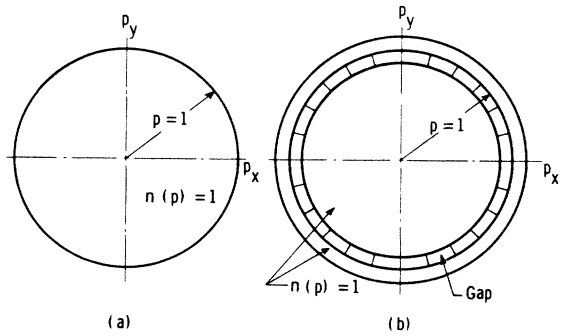

FIG. 1. Surfaces enclosing the occupied one-electron states of the zeroth-order wave functions for (a) the normal state and (b) the Fröhlich state.

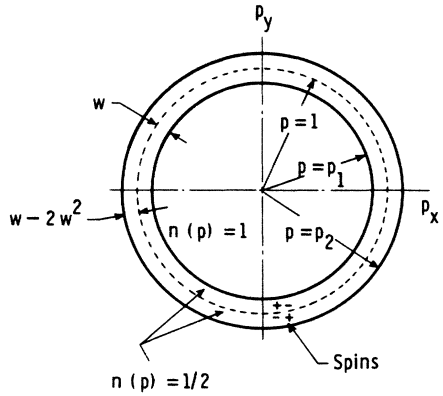

FIG. 2. Zeroth-order superconducting wave function. Inside the inner radius p_1, one-electron states are doubly occupied [$n(p)=1$ for each spin]. Between p_2 and p_1 states are singly occupied in an antiferromagnetic arrangement in p space. The average occupation for each spin is $n(p)=\frac{1}{2}$. p is defined by k/k_F.

where

$$\zeta=2\sqrt{3}\left[\frac{4}{9\pi}\right]^{2/3}\left[\frac{r_s m}{M}\right]^{1/2}. \tag{12}$$

ζ can be shown to be the ratio of the longitudinal long-wavelength phonon energy to the free-electron Fermi energy of the normal state. Thus the value of ζ is roughly the same as Migdal's expansion parameter,[14,15] however, it is observed from (11) that the energy does not have a power-series expansion in ζ.

IV. THE WAVE FUNCTION

Figure 1(a) describes the unperturbed wave function which leads to the normal state, consisting of a Slater determinant with wave vectors bounded by a spherical Fermi surface. The possibility of lowering the energy as a result of a different distribution was recognized by Fröhlich who considered a state with an energy gap as shown in Fig. 1(b). However, as discussed in Sec. X this calculation was made with approximations which are not justified in the present analysis. A rigorous proof as to what constitutes the absolute ground state is difficult to give, and will not be attempted, since it is regarded as sufficient to show that superconducting energy levels can exist which lie lower than the normal state. The assumed form of the ground state is given by the configuration $n(\mathbf{p})=\frac{1}{2}$ between the limits p_2 and p_1, with $n(\mathbf{p})=1$ for $p<p_1$ and $n(\mathbf{p})=0$ for $p>p_2$. In the true wave function $n(\mathbf{p})$ is probably a continuous function, but the step function is used for simplicity. Thus the electronic configuration is described by two surfaces as shown in Fig. 2. The first surface gives the limit of double occupancy of one-electron states, while the region between the two surfaces corresponds to single occupancy. Since one expects to find as many plus spins as minus spins in any volume element, the region of single occupancy can be described as an "antiferromagnetic" arrangement in $\mathbf{k}$ space as indicated in the figure. The details of the spin arrangement within a small region are unimportant since only the average occupancy near a point enters the perturbed energy expression. The reasoning behind the choice of the new wave function is as follows: In Eq. (11) the integrand becomes large for $p'\to p$, in which case $n(p)[1-n(p')]$ approaches $n(p)-n^2(p)$, which is maximized by $n(p)=\frac{1}{2}$.

V. ELECTRON-PHONON ENERGY DIFFERENCE

In order to keep the number of electrons fixed it is necessary for

$$\int_{p_1}^{p_2}[n(\mathbf{p})-n_0(\mathbf{p})]d\mathbf{p}=\int_{p_1}^{p_2}n(\mathbf{p})d\mathbf{p}-\int_{p_1}^{1}d\mathbf{p}=0\,. \tag{13}$$

For $n(\mathbf{p})=\frac{1}{2}$ this is accomplished approximately by

$$p_1=1-w\,, \tag{14}$$

$$p_2\approx 1+w-2w^2\,, \tag{15}$$

where $w=1-p_1$ is shown in Fig. 2. With the results of Appendix A, which show that the terms for $p'>p$ in Eq. (11) represent the normal state energy it follows that

$$\frac{\Delta E^{(2)e\text{-ph}}}{N}\approx\frac{1}{3\pi^2}\left[\frac{9\pi}{4}\right]^{4/3}\frac{\zeta}{r_s}\int_{1-w}^{1+w-2w^2}dp\,p\int_{1-w}^{1+w-2w^2}dp'\frac{p'\ln|(p'-p)/(p'+p)|}{(p')^2-p^2+\zeta}\,, \tag{16}$$

where both ζ and w are assumed to be small compared with unity. By neglecting w^2 in the upper limit, setting $p=p'=1$ except where the two are subtracted, and using the transformations $p=1+wx$, $p'=1+wx'$ one obtains

$$\frac{\Delta E^{(2)e\text{-ph}}}{N}\approx\frac{1}{3\pi^2}\left[\frac{9\pi}{4}\right]^{4/3}\frac{w^2}{r_s}\int_{-1}^{1}dx\int_{-1}^{1}dx'\frac{[\ln(w/2)+\ln|x'-x|]}{\gamma(x'-x)+1}\,, \tag{17}$$

where $\gamma=2w/\zeta$. Integration of the $\ln w/2$ term can be performed and the expression arranged to read

$$\frac{\Delta E^{(2)e\text{-ph}}}{N}\approx\frac{4}{3\pi^2}\left[\frac{9\pi}{4}\right]^{4/3}\frac{w^2}{r_s}[g_1(\gamma)\ln(w/2)+g_2(\gamma)]\,, \tag{18}$$

where

$$g_1(\gamma)=\tfrac{1}{4}\int_{-1}^{1}dx\int_{-1}^{1}dx'\frac{1}{\gamma(x'-x)+1}$$
$$=\frac{1}{4\gamma^2}[(1+2\gamma)\ln(1+2\gamma)$$
$$+(1-2\gamma)\ln|1-2\gamma|] \tag{19}$$

and

$$g_2(\gamma)=\tfrac{1}{4}\int_{-1}^{1}dx\int_{-1}^{1}dx'\frac{\ln|x'-x|}{\gamma(x'-x)+1}\,. \tag{20}$$

Both g_1 and g_2 are well-behaved functions with no singularities. $g_1(0)=1$, $g_2(0)=\ln 2-\frac{3}{2}$; while as $\gamma\to\infty$ both functions approach zero, with a slower approach for g_2, which is equal to $-\pi^2/4\gamma$ in this limit. It follows that (18) ranges from an expression completely independent of nuclear mass to a value proportional to w times $(m/r_sM)^{1/2}$, which is the principal dependence of the normal-state electron-phonon energy. $g_1(\gamma)$ is positive and leads to a negative contribution to the energy because of the factor $\ln w$. $g_1(\gamma)-1$ is plotted in Fig. 3 as $f_1(\gamma)$, showing a spike near $\gamma=0.54$.

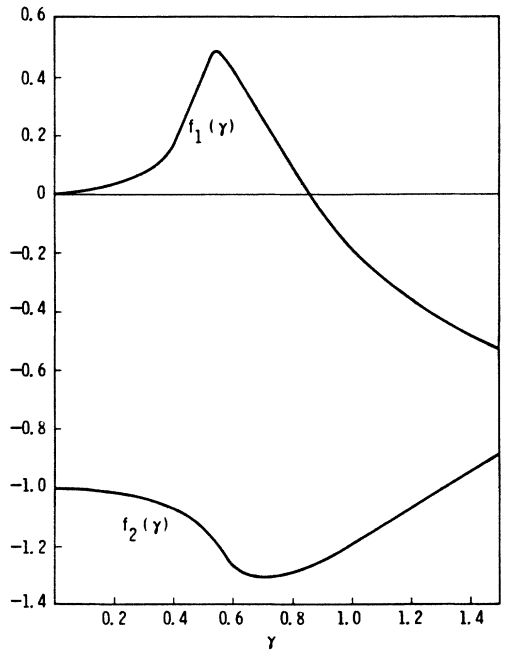

FIG. 3. Plot of $f_1(\gamma)$ and $f_2(\gamma)$. For values of γ large compared with unity $f_1(\gamma)\to-1$ and $f_2(\gamma)\to\frac{1}{2}-2.47/\gamma$.

VI. THE CHANGE IN KINETIC AND EXCHANGE ENERGY

The difference in unperturbed energy between an arbitrary state with spherical symmetry and the normal state is

$$\frac{\Delta\varepsilon}{N}=\frac{1}{3\pi^2}\left[\frac{9\pi}{4}\right]^{5/3}\frac{1}{r_s^2}\int d\mathbf{p}\,p^2[n(\mathbf{p})-n_0(\mathbf{p})]=-\frac{2}{3\pi}\left[\frac{9\pi}{4}\right]^{5/3}\frac{1}{r_s^2}\left[\int_{1-w}^{1}p^4dp-\int_{1}^{1+w-2w^2}p^4dp\right] \tag{21}$$

with the result

$$\frac{\Delta\varepsilon}{N}=\frac{4}{3\pi}\left[\frac{9\pi}{4}\right]^{5/3}\frac{w^2}{r_s^2}+O(w^3)\,. \tag{22}$$

The exchange energy difference is

$$\frac{\Delta E^{\text{ex}}}{N}=-\frac{4}{3\pi^2}\left[\frac{9\pi}{4}\right]^{4/3}\frac{1}{r_s}\int dp\,p\int dp'\,p'\ln\left|\frac{p'+p}{p'-p}\right|[n(\mathbf{p})n(\mathbf{p}')-n_0(\mathbf{p})n_0(\mathbf{p}')]\,. \tag{23}$$

The integrals can be evaluated to give

$$\frac{\Delta E^{\text{ex}}}{N}=-\frac{4}{3\pi^2}\left[\frac{9\pi}{4}\right]^{4/3}\frac{1}{r_s}w^2(\ln w-\tfrac{1}{2})+O(w^3)\,. \tag{24}$$

VII. CONDITION FOR SUPERCONDUCTIVITY

Collecting the results of (18), (22), and (24) gives the following expression for the change in energy per electron from the normal state

$$\frac{\Delta E}{N}=\frac{11}{r_s^2}w^2-\frac{1.83}{r_s}w^2(\ln w-\tfrac{1}{2})$$
$$+\frac{1.83}{r_s}w^2[g_1(\gamma)\ln(w/2)+g_2(\gamma)]\,, \tag{25}$$

where

$$\zeta=0.94\left[\frac{r_sm}{M}\right]^{1/2}, \tag{26}$$

$$\gamma=\frac{2w}{\zeta}=2.13\left[\frac{M}{r_sm}\right]^{1/2}w\,. \tag{27}$$

For small w it is not obvious that the expansion (25) is converging, since the exchange and electron-phonon energies can be larger than the lower-order kinetic energy term. But this occurs only because pair interactions introduce an extra factor $\ln w$ not present in a single particle term. It is expected (though not proved) that the succeeding higher-order terms will rapidly converge for $r_s \lesssim 1.6$, as they seem to do for the normal-state energy expansion.[9]

It is observed that the second-order perturbation term in (25) is similar in form to the exchange term as γ approaches zero. Since $g_1(0)=1$, the $\ln w$ terms cancel for small γ, but as γ increases the electron-phonon energy begins to dominate. Let $f_1(\gamma)$ and $f_2(\gamma)$ be defined by

$$f_1(\gamma)=g_1(\gamma)-1 , \tag{28}$$

$$f_2(\gamma)=g_2(\gamma)-g_1(\gamma)\ln 2+\tfrac{1}{2} . \tag{29}$$

Then

$$\frac{\Delta E}{N}=\frac{11}{r_s^2}w^2+\frac{1.83}{r_s}w^2[f_1(\gamma)\ln w+f_2(\gamma)] , \tag{30}$$

or in terms of γ

$$\frac{\Delta E}{N}=0.40\frac{m}{M}\gamma^2\left[\frac{6}{r_s}+f_1(\gamma)\ln(\zeta\gamma/2)+f_2(\gamma)\right] . \tag{31}$$

The value of ΔE will be examined at the equilibrium density $r_s \approx 1.6$. By substituting $r_s=1.6$ and introducing the atomic mass A_m one can write Eq. (31) as

$$\frac{\Delta E}{N}=-2.19\times 10^{-4}\frac{\gamma^2}{A_m}\{f_1(\gamma)[4.276+0.5\ln(A_m/\gamma^2)] -3.75-f_2(\gamma)\} . \tag{32}$$

A plot of the functions $f_1(\gamma)$ and $f_2(\gamma)$ is shown in Fig. 3. Since $f_2(\gamma)$ is relatively constant, the point of minimum energy is determined by $f_1(\gamma)$. Thus ΔE is a minimum either at $\gamma=0$, or near the peak in f_1 which occurs at $\gamma=0.54$, depending on the sign of the expression within the brackets in Eq. (32). In the first case, the ground state of the system is the normal state, while in the second case a new type of ground state results, as described by Fig. 2 with $w=0.27\zeta$. While it remains to be demonstrated, this state is presumed to be a superconducting state. With $\gamma=0.54$ the energy at the equilibrium density finally becomes

$$\frac{\Delta E}{N}=-1.53\times 10^{-5}\frac{1}{A_m}(\ln A_m-0.88) , \tag{33}$$

although the constant 0.88 is not regarded as having significance beyond its order of magnitude (see Sec. IX). Nevertheless, Eq. (33) implies that a sufficient condition for superconductivity is

$$\ln A_m \gtrsim 1 . \tag{34}$$

The condition given by (34) is not satisfied for a proton mass $A_m=1$ but is satisfied for tritium, which leads to an energy difference of -1.1×10^{-6} Ry as given by (33). The maximum energy difference given by (33) is -2.3×10^{-6} which occurs for $A_m=6.54$.

VIII. THE CRITICAL FIELD AND TEMPERATURE

The thermodynamic critical magnetic field H_c is defined as

$$\frac{H_c^2}{8\pi}V=-\Delta E\frac{e^2}{2a_B} , \tag{35}$$

where V is the volume and $e^2/2a_B$ the Rydberg unit, with e the electronic charge and a_B the Bohr radius. Since $V=4\pi r_s^3 a_B^3 N/3$ it follows that

$$H_c=\frac{2.97\times 10^7}{r_s^{3/2}}\left[-\frac{\Delta E}{N}\right]^{1/2} . \tag{36}$$

For $A_m=3$ one obtains the relatively large value $H_c=1.54\times 10^4$ Oe. The isotope effect ($H_c \sim A_m^{-1/2}$) does not begin to hold until A_m gets in the range of 100.

Although the critical temperature cannot be accurately deduced from the ground state, an estimate can be made through the use of an individual particle approximation. If the number of **p** vectors (multiplied by two for spin) between $p=1$ and $p=p_1$ in the normal Fermi sphere is regarded as the number of electrons N^* involved in the superconducting interaction, then

$$\frac{N^*}{N}=3w . \tag{37}$$

By assigning all the energy difference with the normal state to these electrons, and assuming the energy divided by N^* is the order of $k_B T_c$, where k_B is the Boltzman constant and T_c the critical temperature, one obtains

$$k_B T_c \sim -\frac{\Delta E}{N^*}\frac{e^2}{2a_B} , \tag{38}$$

or

$$T_c \sim -\frac{\Delta E}{N}\frac{1}{w}\times 5.3\times 10^4 \sim -\frac{\Delta E}{N}\times 8.9\times 10^6\left[\frac{A_m}{r_s}\right]^{1/2} . \tag{39}$$

For $A_m=3$ the value obtained is $T_c \sim 14$ K. The maximum value of the right-hand side of (39) for $r_s=1.6$ is 51 which occurs for $A_m=17.7$.

IX. THE EFFECT OF HIGHER-ORDER TERMS

An exact catalog of all higher-order terms in the parameter expansion would include a large number of terms depending on fractional and integral powers of $(m/r_s M)$, which arise, principally, from anharmonic effects and higher approximations for the matrix elements of $H^{e\text{-ph}}$. The next-order terms believed to be most important in the energy difference expansion are 0(const., $\ln r_s$) coming from (a) electron correlation energy, (b) a term from the motion of electrons in a fixed lattice, and (c) electron-phonon coupling from third-order perturbations. Only the part (b), which is a one-particle term and should be compared with the kinetic energy, is easy to calculate, and this part is found to be less than 5% of the r_s^{-2} term in (25), and of opposite sign. One way to estimate the effect

of (a) is to assume that the convergence of the ΔE expansion is similar to the convergence for the normal-state energy. At the equilibrium density the correlation energy terms in the normal-state energy represent 8% of the zeroth-order kinetic energy, and 12% of the exchange energy. Thus the higher-order terms in ΔE are unlikely to appreciably change the coefficient of $\ln A_m$ in Eq. (33), but since the constant -0.88 results from a near cancellation at the equilibrium density of two terms an order of magnitude larger, this value may be changed considerably. Assume, for example, that the higher-order terms of interest at $r_s=1.6$ are positive and equal to 8% of the kinetic energy $11w^2/r_s^2$ in Eq. (25). Then in (33) the constant -0.88 will be changed to -2.1. The result still leads to strong superconductivity, but a larger atomic mass is required.

In a different context several authors, including Caron[5] and Whitmore, Carbotte, and Shukla[6] have pointed out that higher-order corrections to the screening are important for the stability of metallic hydrogen, but this point is bypassed in the present analysis.

X. COMPARISON WITH OTHER THEORIES

In the BCS model of superconductivity direct electron-phonon coupling is neglected in favor of a phonon-mediated indirect coupling between electrons, whereas the opposite is assumed here. In the present formalism processes involving other electrons arise only in higher-order perturbations, where, for example, electron-electron matrix elements mix with electron-phonon elements. These terms have not yet been investigated, but it is argued that they are smaller than the second-order terms. As noted in Sec. II B it is possible that an exact treatment of degeneracy will also lead to an indirect coupling.

The present approach represents an attempt to derive the energy for a simple system from the exact Coulomb interactions, with no arbitrary constants. Although it has been argued in the past[16] that perturbation theory breaks down when applied in second-order to electron-phonon terms, this objection seems to be based on one-particle approximations and the effects of acoustic phonons.[7] The many-body calculation given here shows the objection to be invalid.

The present theory has a formal similarity to Fröhlich's first theory,[1] which was later abandoned in favor of an alternate approach.[17] In Fröhlich's first attempt to construct a theory, the scattering of free electrons by phonons was considered, and second-order perturbation theory was used to obtain the energy in terms of $n(\mathbf{p})[1-n(\mathbf{p}')]$. The expression obtained had the same form as the many-body result derived here, except that Fröhlich's interest was in acoustic (screened) phonons (which lead to different results). Fröhlich then concluded that the term $n(\mathbf{p})$ could be deemphasized compared with the term $n(\mathbf{p})n(\mathbf{p}')$, and this allowed a transformation to be performed on the energy denominator to a more symmetric form. Essentially the same form was used by Bardeen, Cooper, and Schrieffer.[2] But in Appendix B it is shown that in the context of the present analysis Fröhlich's assumption is not correct. The full expression $n(\mathbf{p})-n(\mathbf{p})n(\mathbf{p}')$ has been retained here, and it is this form which suggests that the ground state is given by $n(\mathbf{p})=\frac{1}{2}$ near the Fermi surface. The wave function leads to the result that the interaction of interest comes exclusively from the region of $\mathbf{p}$ and $\mathbf{p}'$ space where occupied and unoccupied one-electron states coexist. To good approximation only longitudinal phonons interact with electrons in this region, whereas in BCS theory transverse modes dominate the interaction.

A brief comparison of the present approach with other theories, such as "strong-coupling" theory[15] is given below. Strong-coupling theory is understood to imply a generalization of the BCS model based on a Green's-function expansion and damped quasiparticle excitations; some discussion of the theory has already been given in Sec. III. In the present perturbation expansion no assumptions are made concerning weak or strong coupling, but it is found that the electron-phonon energy is small, and depends upon a small parameter ζ which is similar to the parameter used by Migdal as an expansion parameter. However, in general, it was noted in Sec. III that an expansion of the energy in powers of ζ is not allowed. A further criticism may be noted as follows: it is an axiom of strong-coupling theory[18] that the superconducting state can be obtained from measurements on the normal states, but considering the fact that the two types of states are orthogonal, the arguments behind this assumption are not obvious. For example, measurements on the normal state tend to involve real phonons, and most electron-phonon theories of superconductivity reduce to approximations where electrons interact with real phonons; whereas in the perturbation expansion they interact with virtual phonons (no real phonons exist in the ground state). Virtual phonons are bare, and in a qualitative sense differ from real screened phonons only for the long-wavelength longitudinal modes. But these are just the phonons which lead to the new coupling.

XI. EXCITED STATES

Two types of electronic excitations are expected for the wave function of Fig. 2. The low-lying excited states correspond to redistributing the electrons in the half-occupied region, but these states are superconducting. To obtain a normal electron, an energy the order of $|\Delta E|/N^*$ is first required to lift the electron out of its energy well in the half-filled region. Thus at low temperatures an energy gap exists between the ground state and the normal excitations, but superconducting states exist within the gap. In a qualitative sense the latter may be expected to (a) introduce a temperature dependence in the effective gap between normal and superconducting states as a result of the thermal population of higher-energy superconducting levels and (b) to introduce a term in the specific heat which is proportional to some power of T, in addition to the usual exponential term in $1/T$ produced at low temperatures by the energy gap. A detailed investigation of the thermal properties is beyond the scope of the present analysis.

XII. EXTENSION OF THE THEORY TO OTHER METALS

It should not be expected that the results for metallic hydrogen can be directly applied to other metals because (1) the electron density of other metals is much lower, (2) the correct Fermi surface should be used for the normal state, as opposed to a Fermi sphere (results of Min, Jansen, and Freeman[19] indicate that even in metallic hydrogen the Fermi surface deviates considerably from a sphere for hcp and sc lattices), and (3) for a large number of electrons per atom one must abandon all hope for an exact series expansion, inasmuch as some type of ion-core model must be used. Nevertheless, for other metals the principle of the calculation remains the same: The total energy may be divided into an electronic part which applies for a fixed perfect lattice, and a second smaller part which results from lattice dynamics when the nuclei are no longer held fixed. In going from the normal state to the superconducting state, the first part is expected to increase, with the second decreasing. The ground state is superconducting if the decrease in the energy associated with the lattice dynamics is greater than the increase in the fixed-lattice energy. The results for metallic hydrogen indicate that Coulomb correlation is relatively unimportant, and therefore as a first attempt, the following approach suggests itself. One can compute the fixed-lattice energy in terms of a one-electron approximation, where the one-electron states are doubly occupied, and the Fermi surface is that which leads to lowest total normal-state energy. The results for metallic hydrogen then indicate that the energy of the lattice dynamics will be lowered if the one-electron states near the Fermi surface are taken to be singly occupied, and this may be used to represent the superconducting wave function. The slight difference in fixed-lattice energy between the two states can be computed because of exact cancellations which occur in terms off the Fermi surface. The extent of the single occupancy is determined by that which maximizes the total energy difference between the two states. The difference in energy of the lattice dynamics for the superconducting and normal states can be estimated from second-order perturbation theory, with the region in $\mathbf{k}$ space which is singly occupied providing the dominant contribution.

XIII. SUMMARY AND DISCUSSION

The leading terms have been computed in a series expansion for the energy difference between low-lying levels and the normal state for metallic hydrogen. The leading terms are believed to be precise, and no arbitrary constants appear. The terms are computed from a many-body perturbation theory in configuration space, where stationary energy levels for the system are emphasized rather than single-particle behavior. Insofar as the leading terms approximate the total energy difference, energy levels are found which lie lower than the normal state, where the lower levels occur only if the nuclear mass is sufficiently large. The interaction responsible for the lower levels is a direct coupling between electrons and bare long-wavelength longitudinal phonons. This coupling leads to an energy which has the same form as the correlation energy for electron exchange. In zeroth order the electronic wave function is a single Slater determinant, where in a region near the Fermi surface only half the one-electron states are occupied. Opposite spins are taken to have an antiferromagnetic arrangement in $\mathbf{k}$ space. It is assumed that the lower-level states are superconducting, and that the condition for the onset of superconductivity requires that the lowering of the energy due to the electron-phonon interaction must overcome the increase in kinetic and exchange energy relative to the normal state. An estimate of the critical temperature shows that the coupling can lead to a T_c the order of several tens of degrees.

To make the calculation exact for metallic hydrogen, higher-order terms and the effects of degeneracy of the unperturbed wave functions must be examined more closely. An extension of the calculation to other metals, and an investigation of how the theory overlaps with conventional theory is suggested but remains to be given. The principal importance of the calculation is the demonstration that direct electron-phonon coupling can introduce a strong superconducting interaction.

APPENDIX A: CALCULATION OF THE TERMS FOR $p'>p$

It is desired to show that the terms for $p'>p$ in Eq. (11) correspond within $O(w^3)$ to the energy of the normal state. Let

$$C=\left[\int_0^{p_1} d\mathbf{p}\int_{p_1}^{\infty} d\mathbf{p}'+\int_{p_1}^{p_2} d\mathbf{p}\int_{p_2}^{\infty} d\mathbf{p}'\right] n(\mathbf{p})[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}',s)$$
$$=\left[\int_0^{p_1} dp\,p^2\int_{p_1}^{\infty} dp'(p')^2+\int_{p_1}^{p_2} dp\,p^2\int_{p_2}^{\infty} dp'(p')^2\right] n(p)[1-n(p')]G(p,p',s)\,, \tag{A1}$$

where it is assumed that $n(\mathbf{p})$ does not depend on angle, and

$$G(p,p',s)=\int d\Omega_p\int d\Omega_{p'}F(\mathbf{p},\mathbf{p}',s) \tag{A2}$$

with $d\Omega_p$ the angular part of the differential. In the normal state $p_1=p_2=1$, $n(p)=n_0(p)$, and C has the value

$$C_0=\int_0^1 dp\,p^2\int_1^{\infty} dp'(p')^2G(p,p',s)\,. \tag{A3}$$

For the wave function of Sec. IV where $n(\mathbf{p})=\frac{1}{2}$ for $p_1<p<p_2$, $n(p)=1$ for $p<p_1$, $n(p)=0$ for $p>p_2$,

$$C=\left[\int_0^{p_1}dp\int_{p_2}^{\infty}dp'+\tfrac{1}{2}\int_0^{p_1}dp\int_{p_1}^{p_2}dp'+\tfrac{1}{2}\int_{p_1}^{p_2}dp\int_{p_2}^{\infty}dp'\right]p^2(p')^2G(p,p',s)$$
$$=\tfrac{1}{2}\left[\int_0^{p_1}dp\int_{p_1}^{\infty}dp'+\int_0^{p_2}dp\int_{p_2}^{\infty}dp'\right]p^2(p')^2G(p,p',s)\ . \tag{A4}$$

By means of a scale transformation and by subtracting C_0 one can write

$$C-C_0=\tfrac{1}{2}\int_0^1 dp\int_1^{\infty}dp'\,p^2(p')^2[p_1^6G(p_1p,p_1p',s)-G(p,p',s)]$$
$$+\tfrac{1}{2}\int_0^1 dp\int_1^{\infty}dp'\,p^2(p')^2[p_2^6G(p_2p,p_2p',s)-G(p,p',s)]\ . \tag{A5}$$

Introducing the notation $G_1=G(p_1p,p_1p',s)$, $G_2=G(p_2p,p_2p',s)$, and $G=G(p,p',s)$, and using the fact that according to Eqs. (14) and (15) $p_1^6+p_2^6-2$ is of order w^2, one may subtract $\frac{1}{2}(p_1^6+p_2^6-2)C_0$ from (A5) to obtain

$$C-C_0\approx\tfrac{1}{2}\int_0^1 dp\int_1^{\infty}dp'\,p^2(p')^2[p_1^6(G_1-G)+p_2^6(G_2-G)]\ , \tag{A6}$$

where terms of order w^2 are neglected. If it can be assumed that G_1 has a first derivative in the domain where $p'>p$, then

$$G_1\approx G+(p_1-1)\left[\frac{\partial G_1}{\partial p_1}\right]_{p_1=1} \tag{A7}$$

and

$$G_1-G\approx(p_1-1)\left[p\frac{\partial G}{\partial p}+p'\frac{\partial G}{\partial p'}\right]\ , \tag{A8}$$

$$G_2-G\approx(p_2-1)\left[p\frac{\partial G}{\partial p}+p'\frac{\partial G}{\partial p'}\right]\ . \tag{A9}$$

Substituting the values of p_1 and p_2 in terms of w, one obtains

$$p_1^6(G_1-G)+p_2^6(G_2-G)\approx w(p_2^6-p_1^6)\left[p\frac{\partial G}{\partial p}+p'\frac{\partial G}{\partial p'}\right]\ , \tag{A10}$$

which is the order of w^2, and integration in (A6) leaves the order unchanged. Since in Eq. (2) C becomes multiplied by a factor $\zeta/r_s\sim w/r_s$, terms of order w^2 in C become of order w^3/r_s in the energy. Thus it is concluded that the difference between C and C_0 is negligible. In a similar way it can be shown that the terms referred to in Ref. 9 as "mixed" terms in the second-order perturbation expression are also approximately the same for the superconducting and normal states, with an energy difference of order w^3/r_s.

APPENDIX B: CONTRIBUTION OF $n(\mathbf{p})$ IN THE FACTOR $n(\mathbf{p})-n(\mathbf{p})n(\mathbf{p}')$

It is of interest to investigate the contribution of the term in $n(\mathbf{p})$ to the electron-phonon energy given by Eq. (2), since Fröhlich assumed that this term could be ignored. Let

$$D=\int d\mathbf{p}\int d\mathbf{p}'[n(\mathbf{p})-n_0(\mathbf{p})]F(\mathbf{p},\mathbf{p}',1)\ , \tag{B1}$$

which gives the difference with respect to the normal state. Since $\Delta n=n-n_0$ vanishes except between p_1 and p_2

$$D=8\pi^2\int_{p_1}^{p_2}dp\,p\,\Delta n(p)\int_0^{\infty}dp'\,p'\frac{\ln[(p'+p)/|p'-p|]}{[(p')^2-p^2+\zeta]}\ , \tag{B2}$$

where the approximations of Sec. III have been used. For the wave function used here $\Delta n(p)=(p-1)/2|p-1|$ between p_1 and p_2, and the transformation $p^2=x$, $(p')^2=x'$ gives

$$D=\pi^2\left[\int_1^{p_2^2}dx-\int_{p_1^2}^1 dx\right]\times\int_0^{\infty}dx'\frac{\ln[(\sqrt{x'}+\sqrt{x})^2/|x'-x|]}{x'-x+\zeta}\ . \tag{B3}$$

The transformation to a new variable z given by $x'=\zeta xz+x$ leads to

$$D=\pi^2\left[\int_1^{p_2^2}dx-\int_{p_1^2}^1 dx\right]\times\int_{-1/\zeta}^{\infty}dz\frac{x}{xz+1}\ln\left[\frac{(\sqrt{\zeta z+1}+1)^2}{\zeta|z|}\right]\ , \tag{B4}$$

where the result can now be integrated over x to give

$$D=\pi^2\int_{-1/\zeta}^{\infty}dz\ln\frac{(\sqrt{\zeta z+1}+1)^2}{\zeta|z|}\left[\frac{p_2^2-1+p_1^2-1}{z}+\frac{1}{z^2}\ln\left|\frac{(z+1)^2}{(p_2^2z+1)(p_1^2z+1)}\right|\right]\ . \tag{B5}$$

Consider only the portion of the integral given by the element of z space between $-1+2w$ and $-1-2w$, and let this portion be denoted by D':

$$D' \approx \pi^2 \ln\left|\frac{4}{\zeta}\right| \int_{-1-2w}^{-1+2w} dz \ln\left|\frac{(z+1)^2}{(p_2^2 z+1)(p_1^2 z+1)}\right| . \tag{B6}$$

The term $(p_2^2-1+p_1^2-1)/z$ has been neglected since it is proportional to w^2. The transformation $z=-1+2wt$ gives

$$D' \approx 2\pi^2 w \ln\left|\frac{4}{\zeta}\right| \int_{-1}^{1} dt \ln\left|\frac{t^2}{p_2^2 p_1^2\left[\frac{1-p_2^2}{2wp_2^2}+t\right]\left[\frac{1-p_1^2}{2wp_1^2}+t\right]}\right| . \tag{B7}$$

Substituting the values for p_1 and p_2 from Eqs. (14) and (15) finally gives

$$D' \approx 2\pi^2 w \ln\left|\frac{4}{\zeta}\right| \int_{-1}^{1} dt \ln\left|\frac{t^2}{1-t^2}\right| = -8\pi^2(\ln 2) w \ln(4/\zeta) . \tag{B8}$$

The remaining part of the D integral tends to give smaller terms of order w^2. From the result (B8) one may conclude that the contribution of $n(\mathbf{p})$ to the difference in electron-phonon energy is the same order of magnitude as the contribution of $n(\mathbf{p})n(\mathbf{p}')$.

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