High Temperature Superconductivity in Metallic Hydrogen: Electron-Electron Enhancements

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We investigate the possibility of superconductivity in a dense phase of hydrogen which becomes metallic while retaining diatomic character. Correlated fluctuations between electrons and holes in the ensuring band-overlap state can lead to significant enhancements in the transition temperature (compared with monatomic phases) principally through a reduction in the associated Coulomb pseudopotential. The effective electron-electron interaction is determined by a method which treats electrons and phonons on an equivalent footing, an approach which confirms that monatomic phases also remain candidates for high temperature superconductivity. [S0031-9007(96)01982-5]

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It was proposed some time ago [1] that certain monatomic forms of dense metallic hydrogen could exhibit superconducting order at quite high temperatures. At the level of BCS theory, the argument had three key elements, each with features unique to the case of hydrogen. First, the exchange bosons are ordinary phonons but because the "ion" in the system is but a single proton (just 1836 times more massive than the electron itself) the vibrational energy scale setting the prefactor in the BCS expression for T_c is already exceedingly high: $\langle \hbar w_{\mathrm{ph}} \rangle \cong 4000$ K. Second, since the proton as an ion lacks any inner core structure, the bare electron-ion interaction is strong (there is no pseudopotential reduction) and so also is the electron-phonon coupling λ. Third, the system is one of high density, $r_s \sim 1.5$ (to be compared, for example, with $r_s \sim 2.07$ in Al) and the density of states $N(0)$ at the Fermi energy ϵ_f is also high. The Coulomb pseudopotential is then typical of high density systems, namely, $\mu^* \sim 0.1$. Taken together, these attributes lead to an expectation of large values of T_c (of order 10^2 K) implying that lone among the elements, metallic hydrogen might exhibit high temperature superconductivity.

The problem has been revisited at the level of *approximate* solutions to the Eliashberg equations [2], again giving T_c values of order 10^2 K. It has also been examined from the standpoint of more accurate representations of the electronic structure, for example, by Papaconstantopoulos and Klein [3], Switendick [4], and Min *et al.* [5], again obtaining T_c's of order 10^2 K. The structural sensitivity of the transition temperature was especially emphasized in a calculation by Whitmore *et al.* [6] which also included nonlinear screening of the protonic charges. The possibility of superconductivity in a distorted hexagonal structure (suggested by a corresponding total energy calculation) was studied by Barbee *et al.* [7]; they reported a transition temperature in the range 230 ± 85 K.

The calculations just summarized generally approach the problem either from the McMillan equation, or from the Eliashberg equation but in either case, the direct electron-electron interaction has been treated through the Coulomb pseudopotential approximation, i.e.,

$$\mu^* = \frac{N(0)V_c}{1 + N(0)V_c \ln(\epsilon_f/\hbar\omega_{\mathrm{ph}})}. \tag{1}$$

Here V_c is taken as an approximate static Fermi surface average of Coulomb interactions between electrons, and ω_{ph} is a typical phonon frequency. For the McMillan formula, ω_{ph} is an average phonon frequency and in the Eliashberg equation it is a cutoff frequency on the order of several times the Debye frequency. Because of differences in possible choices for ω_{ph}, the parameter μ^* used in the McMillan equation is also different (generally only by a small amount) from the value of μ^* in the original Eliashberg equation [8]. As noted, typical values of μ^* are in the vicinity of 0.1 at least for high density systems (which, as we establish, includes monatomic phases of metallic hydrogen).

We shall now examine in more detail the role electron-electron interactions play in the context of possible superconductivity in *monatomic* metallic hydrogen. The reason for this is that in such a structure hydrogen would be classified as a group I element, an alkali metal: No other alkali metal has so far been verifiably found to be superconducting under normal conditions, and it is important to understand the key differences between metallic hydrogen (in the so-called Wigner-Huntington phase) and the other alkali metals. So far as superconductivity is concerned, a crucial consideration is the mean electronic density and the role this plays in influencing the manifestation of *direct* electron-electron interactions in this problem. But it has also been proposed that *paired* hydrogen could become metallic at high densities through a band-overlap transition [1,9]. Exactly such a paired-proton state has recently been suggested by Weir *et al.* [10] as the dominant character of a high temperature metallic phase of dense liquid hydrogen they create by shock compression. In equivalent low temperature phases, both electron and hole carriers are then expected to be present, and we have shown [11,12] that under certain conditions, correlated fluctuations between them can lead to significantly enhanced transition temperatures. The necessary conditions can prevail in hydrogen and we report here that this electronic effect works constructively with the phonon mediated interaction in paired metallic hydrogen to produce transition temperatures even larger than those predicted for monatomic phases.

We therefore proceed with a *complete* solution of the Eliashberg equations for metallic hydrogen by a method which treats electrons and phonons on an entirely equal footing. We have already used this approach in a number of metallic systems [11,12] and have found that the ubiquitous use of $\mu^* \approx 0.1$ can fail in lower density systems, particularly multiband systems. Though computationally intensive because of the disparity in frequency scales characterizing phonon and electron systems, a full numerical solution of the Eliashberg equations is nonetheless possible and, especially for low density metals and for some multiband metals, this first-principles approach can lead to results interestingly different from approximate solutions that traditionally assume $\mu^* \approx 0.1$. Our starting point is the fundamental equation for the pairing function $\Phi_l(k, i\omega_n)$ of l-wave superconductivity, i.e.,

$$\Phi_l(k, i\omega_n) = -T \sum_{\omega_{n'}} \int_0^\infty dk' \, K_l(k, i\omega_n; k', i\omega_{n'}) \times \Phi_l(k', i\omega_{n'}) \,, \tag{2}$$

where

$$K_l(k, i\omega_n; k', i\omega_{n'}) = \frac{k'}{4\pi^2 k} |G(k', i\omega_{n'})|^2 \times \int_{|k-k'|}^{k+k'} dq \, P_l\left(\frac{k^2 + k'^2 - q^2}{2kk'}\right) \times q V_{\mathrm{eff}}(q, i\omega_n - i\omega_{n'}) \,. \tag{3}$$

Here $G(k', i\omega_{n'})$ is the fully interacting Green's function and $V_{\mathrm{eff}}(q, i\omega)$ is the irreducible electron-electron interaction; it is important to note that V_{eff} includes *both* the phonon mediated interaction *and* the direct Coulomb terms.

We take the direct Coulomb part of $V_{\mathrm{eff}}(q, i\omega)$ to be given by the Kukkonen-Overhauser approximation [13–15] but modified to include self-energy effects [12]; for the case of a single band, it is given by

$$V_{\mathrm{eff}}^C = v_q + \frac{v_q^2 (1 - G_s)^2 \overline{\Pi}_o}{1 - v_q (1 - G_s) \overline{\Pi}_o} - (2\nu + 1) \frac{v_q^2 (G_a)^2 \overline{\Pi}_o}{1 + v_q G_a \overline{\Pi}_o} \,. \tag{4}$$

In (4) v_q is the bare Coulomb interaction, ν is the valley degeneracy (which is equal to unity for atomic hydrogen in simple structures), and $\overline{\Pi}_0$ is the Lindhard approximation to the density-density response function but modified to include self-energy effects. The quantities G_s and G_a are standard local field factors and are determined by interpolation between known limits as discussed in Ref. [12]. For the two-band case (which is an appropriate model for metallic diatomic hydrogen), the direct Coulomb part of the effective interaction between electrons in band (1) differs in a crucial way and is given as [15]

$$V_{\mathrm{eff}}^C = v_q + \frac{v_q^2 (1 - G_s^{11})^2 \overline{\Pi}_o^{(1)}}{1 - v_q (1 - G_s^{11}) \overline{\Pi}_o^{(1)}} - (2\nu + 1) \frac{v_q^2 (G_a^{11})^2 \overline{\Pi}_o^{(1)}}{1 + v_q G_a \overline{\Pi}_o^{(1)}} + v_{12}^2 \Pi^{(2,2)}, \tag{5}$$

where

$$v_{12} = (1 - G_s^{12}) v_q / [1 - v_q (1 - G_s^{11}) \overline{\Pi}_o^{(1)}], \tag{6}$$

and $\Pi^{(2,2)}$ is the density-density response function for carriers in band (2). The important additional term in the effective interaction is traced to correlated charge fluctuations between the two bands. It is *attractive* and, as we have found, in some circumstances it can overcome the effects of direct Coulomb repulsion. An essential point is that the local fields are *all* constrained by compressibility sum rules and Ward identities with the particular consequence that the attractive term is actually *exact* in the static, long-wavelength limit for electrons on the Fermi surface. The part of $V_{\mathrm{eff}}(q, i\omega)$ arising from phonon exchange is relatively standard and with sufficient accuracy may be taken to be [11]

$$V^{\mathrm{ph}}(q, i\omega) = -\frac{\alpha}{1 + (1/2k_f)^2} \frac{\omega_q^2}{\omega^2 + \omega_q^2} \,, \tag{7}$$

where the constant α is chosen to reproduce the correct electron-phonon coupling constant λ and w_q is then assumed to be equal to the characteristic frequency $\langle w_{\mathrm{ph}} \rangle$. The self-energy corresponding to the Green's function in (3) is given by

$$\Sigma(k, i\omega_n) = -T \sum_{\nu_n} \int \frac{d^3 q}{(2\pi)^3} \times V_{se}(\mathbf{q}, i\nu_n; \mathbf{q} - \mathbf{k}, i\nu_n - i\omega_n) G(q, i\nu_n) \,. \tag{8}$$

An approximation for V_{se} can be derived from the Kukkonen-Overhauser formalism and it can be expressed as

$$V_{se} = V^{\mathrm{ph}} + \frac{1}{\overline{\Pi}_o^i} \sum_j v_c^{ij} \Pi_s^{ij}, \tag{9}$$

where again the Π_s^{ij} are elements of the density-density response matrix for the two-band system.

Equation (2) can be solved by using a technique originating with Rietschel and Sham [16] and with Takada [17] where the anomalous self-energy $\Phi_l(k, i\omega_n)$ is evaluated by interpolation on a finite grid in both k and ω_n. This method of evaluating $\Phi_l(k, i\omega_n)$ than converts Eq. (2) into a matrix equation with the formal structure

$$\mathbf{M}_l \mathbf{\Phi}_l = \mathbf{\Phi}_l \,, \tag{10}$$

which in turn can be straightforwardly converted into an eigenvalue problem by writing

$$\mathbf{M}_l \mathbf{\Phi}_l = \gamma \mathbf{\Phi}_l \,, \tag{11}$$

Equation (2) is immediately recovered when one of the eigenvalues γ is equal to unity. To calculate the transition temperature, it is necessary to solve Eq. (11) for the largest eigenvalue as a function of T. For high temperatures this largest eigenvalue is always less than unity; a T_c is then determined as that temperature for which the largest eigenvalue eventually equals unity.

The available estimates of T_c for monatomic forms of hydrogen have all assumed that $\mu^* \approx 0.1$. Since our results for the ordinary simple metals [11] clearly indicate that μ^* grows with increasing r_s, a somewhat smaller μ^* for monatomic hydrogen (where $r_s 1.5$) might initially be expected. However, the phonon energy in metallic hydrogen is actually a larger fraction of the Fermi energy than in most metals and this tends to increase the Coulomb pseudopotential μ^*. Nevertheless we confirm that $\mu^* \approx 0.1$ remains a reasonable assumption in monatomic hydrogen (but *not* in the other alkalis) by directly calculating the transition temperature for metallic monatomic hydrogen using the modified Kukkonen—Overhauser interaction and parameters taken from the calculation of Ref. [7]. Accordingly, if we take $r_s = 1.3$, $\lambda = 1.5$, and $\langle \omega_{\text{ph}} \rangle = 1830$ K, we then find from the solutions of (11) that $T_c = 215$ K. For $\lambda = 1.5$, the McMillan formula should be reasonably accurate [17] and if we solve it for μ^* *given* $T_c = 215$, we deduce that $\mu^* = 0.089$. For purposes of comparison, we also calculate T_c using the McMillan equation but with μ^* *set* to the value 0.1; we then find $T_c = 209$ K which is actually within 3% of the result using our *ab initio* treatment of the Coulomb interaction. The conclusion therefore is that the somewhat standard value $\mu^* \approx 0.1$ is indeed a reasonably good approximation for *monatomic* metallic hydrogen. The transition temperature calculated in Ref. [7], namely, $T_c = 230$ K, differs in a minor way from our result merely because more realistic phonon dispersion relations are used there. (This difference will be much smaller if we use $\langle \omega_{\text{ph}} \rangle_{\log}$ instead of $\langle \omega_{\text{ph}} \rangle$ [18].) It should be especially noted that applications of exactly the techniques used here given reasonable T_c values (i.e., close to experimental) for the conventional metals [11].

A far more interesting situation arises for the case of the proposed metallic state of hydrogen in which proton pairing is retained [1]. As molecular hydrogen is compressed, there can be a band-overlap transition (generally from the closure of an indirect gap) and it results in a metallic phase with an exchange stabilized diatomic structure preserved [1,9]. In this metal there will be electronlike bands and holelike bands with approximately equal effective masses, and as we note below under certain conditions the correlated charge fluctuations arising in this situation can give rise to electron pairing even without phonons [11]. The details of the actual one-electron structure are so far undetermined and for this reason the new effect arising from this distinct manifestation of electron-electron interactions is demonstrated with representative values of electron and hole band densities and masses.

Consider therefore a model of proton-paired metallic hydrogen consisting of a free electronlike band, and a free holelike band with a valley degeneracy of 2 (since there are two equivalent hole bands in a typical Brillouin zone taken here to be of the hexagonal class). To demonstrate the interesting differences presented by this phase, we take λ to be 1.5 and assume a characteristic frequency of 1830 K. (These are simply the values obtained in Ref. [19] for monatomic hydrogen, and we will assume that similar values are obtained in the diatomic phase.) This form of electronic structure leads of course to a general expectation of a *decline* in the overall density of states but it does not necessarily mean that λ will be significantly reduced, and in any case we find that any such reductions can be more than recoupled by the new effect originating with correlated charge fluctuations in the electron-electron terms. The largest T_c's are not greatly sensitive to these details since the electronic pairing mechanism is now providing a very significant contribution to the overall pairing. We define r_{se} through the relation $4/3\pi r_{se}^3 = 1/\rho_e$ (ρ_e is the density of electrons in the conduction band and is also equal to the density of holes in the valence band). Here superconductivity first occurs via pairing in the electron band; for $r_{se} = 3$ we find by direct solution of (11) that $T_c = 314$ K. For $r_{se} = 3.5$, $T_c = 409$ K and T_c can increase even further as r_{se} is taken to larger values Three points should be noted immediately: First, as stated above when this approach is applied to more conventional systems, entirely standard transition temperatures are found [11]. The densities and couplings utilized here are not significantly outside of those of other known superconductors. Second, a large rise in T_c occurs above $r_{se} = 3.5$ because $r_{se} = 4$ is near a singularity appearing in the long-wavelength limit of the effective interaction (see below). Third, the results just quoted correspond to equal electron and hole masses ($m_e = m_h = m$). For lower masses, the transition temperature is also lower but can still exceed room temperature. If the hole mass is increased over the electron mass, the static effective interaction tends to become more attractive and the transition temperature will also increase, behavior which parallels the earlier findings of Vignale and Singwi [15] in electron-hole liquids.

Superconductivity in the proton-paired metallic phase of hydrogen is now being driven by both phonons and correlated charge fluctuations. Their relative importance can be easily ascertained by calculating the transition temperatures in the two-band electron gas *without* phonons present. This is the generalization to two bands of the question originally raised by Kohn and Luttinger [20] concerning the possibility [11] that the true ground state of the interacting electron gas might exhibit off-diagonal long-range order. The presence of correlated charge fluctuations between electron and hole bands very much enhances this possibility; for example, for $r_{se} = 4$, the transition to superconductivity sets in at approximately $\epsilon_{fe}/20$, and is entirely attributable to a purely electronic phenomenon. It is strikingly different from pairing (without intermediaries) in the single band case [11]. The large values of T_c result largely from the fact that the energy scale in the absence of intermediaries is set entirely by the Fermi energy and if, as here, correlated fluctuations can reduce the Coulomb pseudopotential, even modestly, this Fermi energy scale can be very effectively revealed. Further, as noted above, the choice of relative densities can significantly affect T_c, and it can be understood this way: At $r_{se} = 3$, for example, the attractive term in the effective interaction [i.e., the fourth term in Eq. (5)] approximately balances the repulsive part of the interaction [i.e., the first three terms in Eq. (5)] and the transition temperature is low. At $r_{se} = 4$, however, the attractive term (which is more sensitive to density than the other terms) exceeds the repulsive terms, and superconductivity can then be mediated by the net attractive interaction. It follows that the details of the one-electron structure (brought about by increase in density) are not unimportant. For the pairing state these are not known at present and the issue is therefore an interesting one to pursue both experimentally and theoretically.

The possibility of superconductivity in metallic hydrogen with the very large T_c's clearly depends on whether or not the system remains unaffected by other instabilities, such as a compressional instability, a charge density wave instability, an exitonic insulator transition, or even a structural phase transition. These may be expected to occur near $r_{se} = 4$ since this is close to the point where the effective interaction becomes singular. Nevertheless, because we find a relatively wide *range* of densities where the transition temperature is expected to be greater than room temperature, there appears to be a reasonable possibility that dense metallic hydrogen in a diatomic phase will exhibit interesting high temperature superconductivity. Note also that with conventional approximations for μ^* the transition temperature for superconductivity induced by fluctuations in proton density can continue to rise in monatomic arrangements up to quite high density before an eventual decline [21]. This is also expected in the paired context.

The primary assumption made is that in these ranges of high density the system is in fact metallic, i.e., that recent evidence of ionic tendencies will eventually give way to itinerant electron systems. If this is indeed the case, metallic diatomic hydrogen could therefore be a superconductor, over a *range* of densities but with transition temperatures considerably higher than in the monatomic case. Even if the monatomic phase should eventually prevail full inclusion of recent developments in both many-body theory and the theory of superconductivity indicates that the transition temperature is still predicted to be high. It is worth recapitulating the crucial difference between the two cases; for the proton-paired band-overlap state, the nature of the effective electron-electron contribution to the pairing kernel differs markedly from that in the monatomic phase. The presence of both electronlike and hole like bands leads to correlated charge fluctuations resulting in an attractive term in the effective interaction, a key physical aspect which, in a system where the phonon energy scale is already high, is nevertheless absent in the single band case.

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