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Critical temperature of superconducting FCC and HCP metallic hydrogen

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Abstract. We have calculated the critical temperature, T_c, of superconducting metallic hydrogen from first principles. We obtained the interionic potential, the phonon dispersion curves, the electron-phonon spectral density $\alpha^2F(\omega)$, and solved the Eliashberg equations to calculate T_c. We considered FCC and HCP hydrogen.

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I. Introduction

Metallic hydrogen, which can be obtained at high enough pressure (of the order of megabars) has atracted the interest of many researchers through the years [1 to 8]. The interest on metallic hydrogen comes from the possibility that this material could be a high temperature superconductor.

There have been several first principles calculations of the superconducting transition temperature of metallic hydrogen. We have, among others, the work of Whitmore *et al.*, who used perturbation theory [5] and of Magaña *et al.* [6,7] who made an extension of the perturbative approach by using the Hellmann-Feynman Theorem. The approaches in these calculations did not use pseudopotentials.

To define a pseudopotential for metallic hydrogen is not simple. The metallic hydrogen ion has no inner core. Because of this, it is clear that we can not use an Ashcroft type pseudopotential. However, following the suggestion made by Magaña *et al.* [8], we could use the approach by Manninen *et al.* [9] to obtain, from first principles, a local pseudopotential for the metal, using the density functional formalism [10,11]. This approach is inspired in the work of Rasolt *et al.* [12]. This kind of pseudopotential has been used successfully in the calculation of properties (like cohesion energy, phonon dispersion curves, elastic constants, lattice specific heat, phonon limited resistivities, etc.) of several metals [13 to 20]. In what follows we describe the method briefly. For more details see Refs. [9, and 13 to 20].

II. Interionic potential

In the method we have used the starting point is the displaced electronic density around an impurity in an electron gas, which has an equilibrium density equal to that of metallic hydrogen, for which we took $r_s = 0.6$ to 1.8 in steps of 0.2 (in units of the Bohr radius). This calculation is made by non-linear screening theory, (density functional formalism [10,11]), and considering the screening of the ion within the model of the nucleus embedded in a jellium vacancy [9], which has been very good for the prediction of properties of metals [9, 13 to 20]. Taking into account that in the pseudopotential formulation the pseudodensity must not contain wiggles near the ion, these wiggles in the calculated density, if present, have to be removed. The wiggles in that region can be present in the induced density calculated from density funcional theory because of the orthogonalization of conduction states to core orbitals. In our case there are not bound states, so that the procedure to eliminate them [9,13], was not used. In what follows we have used atomic units (*i. e.*, magnitude of the electron charge = electron mass = $\hbar = 1$). The energy is given in double Rydbergs.

From pseudopotential theory and linear response theory [21], the interionic potential is given by

$$\Phi(r) = \frac{Z^2}{r}\left(1 + \frac{2}{\pi Z^2}\int_0^\infty \frac{dq\,\sin(qr)\epsilon(q)[\delta n(q)]^2}{q[1-\epsilon(q)]}\right), \tag{1}$$

where r is the separation between the two ions, Z is the charge of the metal ion, $\epsilon(q)$, is the dielectric response function of the electron gas and $\delta n(q)$ is the Fourier fransform of the induced charge pseudodensity.

For the model of the nucleus embedded in a jellium vacancy [9,13], the induced electronic density is calculated by taking the difference [9]:

$$\delta n(r) = n(r) - n_v(r) - 2\sum_b |\psi_b(r)|^2, \tag{2}$$

where $n(r)$ is calculated with the total charge density corresponding to a nucleus located at the center of a vacancy in jellium, and $n_v(r)$ is the electron density around a jellium vacancy alone. Charge neutrality of the metal is a necesary condition. The bound states, which are represented by $\psi_b(r)$, in this case are zero.

We calculated $\delta n(q)$, the Fourier transform of the displaced electron pseudodensity, taking the Fourier transform of the density given by Eq. (2). (remember that smoothing was not necessary).

The unscreened pseudopotential form factor, $\nu(q)$, is related to $\delta n(q)$ by

$$\nu(q) = \frac{4\pi\delta n(q)\epsilon(q)}{q^2[1-\epsilon(q)]}. \tag{3}$$

Eq. (3) is used to obtain an effective local pseudopotential, which in linear response will give the exact induced displaced electronic density outside the region of smoothing (which in this case was not necessary). In this way some of the non linear screening effects are included into the pair potential calculated from this pseudopotential.

In the approach of Rasolt *et al.* [12] the displaced electronic density around an impurity in an electron gas is also previously calculated by non-linear screening theory. Then a non local pseudopotential is defined in order to reproduce, as close as possible, the non-linear displaced electronic density by linear response theory, except in a region close to the ion. In this way, the non-linear effects are also partially included.

The dielectric function we used satisfies by construction, the compressibility theorem which is important in connection with the interionic potential [9, 22]. It is given by [1, 22]

$$\epsilon(q) = 1 + \left(\frac{4\pi}{q^2}\right) G(q), \tag{4}$$

where

$$G(q) = \frac{G_0(q)}{1 - \left(\frac{4\pi}{k_{\mathrm{TF}}^2}\right) G_0(q)(1 - L)} \tag{5}$$

and $G_0(q)$ is the usual Lindhard polarizability, k_{TF} is the Fermi-Thomas screening constant, and L is the ratio

$$L = \frac{\dfrac{\partial\mu}{\partial r_S}}{\dfrac{\partial E_{\mathrm{F}}}{\partial r_S}}. \tag{6}$$

In equation (6) μ is the chemical potential, E_{F} is the Fermi energy and

$$\mu(r_S) = E_{\mathrm{F}}(r_S) + \mu_{\mathrm{xc}}(r_S),$$

where $\mu_{\mathrm{xc}}(r_S)$ is the exchange-correlation contribution to the chemical potential.

On the other hand, the screened pseudopotential form factor, $W(q)$, given by

$$W(q) = \frac{\nu(q)}{\epsilon(q)} C(q), \tag{7}$$

is important in the calculation of the resistivity. The vertex correction is $C(q)$ which,

r_S	1	2	3	4	5	6
$H(E_F)$	1.164	1.302	1.429	1.547	1.660	1.766

TABLE I. Quasiparticle renormalization constant at the Fermi level as given by Hedin [26]. This is a function of r_S.

following the work of Rasolt [24] and the work of Shukla and Taylor [25] is given by

$$C(q) = \frac{1}{H(E_{\mathrm{F}})}\left[1 - \frac{G(q)}{G(0)}\left(1 - \frac{H(E_{\mathrm{F}})B}{B_0}\right)\right],$$

where $H(E_{\mathrm{F}})$ is the quasiparticle renormalization constant at the Fermi level given by Hedin [26] and it is a function of r_s, (B/B_0) is the ratio of the electron gas compressibility (B) with that of the non-interacting electron gas (B_0), and the quasiparticle electron mass has been taken equal to the electron mass. In Table I we reproduce the tabulated values of $H(E_{\mathrm{F}})$, from the work by Hedin [26].

In the derivation of this expression for $C(q)$, a non local electron-electron interacction, and scattering on the Fermi surface were considered [24,25].

Using the expression of Gunnarson and Lundquist [27], for exchange-correlation (which is the one we used in the calculation of the induced electronic density), the corresponding value of L is

$$L = 1 - \left(\frac{4}{9\pi^4}\right)^{1/3} r_S\left(1 + \frac{0.6213}{r_S + 11.4}r_S\right). \tag{8}$$

With the induced charge pseudodensity and the dielectric function already given, we used Eq. (1) to calculate the interionic potential.

III. Phonons and T_c

From the interionic potential we calculated the phonons and associated force constants, using the Self-Consistent Harmonic approximation (SCHA) [28, 29, 30].

The expression for the effective phonon distribution function, $\alpha^2F(\omega)$, which is useful to calculate T_c, can be given as [5]

$$\alpha^2F(\omega) = N(0)\int \frac{d\Omega_k}{4\pi}\frac{d\Omega_{k'}}{4\pi}\sum_\lambda \left|g_{\mathbf{kk}',\lambda}\right|^2 \delta(\omega - \omega_\lambda(\mathbf{k}-\mathbf{k}')) \tag{9}$$

where $N(0)$ is the electron density of states at the Fermi level, $d\Omega_k$ and $d\Omega_{k'}$ are solid angle elements on the Fermi surface, $\mathbf{k}$ and $\mathbf{k}'$, $\omega_\lambda(\mathbf{k}-\mathbf{k}')$ are the phonon frequencies, and $g_{\mathbf{kk}',\lambda}$ is the electron-phonon coupling constant which, for the one

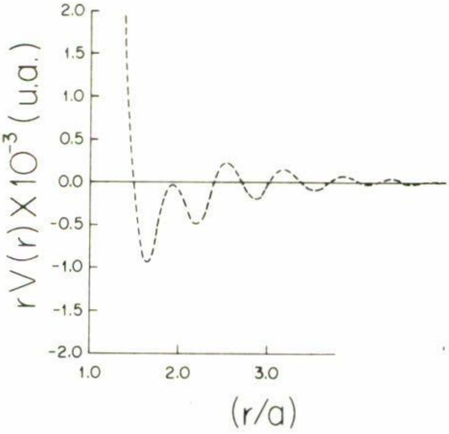

FIGURE 1. Calculated interionic potential for metallic hydrogen. We are using $r_s = 0.8a_0$ where a_0 is the Bohr radius.

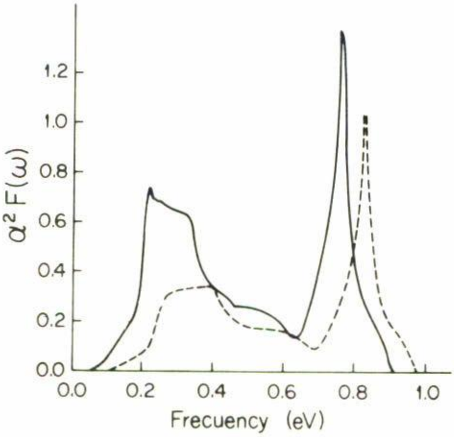

FIGURE 2. Calculated Eliashberg function $\alpha^2F(w)$ for FCC metallic hydrogen, with $r_s = 0.8$ (in atomic units). Predicted in this work: —; From Ref [1]: - - -.

plane wave theory, is given by

$$g_{\mathbf{kk}',\lambda} = -\frac{i\mathbf{q}\cdot\boldsymbol{\epsilon}_\lambda(\mathbf{q})W_{k_\mathrm{F}}(\mathbf{q})}{\left[2MN\omega_\lambda(\mathbf{q})\right]^{1/2}} \tag{10}$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, $\boldsymbol{\epsilon}_\lambda(\mathbf{q})$ is the polarization vector of the lattice vibration with wave vector $\mathbf{q}$ and frequency $\omega_\lambda(\mathbf{q})W_{k_\mathrm{F}}(\mathbf{q})$ is the form factor for scattering on the Fermi surface, M is the ion mass and N is the number of ions.

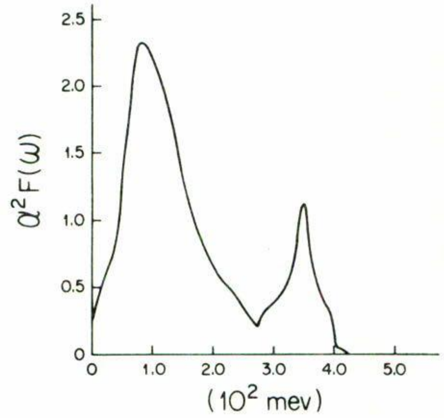

FIGURE 3. Calculated Eliashberg function $\alpha^2 F(w)$ for HCP metallic hydrogen, with $r_s = 1.0$ (in atomic units).

FCC		
r_S	T_c (K)	T_c (K) (from Ref. [6])
0.8	131	243

HCP	
r_c	$T_c(K)$
0.8	196
1.0	172
1.2	155
1.6	140

TABLE II. Predicted values for the superconducting transition temperature of FCC and HCP metallic hydrogen. It is predicted with this approach that FCC is unstable for $r_S \geq 1.0$ and that HCP is unstable for $r_S \geq 1.8$, in units of the Bohr radius. The maximum temperature predicted is for HCP hydrogen, 196 K.

The force constants generated from the interionic potential using the the SCHA are used to calculate the function $\alpha^2 F(\omega)$. To calculate all the phonon frequencies and polarization vectors entering in equation (9), from the force constants obtained in the phonon dispersion curve, we followed the method of Gilat and Raubenheimer [31]. This method consists in solving the secular equations associated with the dynamical matrix only at a relatively small number of points (3000) in the irreducible first Brillouin zone. Then, by means of linear extrapolation the other phonon eigenfrequencies are extracted from within small cubes, each centered at one point. These cubes can be arranged to fill the entire irreducible first Brillouin zone and thus can yield the complete frequency distribution of the crystal.

With this information we can solve the Eliashberg equations in order to find T_c.

In Fig. (1) we show the resulting interionic potential. From the interionic potential we obtained the electron-phonon interaction, $\alpha^2 F(\omega)$, and the force constants by the SCHA and the method of Gilat and Raubenheimer [31]. The resulting electron-phonon interaction for FCC and HCP hydrogen are shown in Figs. (2) and (3). In Fig. (2) we show a comparison with the results of other calculations for FCC hydrogen. In Table II we show some superconductivity parameters for FCC and HCP hydrogen. We found a value for T_c which is similar to previous calculations, confirming the idea of metallic hydrogen as a possible high temperature superconductor.

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Resumen. Hemos calculado la temperatura crítica del hidrógeno metálico superconductor, a partir de primeros principios. Obtuvimos el potencial interiónico, las curvas de dispersión de fonones, la densidad espectral $\alpha^2F(\omega)$ y resolvimos las ecuaciones de Eliashberg para calcular T_c. Consideramos hidrógeno en las estructuras FCC y HCP.