PHYSICAL REVIEW B VOLUME 33, NUMBER 10 15 MAY 1986

Extension of the Lang-Kohn work-function calculation to the density of metallic hydrogen

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(Received 14 May 1985)

We have made a calculation of the work function of metallic hydrogen using the approach given by Lang and Kohn. We made the calculation using the jellium model and taking for metallic hydrogen $r_s = 1.0$. The value we obtained for the work function is 4.67 eV.

Metallic hydrogen is a material which has attracted considerable interest recently.[1-10] The prediction and knowledge of its properties is becoming important.

It is known from experiment[11] and theory[12-14] that the value of the work function depends on the crystalline face considered. It is clear that the ionic potential plays a crucial role in this anisotropy of the value of the work function.

On the other hand, when the jellium model is used to compute the work function for simple metals in polycrystalline form, a good agreement with experimental results is obtained.[12-14]

If the effect of each metal ion on the conduction electrons is taken into account in order to calculate the work function in a realistic way, a very difficult problem arises: solving a self-consistent, three-dimensional system of equations.[12] What Lang and Kohn[12] did in order to avoid this difficulty was to use pseudopotentials and perturbation theory. They considered that the replacement of the uniform background by the ion pseudopotentials represents a small perturbation $\delta v(\mathbf{r})$, and taking the perturbation to first order, they gave an expression for the change of the work function with respect to the value they found using the jellium model. Within this approximation Lang and Kohn calculated the variation of the value of the work function from one crystal face to another for some metals. Monnier and Perdew[13] and Monnier, Perdew, Langreth, and Wilkins[14] made a generalization of the approach given by Lang and Kohn to deal with the inclusion of the effect of the ions on the conduction electrons, and treated the discrete lattice perturbation $[\delta v(\mathbf{r})]$ variationally. Their calculation is reduced to the one by Lang and Kohn in the limit of weak $\delta v(\mathbf{r})$. The results obtained in Ref. 13 for the jellium model and for the value of the work function for different crystal faces in Ref. 14 agree with the results of Lang and Kohn, although the approach in Ref. 14 is more accurate. The pseudopotential used in all cases was an Ashcroft pseudopotential.[15]

If we were interested in calculating the work function of metallic hydrogen for different crystal faces, we would have to assume a specific crystal structure for this material and to choose a pseudopotential different from Ashcroft's pseudopotential because a metallic hydrogen ion has no inner core. Perhaps we could construct a pseudopotential for metallic hydrogen using the method given by Manninen *et al.*,[16] which has been applied with some success to aluminum. In this method the pseudopotential is constructed using the electronic density around a metal ion. It is a first principles pseudopotential.

We are interested here in the value of the work function for metallic hydrogen in polycrystalline form. From Refs. 12—14 we conclude that the jellium model is adequate for this purpose.

On the other hand, following Lang and Kohn,[12] if we take a simple arithmetic average, for qualitative purposes, of the values of the work function for different crystal faces for every one of the metals studied in Refs. 12—14 we get values which are very close to those obtained using the jellium model.

In this work we made a calculation of the work function of polycrystalline metallic hydrogen, using the jellium model for the metal. We have followed the approach given by Lang and Kohn.[12,17] They use the formalism of Hohenberg, Kohn, and Sham,[18,19] and perform the calculation of the work function for values of r_s between 2.0 and 6.0. It seems that for metallic hydrogen we should expect a value of r_s between 1.0 and 2.0,[10] so we have extended their calculations to the case $r_s = 1.0$. Their results obtained using the jellium model are in good agreement with experimental values. These results are even improved a little ($\sim$5—8 %) when they include the effect of the lattice using a pseudopotential.

For the convenience of the reader we describe briefly the method we followed and for more details the reader may see Refs. 12 and 17.

Defining the work function Φ as the minimum energy required to remove an electron from the metal at 0 K, it can be shown that[12]

$$\Phi = \Delta\phi - \bar{\mu} \, , \tag{1}$$

where $\Delta\phi$ is the change in the electrostatic potential across the dipole layer create by the "spilling out" of the electrons at the surface and $\bar{\mu}$ is the chemical potential of the electrons in the bulk relative to the mean electrostatic potential there. All many-body effects are contained in the exchange and correlation contribution to $\bar{\mu}$ and in their effect on the barrier potential.

A schematic representation of the system considered is given in Fig. 1. The expression for $\Delta\phi$, imposing charge neutrality is

$$\Delta\phi=4\pi\int_{-\infty}^{\infty}x\,[n(x)-n_+(x)]dx\ , \tag{2}$$

where $n(x)$ is the electronic density and $n(x)$ is the positive uniform background density

$$n_+(x)=\begin{cases} n, & x<0\\ 0, & x>0\ .\end{cases} \tag{3}$$

The corresponding expression for $\bar{\mu}$ is

$$\bar{\mu}=\tfrac{1}{2}k_F^2+\mu_{\rm xc}[n_0]\ , \tag{4}$$

where k_F is the bulk Fermi wave vector and $\mu_{\rm xc}[n_0]$ is the exchange-correlation contribution to the chemical potential.

Notice that in order to find $\Delta\phi$ we need to know $n(x)$ and to know $n(x)$ we need to know the effective potential on the electrons. This effective potential includes $\Delta\phi$. In this way we have a self-consistent problem.

When the Hohenberg-Kohn-Sham formalism is used to find the electronic density, the resulting self-consistent equations to be solved are the following:[12]

$$\left[-\frac{1}{2}\frac{d^2}{dx^2}+V_{\rm eff}[n(x)]\right]\psi_k(x)=\tfrac{1}{2}(k^2-k_F^2)\psi_K(x)\ , \tag{5}$$

$$V_{\rm eff}[n(x)]=\Phi[n]-4\pi\int_x^{\infty}dx'\int_{x'}^{\infty}dx''[n(x'')-n_+(x'')] +\mu_{\rm xc}[n(x)]\ , \tag{6}$$

$$n(x)=\frac{1}{\pi^2}\int_0^{k_F}(k_F^2-k^2)\,|\,\psi_k(x)\,|^2dk\ . \tag{7}$$

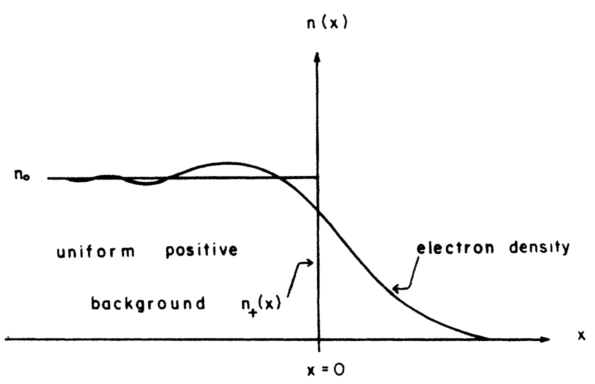

FIG. 1. Schematic representation of the charge densities in the metal.

The wave function $\psi_k(x)$ when $x\to-\infty$ has the asymptotic form

$$\psi_k(x)=\sin[kx-\gamma(k)]\ , \tag{8}$$

where $\gamma(k)$ is the corresponding phase shift.

TABLE I. Electronic densities for $r_s=2.0$; $n(x)$ is obtained in this work; $n_{\rm LK}(x)$ is by Lang and Kohn (Ref. 11). For $r_s=1.0$ the obtained electronic density and the effective potential are shown. The distance x is given in fractions of the Fermi wave length. The densities are given in fractions of n_0. The effective potential energy $V_{\rm eff}$ is given in fractions of the Fermi energy. (For $r_s=1.0$, $E_F=50.1$ eV, $\lambda_F=3.27$ a.u.)

Position	$r_s=2.0$		$r_s=1.0$	
x/λ_F	$n(x)$	$n_{\rm LK}(x)$	$n(x)$	$V_{\rm eff}(x)/E_F$
−1.20	1.0051	1.0036	0.9953	−0.9976
−1.15	1.0028	0.0013	0.9951	−0.9973
−1.10	0.9953	0.9982	0.9943	−0.9969
−1.05	0.9966	0.9954	0.9927	−0.9965
−1.00	0.9953	0.9941	0.9908	−0.9960
−0.95	0.9963	0.9953	0.9890	−0.9955
−0.90	0.9994	0.9986	0.9876	−0.9948
−0.85	1.0036	1.0029	0.9869	−0.9940
−0.80	1.0071	1.0065	0.9867	−0.9931
−0.75	1.0078	1.0076	0.9866	−0.9920
−0.70	1.0053	1.0051	0.9859	−0.9907
−0.65	0.9995	0.9995	0.9840	−0.9892
−0.60	0.9923	0.9925	0.9806	−0.9861
−0.55	0.9864	0.9869	0.9756	−0.9853
−0.50	0.9847	0.9852	0.9687	−0.9829
−0.45	0.9877	0.9884	0.9592	−0.9799
−0.40	0.9937	0.9944	0.9455	−0.9761
−0.35	0.9971	0.9979	0.9249	−0.9587
−0.30	0.9895	0.9904	0.8956	−0.9332
−0.25	0.9615	0.9626	0.8561	−0.9036
−0.20	0.9057	0.9070	0.8051	−0.8691
−0.15	0.8194	0.8209	0.7419	−0.8285
−0.10	0.7069	0.7084	0.6674	−0.7807
−0.05	0.5791	0.5805	0.5843	−0.7240
0.00	0.4508	0.4521	0.4968	−0.6584
0.05	0.3361	0.3373	0.4101	−0.5673
0.10	0.2427	0.2437	0.3301	−0.4688
0.15	0.1712	0.1721	0.2607	−0.3838
0.20	0.1187	0.1194	0.2034	−0.3512
0.25	0.0813	0.0819	0.1572	−0.4688
0.30	0.0551	0.0556	0.1206	−0.3212
0.35	0.0371	0.0375	0.0921	−0.1812
0.40	0.0248	0.0251	0.0700	−0.1487
0.45	0.0166	0.0168	0.0531	−0.1217
0.50	0.0110	0.0112	0.0401	−0.0984
0.55	0.0073	0.0074	0.0302	−0.0787
0.60	0.0048	0.0049	0.0227	−0.0524
0.65	0.0032	0.0033	0.0169	−0.0260
0.70	0.0021	0.0022	0.0126	−0.0055
0.75	0.0014	0.0014	0.0094	0.0060
0.80	0.0009	0.0010	0.0070	0.0150
0.90	0.0004	0.0004	0.0028	0.0298
1.00	0.0001	0.0002	0.0020	0.0415

For μ_{xc} we took the expression given by Hedin and Lundquist,[20] based on the work of Singwi *et al.*:[21]

$$\mu_{xc}[n(x)] = -0.02902\left[\frac{21}{r_s(x)} + 0.7734\ln\left[1+\frac{21}{r_s(x)}\right]\right] \tag{9}$$

in a.u. (double rydbergs), where

$$r_s(x) = \left[\frac{3}{4\pi n(x)}\right]^{1/3} . \tag{10}$$

Notice that the work function is $\phi[n]$ in Eq. (6). For metallic hydrogen we took the electronic equilibrium bulk density in such a way that $r_s = 1.0$.

The self-consistency of the solution to the set of equations (5)–(7) is not achieved automatically. What we did was to propose an adequate trial effective potential and with it to find the wave functions $\psi_k(x)$. From these wave functions we constructed the density and from it we got the new effective potential. When this new effective potential was not close to the trial potential we changed the trial potential and started the procedure again. The procedure was repeated until we got satisfactory self-consistency. Plotting the trial and the effective potentials was very helpful to find out the changes to make in the trial potential.

Using this procedure we could reproduce the results given by Lang and Kohn for $r_s = 2.0$, also obtaining $\Phi = 4.0$ eV. In Table I we show our calculated density and that of Lang and Kohn for $r_s = 2.0$. In the same table we show the density and the effective potential for metallic hydrogen with $r_s = 1.0$. The resulting work function is $\Phi = 4.67$ eV. In Fig. 2 we show the input and the output for the effective potential, $V_{\text{eff}}[n(x)]$ in the final calculation. It is clear that if the expected value for r_s for metallic hydrogen is between 1.0 and 2.0, we should expect the corresponding value of the work function to be between 4.0 and 4.67 eV.

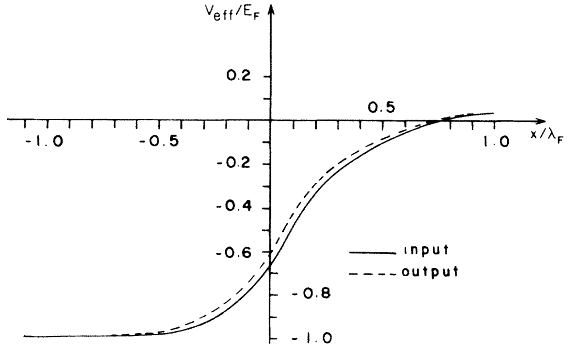

FIG. 2. Self-consistency in the input-output effective potential. Input: ——; output: — — —. The self-consistency is the same as the one obtained for the case $r_s = 2.0$, listed in Table I; $E_F = 50.1$ eV; $\lambda_F = 3.27$ a.u.

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