Two approaches for self consistency in the calculation of screening electron densities

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Abstract. We have calculated the electronic density around an ion in metallic hydrogen using the density functional formalism of Hohenberg, Kohn and Sham. We have a set of self-consistent equations to be solved within this formalism. We have numerically solved these equations using two different approaches. In the first one we have approximate self consistency. This approach had been used previously to calculate the interionic potential and superconducting properties of metallic hydrogen. In the second approach we have full self-consistency by following the method of Manninen *et al.* The results for the density show small differences from one approach to the other and for the effective potentials the differences are even smaller. From the densities we have recalculated the interionic potential for both approaches. The resulting interionic potentials are practically identical.

Resumen. Hemos calculado la densidad electrónica alrededor de un ion en hidrógeno metálico utilizando el formalismo de densidad funcional de Hohenberg, Kohn y Sham. En este formalismo se tiene que resolver un conjunto de ecuaciones autoconsistentes. Resolvimos numéricamente estas ecuaciones utilizando dos enfoques distintos. En el primero, tenemos una autoconsistencia aproximada. Este enfoque ha sido utilizado previamente para calcular el potencial interiónico y las propiedades de superconductividad del hidrógeno metálico. En el segundo enfoque tenemos autoconsistencia completa al seguir el método de Manninen *et al.* Los resultados para la densidad presentan pequeñas diferencias entre ambos enfoques y para los potenciales efectivos las diferencias son todavía más pequeñas. A partir de las densidades hemos recalculado el potencial interiónico con ambos enfoques y resulta prácticamente el mismo.

1. Density Functional Theory

This formalism is due to Hohenberg, Kohn and Sham [1, 2] and states that there exists a local, one body effective potential $V_{\text{eff}}(\mathbf{r})$ which can be used to obtain the exact ground state electron density through solutions of the one particle Schrödinger equation,

$$\left[-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{1}$$

and (μ is the Fermi energy)

$$n(\mathbf{r}) \equiv \sum_{\epsilon_i < \mu}|\psi_i(\mathbf{r})|^2. \tag{2}$$

The effective potential is given by

$$V_{\text{eff}}(\mathbf{r}) = -\phi(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}, \tag{3}$$

where $\phi(\mathbf{r})$ is the total electrostatic potential of the system, and $E_{\text{xc}}[n(\mathbf{r})]$ is the exchange-correlation energy of the system.

When we omit gradient corrections, we can write

$$\frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{d}{dn}\left[n(\mathbf{r})\epsilon_{\text{xc}}(n(\mathbf{r}))\right], \tag{4}$$

where $\epsilon_{\text{xc}}(n(\mathbf{r}))$ is the exchange-correlation energy per particle in a homogeneus electron gas of density n.

Using spherical symmetry, we write the equations to be solved for our case

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + V_{\text{eff}}(r) + \frac{l(l+1)}{r^2} - \epsilon_k\right]r\,R_{lk}(r) = 0, \tag{5}$$

where $R_{lk}(r)$ is a solution to the radial Schrödinger equation of energy $\epsilon_k = (1/2)k^2$, for nonlocalized states.

The potential of the impurity in the electron gas is contained in $\phi(\mathbf{r})$ and, in the absence of the impurity, $R_{lk}(r)$ is proportional to the spherical Bessel function of the first kind, $J_l(kr)$.

Using Eq. (2) we can write the electron displaced density around an ion in the electron gas: $n(\mathbf{r}) - n_0 = \Delta n(\mathbf{r})$,

$$\Delta n(\mathbf{r}) = \frac{1}{\pi^2} \sum_{l=0}^{\infty} (2l+1) \int_0^{k_F} dk \, k^2 \left[|R_{lk}(r)|^2 - |J_l(kr)|^2 \right] + 2 \sum_b |\psi_b(r)|^2, \tag{6}$$

where ψ_b refers to the bound state wave functions.

In order for the impurity to be completely screened, exactly Z electrons must be displaced by it, where Z is the charge of the impurity. For a potential $V_{\text{eff}}(r)$, the number of displaced electrons is given by the Friedel Sum Rule (FSR):

$$Z_F = \frac{2}{\pi} \sum_{l=0}^{l_{\text{max}}} (2l+1) n_l(k_F), \tag{7}$$

where $n_l(k_F)$ are the phase shifts of the potential evaluated at the Fermi level. In this way, for a perfect screening $Z = Z_F$.

For the exchange-correlation contribution to the effective potential, we use the expression given by Hedin and Lundquist [3] which is based on the work of Singwi *et al.* [4] (in double Rydbergs):

$$V_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(r)} = -0.02090 \left[\frac{21}{r_s(r)} + 0.7734 \ln \left(1 + \frac{21}{r_s(r)} \right) \right], \tag{8}$$

where $r_s(r)$ is the local electron gas density parameter evaluated at r, *i.e.*, $(4/3)\pi r_s^3 = 1/n(r)$.

The electrostatic potential obeys Poisson's equation,

$$\nabla^2 \phi = -4\pi D(r), \tag{9}$$

where

$$D(\mathbf{r}) = Z\delta(\mathbf{r}) - \Delta n(\mathbf{r}). \tag{10}$$

In order to have $V_{\text{eff}}(\mathbf{r})$ vanishing at large $\mathbf{r}$, the exchange correlation part is rescaled to

$$V_{\text{xc}}(\mathbf{r}) \to V_{\text{xc}}[n(\mathbf{r})] - V_{\text{xc}}[(n_0)]. \tag{11}$$

We had to solve Eqs. (5), (6), (8), (10) and (11) self consistently in order to obtain the displaced density, and to check the Friedel Sum Rule (Eq. (7)).

2. Methods of Calculation

We have used two approaches in obtaining the solutions for the displaced density.

In the first one we don't have an automatic convergence in successive iterations. We used the method given in Refs. 5 and 6 and we describe it here briefly.

The initial step is choosing a trial potential $V_{tr}(r)$ which satisfies the Friedel Sum Rule, from which we obtain the wave function solving Eq. (1) and we find $\Delta n(r)$ using Eq. (6). This $\Delta n(r)$ is used to generate $V_{eff}(r)$ for which the Friedel Sum is calculated. In general, $V_{eff}(r)$ will not satisfy the Friedel Sum Rule and will not show consistency with $V_{tr}(r)$. The following step was to change $V_{tr}(r)$ and to start the procedure again. The procedure was repeated until we got satisfactory self consistency between $V_{tr}(r)$ and $V_{eff}(r)$ and the correct Friedel Sum. Plotting the trial and effective potentials was very helpful to find out the changes to make in the trial potential. The trial potential we used was

$$V_{tr}(r) = -\frac{1}{r}\left[\frac{e^{-\alpha r}}{1 + \beta r + (\beta^2 + (\alpha + \beta)^2)r^2/2}\right]. \qquad (12)$$

To begin, an initial value of β was chosen, and then α determined so that $V_{tr}(r)$ satisfied the FSR. From this, $\Delta n(r)$ and then $V_{eff}(r)$ and the Friedel Sum were calculated.

Then, a different value of β was chosen, producing a new $V_{tr}(r)$, with an adequate value of α and hence a new $V_{eff}(r)$ with a new Friedel Sum.

For the electronic density parameter we took $r_s = 1.0$ [5, 6, 7]. The Schrödinger equation was solved in steps of $0.05a_0$ (where $a_0 = 0.529$ Å). It was found that going out to $10a_0$ was far enough. The

phase shifts were calculated at $5a_0$. The sums over l were terminated at $l_{max} = 7$.

In the second approach to calculate the displaced density we followed the method of Manninen *et al.* [8], which we describe briefly.

It is always found that by solving the electrostatic potential in each iteration cycle from the equation ($n_+(\mathbf{r})$ is the jellium density)

$$\phi^i(\mathbf{r}) = \int d^3r \left[\frac{n_+(\mathbf{r}) - n^{i-1}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \tag{13}$$

the procedure diverges. The artifice proposed by Manninen *et al* [8] which was found to be successful in solving the Hohenberg-Kohn-Sham equations is the following.

The Poisson equation is written in the form

$$\nabla^2 \phi - k^2 \phi = -4\pi(n_+ - n) - k^2 \phi, \tag{14}$$

with a recursive solution given by [8]

$$\phi^{(i)}(\mathbf{r}) = \frac{1}{4\pi} \int d^3r \frac{e^{-k|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \left[-4\pi(n_+(\mathbf{r}') - n^{(i-1)}(\mathbf{r}')) - k^2 \phi^{(i-1)}(\mathbf{r}') \right]. \tag{15}$$

This equation leads to a sufficient convergence after about 8 iterations, starting with a Thomas-Fermi type potential. The constant k is arbitrary with a convenient numerical value for convergence. The final solution does not depend on the particular value of k.

In this approach we also used a step size of $0.05a_0$ to solve the Schrödinger equation, with a maximum value of r of $10a_0$. The phase shifts were also calculated at $5a_0$ and the sums over l were terminated at $l_{max} = 7$. The value of k for the first seven iterations was $1.7a_0^{-1}$. After that, and in order to increase the speed of conver- gence, we took $k = 1.0a_0^{-1}$. The degree of self-consistency between two succesive iterations we could achieve was of one part in 10^5 for both, the density and the effective potential.

3. Results and Discussion

The calculated displaced densities are shown in Figs. 1,2. We can

see the same overall shape for both densities. We can also see small differences for the value of the density for a given r. In table I we show the density parameter r_s, the Friedel Sum for each calculation and the phase shifts, which were calculated at $r = 5.0a_0$ in both cases. Table II shows the positions of maxima and minima and the values of the densities at these points for both aproaches. In Fig. 3 we present the degree of self-consistency between the input and output effective potentials for the first approach.

The results for the density in the first approach have been used previously to calculate the interionic potential and superconducting properties of metallic hydrogen [5, 7]. Thus, it seems necessary to find out if the small differences in the calculated displaced electron densities are enough to change the predictions made previously for metallic hydrogen [5, 7].

We have used the electron densities obtained from the two approaches to recalculate the interionic potential in metallic hydrogen, following the method described in Refs. 5, 7 and 9. In this method the interionic potential is given by [9]

$$V(R) = \frac{Z^2}{R} - 2Z \int_0^1 d\lambda \left[F_1(\lambda, R) + F_2(\lambda, R) \right], \tag{16}$$

where

$$F_1(\lambda, R) \equiv \int_0^R \frac{4\pi r^2 \Delta n_\lambda(\mathbf{r})}{R} \, dr,$$

$$F_2(\lambda, R) \equiv \int_R^\infty 4\pi r \Delta n_\lambda(\mathbf{r}) \, dr,$$

and λ is such that $0 \le \lambda \le 1$.

We had to calculate $\Delta n_\lambda(\mathbf{r})$ to get $F_1(\lambda, R)$ and $F_2(\lambda, R)$ and the interionic potential. We took $\lambda = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0. The resulting interionic potentials for each approach are shown in Fig. 4, where the interionic potential obtained from the displaced electron densities using the first approach is exactly (one part in 10^5) the one reported in Refs. 5 and 7. The results for the two approaches are practically identical. The phonon dispersion curves and the superconducting properties were obtained in Refs. 5 and 7 from the
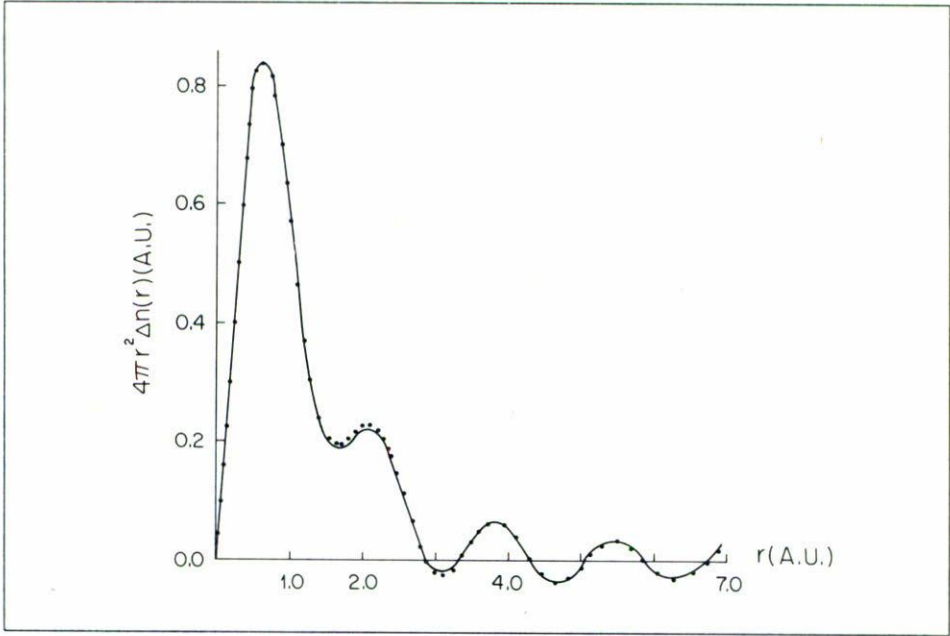
FIGURE 1. Displaced electron densities for metallic hydrogen in a.u. Result using the first approach: ___ ; result using the second approach: ...
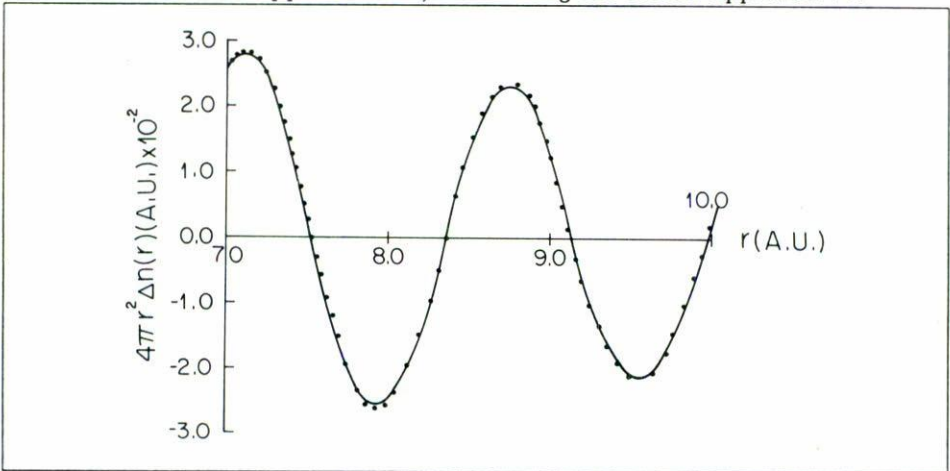

FIGURE 2. Displaced electron densities for metallic hydrogen in a.u. (2nd. part). Result using the first approach: ___ ; result using the second approach: ...

1st. Approach	$r_s = 1.0$ a.u.	2nd. Approach
FSR = 0.99477		FSR = 1.0027
	Phase Shifts	
$n_0 = 0.6273$		$n_0 = 0.6300$
$n_1 = 0.1603$		$n_1 = 0.1590$
$n_2 = 0.4876$		$n_2 = 0.0494$
$n_3 = 0.01670$		$n_3 = 0.01700$
$n_4 = 0.0062$		$n_4 = 0.0061$
$n_5 = 0.0024$		$n_5 = 0.0023$
$n_6 = 0.00010$		$n_6 = 0.0009$
$n_7 = 0.0004$		$n_7 = 0.0004$

TABLE I. Results for the phase shifts and the Friedel Sum Rule (FSR) for metallic hydrogen $r_s = 1.0$ a.u. using both approaches $(4/3)\pi r_s^3 = 1/n_0$.

1st. Approach		$r_s = 1.0$ a.u.		2nd. Approach
$4\pi r^2 \Delta n(r)$ (a.u.)	r (a.u.)		r (a.u.)	$4\pi r^2 \Delta n(r)$ (a.u.)
0.8411	0.65	M	0.63	0.8494
0.1869	1.65	m	1.62	0.1909
0.2184	2.05	M	2.07	0.2282
-0.1792×10^{-1}	3.10	m	3.06	-0.2410×10^{-1}
0.6555×10^{-1}	3.80	M	3.84	0.6410×10^{-1}
-0.3727×10^{-1}	4.70	m	4.68	-0.3970×10^{-1}
0.3446×10^{-1}	5.50	M	5.46	0.3780×10^{-1}
-0.3107×10^{-1}	6.30	m	6.30	-0.3218×10^{-1}
0.2798×10^{-1}	7.10	M	7.14	0.2871×10^{-1}
-0.2522×10^{-1}	7.95	m	7.98	-0.2532×10^{-1}
0.2305×10^{-1}	8.75	M	8.7	0.2338×10^{-1}
-0.2110×10^{-1}	9.55	m	9.54	-0.2138×10^{-1}

TABLE II. Positions of maxima and minima and values of the electronic displaced densities at these points, using both approaches. The positions of the maxima are given by M and the positions of the minima are given by m.
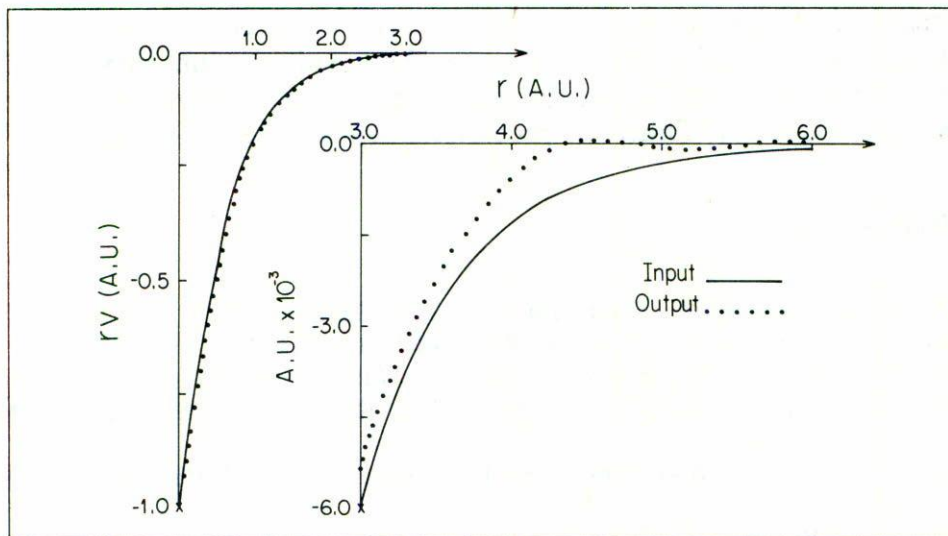
FIGURE 3. Input and output potentials in the first approach. Notice the change of scale in the second frame. This was the degree of self-consistency obtained in Refs. 5, 6 and 7. Input: ___ ; Output: ...
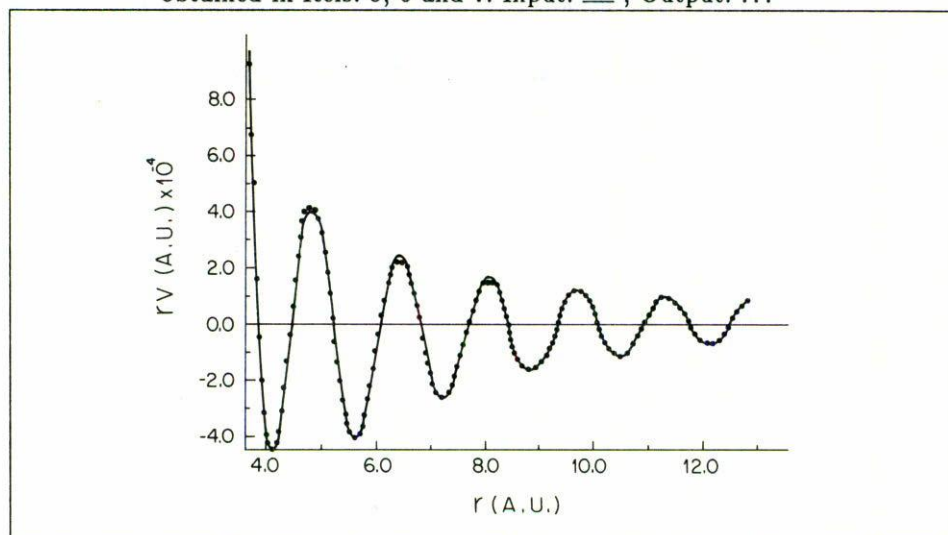

FIGURE 4. Interionic potential for metallic hydrogen. Potential from Refs. 5 and 7 (which was recalculated here): ___ ; potential from the densities obtained from the second approach of this work: ...

interionic potential. In this way, since the interionic potentials are the same, we will obtain the same phonon dispersion curves and the same superconducting properties for metallic hydrogen for the second approach. Thus, the predictions will not be changed.

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