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# Ionic interaction and conductivity of metallic hydrogen

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We calculate the electroresistivity of metallic hydrogen within the framework of perturbation theory in electron-proton interaction. To this end we employ the Kubo linear response theory while using the two-time retarded Green functions method to calculate the relaxation time. The expressions for the second and third order contributions are given. To describe the electron subsystem, the random phase approximation is used, allowing for the exchange interactions and correlations in a local field approximation. Thermodynamics of the proton subsystem is assumed to be given by the Percus-Yevick equation. At a given density and temperature the only parameter of the theory is the hard sphere diameter, which is calculated from effective pair ionic interaction. For a completely degenerated electron gas, the latter is determined by the density of the system. The dependence of the second and the third order contributions on the parameters of the theory is investigated. For all densities and temperatures examined here the third order contribution constitutes more than half of the second order term. The corresponding magnitude of resistivity is about $100 \sim 250 \mu\Omega$ cm.

**Key words:** *metallic hydrogen, electrical conductivity*

**PACS:** *71.10.+x, 72.10.Bg, 72.15.Cz*

## 1. Introduction

Hydrogen is the most widespread element in the universe. The major portion of the mass of the planets in the solar system is contributed by the hydrogen in metallic state. From the theoretical point of view hydrogen is a unique object for which the electon-ion interaction is known exactly. It allows us to perform calculations of various properties involving the minimal number of simplifying assumptions, and therefore, with maximal plausibility.

The possibility for the metallic phase of hydrogen to exist was predicted in 1935 [12]. It was suggested that at high densities hydrogen should exhibit the transition from diatomic molecular state, with insulator properties, to an atomic state with metallic conductivity. The actual discovery of metallic hydrogen and the detailed investigation of conductivity as a function of the pressure and the temperature followed at 1996 [11]. In this study the molecular hydrogen in a liquid state was subjected to shock compression up to 1.80 Mbar at the temperatures in the $2200 - 4400$ K range. The dielectric-metal transition was observed at the pressure of 1.4 Mbar while temperature 3000 K, while the resistivity of metallic phase measured $500\mu\Omega$ cm. In the pressure and the temperature range $1.4 - 1.8$ Mbar and $3000 - 4400$ K the electroresistivity remained virtually unchanged. As a matter of fact, the examined transition was of a metal-semiconductor type, as the band-gap did not vanish completely, but decreased from 15 eV to 0.3 eV, which is almost equal to the temperature of a sample. It should be noted that the earlier experimental and theoretical studies of the conjectured metallic state exist. In the work [6] the electric conductivity of molecular hydrogen was measured at substantially lower pressure of $0.1 - 0.2$ Mbar, the results followed the exponential law with the rate specific to semiconductors with the 12 eV band-gap. The discovery of metallic hydrogen was first reported in [3] in 1978. The authors reported the discovery of metallic hydrogen at the pressure 2 Mbar with the resistivity of $1000\mu\Omega$ cm.

 

When the new substances are discovered, the examination of the static properties usually precede the studies of transport phenomena. At present the research on the static properties of metallic hydrogen is carried out intensively [1,4,5,7–9]. Yet, there are virtually no theoretical investigations of the electron transport phenomena in metallic hydrogen. The distinctive feature of the treatises on static properties of metallic hydrogen is the adoption of the nearly free electron model. Here we are going to employ this model to calculate the electroresistivity of metallic hydrogen. Herein we assume that the hydrogen is in the true metallic state with no band-gap at all, and not in the experimentally observed semiconductor state with the band-gap of 0.3 eV. This state can be realized either at a higher pressure, or at a higher temperature. We should like to note that the Jupiter core with the radius equal to half the radius of the planet, consists of a hydrogen at the pressure of $3-40$ Mbar and the temperature $10000-20000$ K.

## 2. Hamiltonian

We assume the hydrogen to be in a disordered atomic state with all the electrons collectivized. In this case the Hamiltonian of the electron subsystem of metallic hydrogen can be taken in the form similar to that of the liquid simple metals [15]

$$H = H_0 + H_{\mathrm{ie}}. \tag{1}$$

Again, just like in the case of the liquid simple metals, the electron gas is considered degenerated, and the ionic subsystem to be a disordered and static one. Using the nearly free electrons approximation, the Hamiltonian of noninteracting electron gas can be written as

$$H_0 = \sum_{\mathbf{k}} \varepsilon_k a_{\mathbf{k}}^{+} a_{\mathbf{k}}\,, \tag{2}$$

where $a_{\mathbf{k}}^{+}, a_{\mathbf{k}}$ are the operators of nucleation and annihilation of electrons with the wave vector $\mathbf{k}$, $\varepsilon_k = \hbar^2 k^2/2m$ is the free electron energy and $m$ is its mass.

The Hamiltonian of the electron-proton interaction can be taken in line with the diffraction model of a metal, which incorporates the electron-electron interaction via screening of the electron-ion interaction

$$H_{\mathrm{ie}} = V^{-1} \sum_{\mathbf{q}} W(q) \rho^{\mathrm{i}}(\mathbf{q}) \rho^{\mathrm{e}}(-\mathbf{q}). \tag{3}$$

Here $V$ is the volume of the system, $W(q) = -V(q)/\varepsilon(q)$ is the screened potential energy of electron-proton interaction, $V(q) = 4\pi \mathrm{e}^2/q^2$ is the Fourier transform of the Coulomb interaction, $e$ is the electron charge, $\varepsilon(q) = 1 + [V(q) + U(q)]\pi_0(q)$ is the dielectric permittivity of the electron gas in the random phase approximation, $U(q) = -2\pi \mathrm{e}^2/(q^2 + \lambda k_{\mathrm{F}}^2)$ is the potential energy of the exchange interaction and the correlations of the electron gas with $\lambda \approx 2$ [2], $k_{\mathrm{F}}$ is the Fermi wave vector,

$$\pi_0(q) = \frac{m k_{\mathrm{F}}}{\pi^2 \hbar^2} \left( \frac{1}{2} + \frac{4k_{\mathrm{F}}^2 - q^2}{8 k_{\mathrm{F}} q} \ln \left| \frac{2k_{\mathrm{F}} + q}{2k_{\mathrm{F}} - q} \right| \right) \tag{4}$$

is the polarization function of a free electron gas, $\rho^{\mathrm{e}}(q) = \sum_{\mathbf{k}} a_{\mathbf{k}}^{+} a_{\mathbf{k+q}}$ is the Fourier transform of the density operator of the electron gas and $\rho^{\mathrm{i}}(q) = \sum_{\mathbf{n}} \exp(-\mathrm{i}\mathbf{q}\mathbf{R}_n)$ with $\mathbf{R}_n$ denoting the radius-vector of the $n$-th ion.

We should like to stress that the metallic hydrogen is the only system with the exactly known unscreened potential of the electron-ion interaction, which is the Coulomb law. This fact significantly simplifies the calculation of various properties of metallic hydrogen, as long as the problem of modelling the electron-ion interaction, leading to the introduction of additional fitting parameters, is avoided.

Just like in the theory of many of the disordered simple metals, the ratio of the potential energy of the electron-ion interaction to the Fermi energy is the small parameter of the theory not for all values of the wave vector. This situation is illustrated in figure 1. The actual small parameter of the theory is the product of the above mentioned ratio on the structure factor of the ion subsystem.

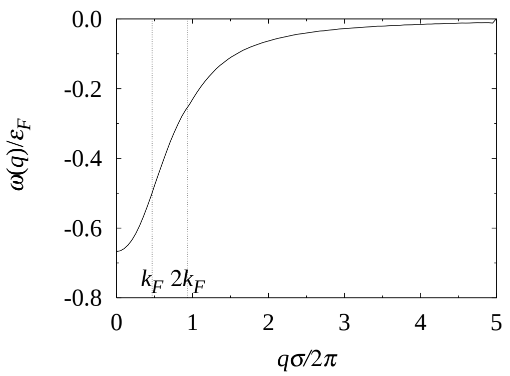


**Figure 1.** The form factor of the screened electron-proton pseudopotential. Two vertical lines denote the values of the wave vector equal to $k_{\mathrm{F}}$ and $2k_{\mathrm{F}}$ correspondingly (scaled with $\sigma/2\pi$). These values correspond to $\sigma = 4au$ and $\eta = 0.45$.

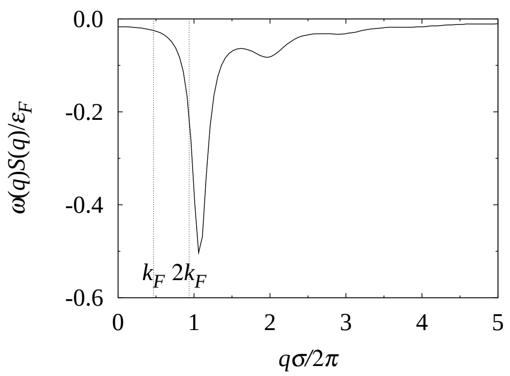


**Figure 2.** The small parameter of the theory. Two vertical lines denote the values of the wave vector equal to $k_{\mathrm{F}}$ and $2k_{\mathrm{F}}$ correspondingly (scaled with $\sigma/2\pi$). These values correspond to $\sigma = 4au$ and $\eta = 0.45$.

From figure 2 it can be seen that again this parameter cannot be considered small for every value of the wave vector. Inasmuch as these values of the wave vector provide substantial contribution to the corresponding integrals, one can expect the perturbation series in this parameter of the theory to converge slowly. This circumstance does not allow us to restrict ourselves to the first term of the perturbation series when calculating the resistivity.

## 3. Resistivity

The electroresistivity of well conducting disordered simple metals can be found using the well known Drude formula

$$R = \frac{m}{ne^2}\tau^{-1}. \tag{5}$$

Here $n$ is the electron gas density and $\tau$ is the relaxation time for the electroconductivity process. We are going to exploit this formula to calculate the resistivity of metallic hydrogen as well. Here we will consider only the electron contribution to the resistivity.

Within the framework of the linear response theory of Kubo and the method of two-time retarded Green functions [2,10] the inverse relaxation time can be written in the form of the series in electron-proton interaction

$$\tau^{-1} = \sum_{n=2}^{\infty} \tau_n^{-1}. \tag{6}$$

The general term of this expansion is of the form

$$\tau_n^{-1} = \frac{N}{V^n} \sum_{\mathbf{q}_1,\dots,\mathbf{q}_n} W(\mathbf{q}_1)\dots W(\mathbf{q}_n) S(\mathbf{q}_1,\dots,\mathbf{q}_n) \Gamma(\mathbf{q}_1,\dots,\mathbf{q}_n). \tag{7}$$

Here $S(\mathbf{q}_1,\dots,\mathbf{q}_n)$ is the $n$-particle structure factor of the ion subsystem, $N$ is the number of ions in the system, $\Gamma(\mathbf{q}_1,\dots,\mathbf{q}_n)$ is the electron multipole for the electric conductivity process.

The second order contribution to the inverse relaxation time for the disordered simple metals, first obtained by Ziman [13], is well explored and reads

$$\tau_2^{-1} = \frac{m}{4\pi\hbar^3\nu k_{\mathrm{F}}^3} \int_0^{2k_{\mathrm{F}}} \mathrm{d}x\, x^3 W^2(x) S(x), \tag{8}$$

where $\nu$ is the inverse proton number density. We now examine the third order contribution in more detail. It is of the form

$$\tau_3^{-1} = \frac{N}{V^3} \sum_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3} W(\mathbf{q}_1)W(\mathbf{q}_2)W(\mathbf{q}_3)S(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\Gamma(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3). \quad (9)$$

For the noninteracting electron gas, the electron multipole, obtained by using the kinetic equation and characterizing the electric conductivity, is of the form

$$\Gamma(\mathbf{k}_1-\mathbf{k}_2,\mathbf{k}_2-\mathbf{k}_3,\mathbf{k}_3-\mathbf{k}_1) = \frac{\beta\pi\hbar}{3mN}(\mathbf{k}_1-\mathbf{k}_2)^2 n(\mathbf{k}_1)[1-n(\mathbf{k}_1)]\frac{\delta(\varepsilon_{\mathbf{k}_2}-\varepsilon_{\mathbf{k}_1})}{(\varepsilon_{\mathbf{k}_2}-\varepsilon_{\mathbf{k}_1})}, \quad (10)$$

where $\beta$ is the inverse temperature and $n(k)$ is the Fermi-Dirac distribution function. With some manipulation [9,11] the third order contribution can be expressed as a principal value integral

$$\tau_3^{-1} = \frac{m^2}{24\pi^5\hbar^5 k_{\mathrm{F}}^2}\int_0^\infty \mathrm{d}k\,\frac{f(k)}{k_{\mathrm{F}}-k}. \quad (11)$$

As long as the electron-electron interaction is exactly known, the major approximation we use is the superposition approximation for the 3-particle structure factor $S(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = S(\mathbf{q}_1)S(\mathbf{q}_2)S(\mathbf{q}_3)$. As a consequence of this approximation we obtain the following expression for the function $f(k)$

$$f(k) = \frac{1}{k_{\mathrm{F}}+k}\sum_{n=0}^{\infty}(2n+1)A_n B_n^2(k), \quad (12)$$

with

$$\begin{aligned} A_n &= \int_0^{2k_{\mathrm{F}}} \mathrm{d}q\, q^3 W(q)S(q)P_n\left(\frac{2k_{\mathrm{F}}^2-q^2}{2k_{\mathrm{F}}^2}\right), \\ B_n(k) &= \int_{|k-k_{\mathrm{F}}|}^{k+k_{\mathrm{F}}} \mathrm{d}q\, qW(q)S(q)P_n\left(\frac{k^2+k_{\mathrm{F}}^2-q^2}{2kk_{\mathrm{F}}}\right), \end{aligned} \quad (13)$$

where $P_n(x)$ is the Legendre polynomial of order $n$.

## 4. The effective pair proton interaction

The effective pair proton interaction is an essential component in estimating the conductivity of metallic hydrogen. It is a particularly valuable feature since the only parameter on which it depends is the number density of the system. Since the effective pair interaction makes it possible to calculate the effective hard sphere diameter for a given temperature, it enables us to determine the hard sphere diameter as a function of density and temperature.

The expression for the effective pair potential is known from the second order perturbation theory in electron-ion interaction and reads

$$V_{\mathrm{eff}}(R) = \frac{\mathrm{e}^2}{R} - \frac{\nu}{\pi^2}\int \mathrm{d}q q^2 \frac{\sin(qR)}{qR}Q(q), \quad (14)$$

where

$$Q(q) = \frac{\nu}{2}V^2(q)\frac{\pi(q)}{1+V(q)\pi(q)}. \quad (15)$$

The polarization function of electron gas with exchange interaction and correlations taken into account in a local field approximation can be written as

$$\pi(q) = \frac{\pi_0(q)}{1+V(q)\pi_0(q)}. \quad (16)$$

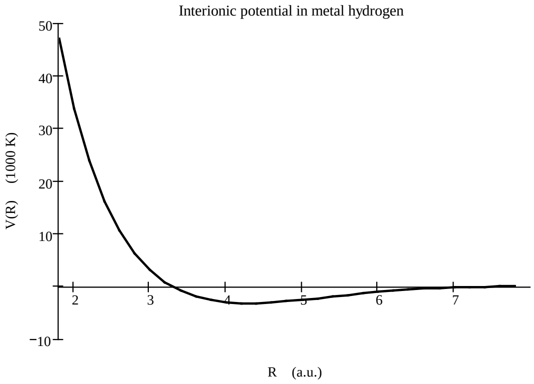


**Figure 3.** The effective pair interaction, $n = 0.001$ gm/cm$^3$.

This expression does not contain any fitting parameters characterizing the ion subsystem and depends only on the Fermi wave vector, i.e. on the number density of the system. The only approximation it involves is the random phase approximation for the electron subsystem taking into account the exchange interaction and electron correlations in a local field approximation.

Figure 3 provides the plot of the effective pair ion interaction for a number density $n = 0.001$ gm/cm$^3$. Now we can introduce the effective hard sphere diameter as the minimum ion approach distance for a given temperature. This distance can be found from equating the total energy of protons to zero at the closest approach

$$V_{\text{eff}}(\sigma) = 3kT/2. \tag{17}$$

Here the reference point for potential energy is the lowest value of the potential well. For instance at $n = 1 mole/cm^3$ and $T = 10^3$ K $\sigma = 2.77$, while raising the temperature to $T = 10^4$ K at the same density we obtain $\sigma = 1.64$. In the first case the packing fraction is $\eta = 0.45$, which roughly corresponds to the value for the liquid alkali metals at melting point, in the second case $\eta = 0.08$.

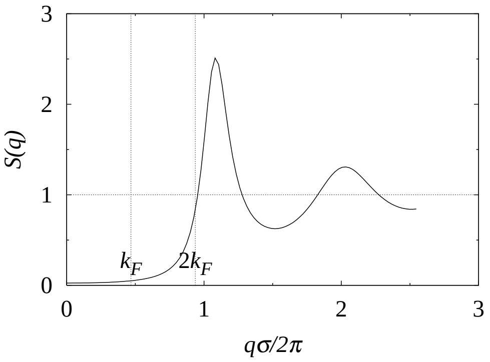


**Figure 4.** The pair structure factor of the ion subsystem. Two vertical lines denote the values of the wave vector equal to $k_\text{F}$ and $2k_\text{F}$ correspondingly (scaled with $\sigma/2\pi$). These values correspond to $\sigma = 4au$ and $\eta = 0.45$.

## 5. Results and discussion

If for the structure factor of the ion subsystem we use the Percus-Yevick equation [14] (see figure 4), then the resistivity depends on three parameters. Namely these are the hard sphere diameter, the packing fraction and the Fermi wave vector. If all the electrons are considered collectivized, then the Fermi wave vector can be related to the number density through $\nu = 3\pi^2/k_\text{F}^3$, while on the other hand $\nu\eta = \pi\sigma^3/6$. It is convenient to choose the hard sphere diameter as the independent parameter. If the temperature is known, this parameter can be uniqely defined as well.

**Table 1.** The coefficients of the series in (12).

| $n$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $A_n$ | –2.031 | 1.210 | –0.487 | 0.168 | –0.050 | 0.013 | –0.002943 | 0.0005285 |

As we see from the table 1 the coefficients $A_n, B_n(q)$ quickly decay with the increase of $n$. This means that we need to allow for only a few terms of the corresponding series. As long as liquid hydrogen exists in nature in a wide pressure and temperature range it is interesting to investigate the dependence of resistivity on parameters $\sigma$ and $\eta$. From figures (5), (6) we can see that the

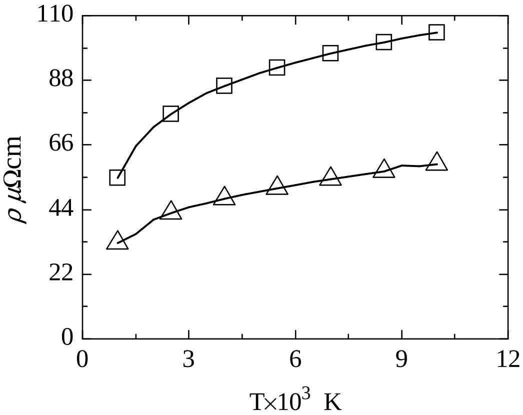


**Figure 5.** The dependence of the resistivity on the temperature. Solid line: 2nd order contribution; dotted line: 3rd order contribution. $n = 0.025$ au$^{-3}$.

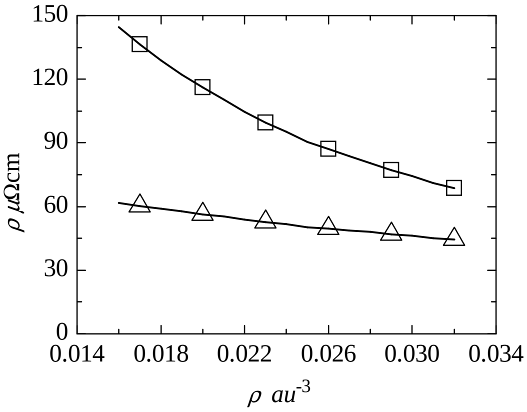


**Figure 6.** The dependence of the resistivity on the number density. Solid line: 2nd order contribution; dotted line: 3rd order contribution. $T = 5000$ K.

electron gas is strongly degenerated at all densities and temperatures considered. The second order contribution to electoresistivity is of the same order as for majority of the liquid metals that are well described using the nearly free electrons approximation. On the other hand, the third order contribution constitutes more than 50% of the second one, which is typical of liquid metals with relatively high resistivity. Consequently, we can expect a slow convergence of the pertutabation theory series for electric conductivity. This is caused by a relatively large magnitude of the above mentioned small parameter of the theory. If we approximate the perturbation series by an infinite geometric progression with the ratio $R_3/R_2 = 0.43$, then the electric resistivity measures $R \approx 250\mu\Omega$ cm at $T = 5000$ K, $n = 0.016$ au and $R \approx 195\mu\Omega$ cm at $T = 5000$ K, $n = 0.032$ au. As the density increases at a fixed temperature, the magnitudes of both second and third contributions decay, while the relative magnitude of the third order contribution increases. The estimated resistivity here decays as well, which is typical of metallic conductivity. If we keep the density fixed and increase the temperature, then both contributions grow together with the estimated resistivity which is again characteristic of metallic conductivity. This can be illustrated with the following numbers: $R \approx 135\mu\Omega$ cm at $T = 1000$ K and $n = 0.025$ au, $R \approx 243\mu\Omega$ cm at $T = 10000$ K and $n = 0.025$ au. The experimentally observed resitivity of $R \approx 500\mu\Omega$ cm was not the intent of this work. However, the values obtained are in reasonable agreement with this value. To provide a better estimate of the experimentally observed resisitivity, the theory should allow for the band gap in the energy spectrum of electrons, and for the presence of the hydrogen in molecular state in experimental setups.

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## Міжіонна взаємодія і провідність металевого водню


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В роботі розрахована провідність рідкого металевого водню в рамках теорії збурень, запропонованої одним з авторів, з урахуванням членів другого і третього порядків за електрон-протонною взаємодією. Запропонований також варіант підсумовування ряду теорії збурень. Коефіцієнт електропровідності знаходився у відповідності до теорії лінійної реакції Кубо і метода двочасових загаяних функцій Гріна. При цьому для електронної підсистеми використовувалось наближення випадкових фаз з урахуванням обмінної взаємодії і кореляцій у наближенні локального поля, а для протонної – точний розв'язок рівняння Перкуса-Євіка для моделі твердих сфер. У цьому разі, при заданій густині і температурі єдиним параметром теорії є діаметр твердих сфер. Для його визначення розраховувалась парна ефективна міжпротонна взаємодія. Для повністю виродженого електронного газу остання повністю визначається густиною системи. За знайденою залежністю міжпротонної взаємодії від відстані і відомій температурі визначався діаметр твердих сфер. Провідність металевого водню досліджена у широкому діапазоні густин і температур, характерних як для експерименту по отриманню металевого водню у земних умовах, так и для газових планет гігантів. Ця залежність є такою ж як і для більшості простих рідких металів. Роль членів старшого порядку теорії збурень виявилась надзвичайно великою, змінюючи у декілька разів результат другого порядку теорії збурень.

**Ключові слова:** *металевий водень, теорія збурень, електроопір*

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