MANYPARTICLE INTERACTIONS AND LOCAL STRUCTURE OF THE METALLIC HYDROGEN AT ZERO PRESSURE

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On the basis of the perturbation expansion for electron gas energy in the third order to the electron-ion potential the pair and irreducible three-ion interaction potentials in metallic hydrogen are calculated. The irreducible potential of three-ion interaction has attractive nature at short interionic separation and oscillates at large ones. The anisotropic character of the three-ion interaction is shown. The potential relief of the ions pair relative to the third ion is constructed. This relief has some potential wells and valleys which connect them. The important role of the irreducible three-ion interaction in formation of the local order in three- and four-ion clusters is shown. The potential relief of an equiangular ion triplet relative to the fourth ion is calculated. This relief has deep potential well for fourth ion at interionic separation corresponding interproton separation in molecule H₂. The quasiclassical probability of ion transition into this well is evaluated. The life time of metallic phase of hydrogen relative to the tunneling nucleation of the H₂ molecules is estimated.

Key words: metallic hydrogen, three-ion interaction, life time.
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1. Introduction

The significance of manyparticle interactions and their role in forming the structure and properties of various condensed systems are not well known yet [1]. For a calculation of manyparticle interaction potentials the knowledge of the linear and nonlinear response functions of electron gas is necessary. At present the explicit form of three-pole diagram expression in ring approximation for homogeneous electron gas is known [2], [3]. It was possible to calculate the equilibrium structures and dynamic properties of simple metal crystals and metallic hydrogen (MH) in the third order to the electron-ion potential (EIP) [3]-[9], to study three-ion interaction potentials in simple metals [3], [7].

The study of the possibility of metastable state of MH at zero pressure is of special importance [4]. In a case of solid MH calculations have been performed by Brovman and Kagan. They calculated the structure, elastic properties, phonon spectrum of the solid MH at zero pressure and proved the local stability of the metastable MH phase in framework of the manyparticle theory of metals [4]. As it turned out in the third order to the EIP the energy minimum exists for twoparameter hexagonal lattices with triangular string structure [4]. For all structures with energy minimum the elementary cell volume was Ω₀ = 20.8a_B³ (a_B is the Bohr radius) and interproton spacing fixed along Z axis was equal to d = 2.04a_B. The investigations of the higher order approximations did not change conclusions essentially. It is connected with the fact that eventually the small parameter in the perturbation expansion for MH energy at P=0 approximately equals to 1/5 [4],[5]. In such a case the sum of all perturbation expansion terms with orders n ≥ 5 gives an error as the dielectric permittivity of the uniform electron gas does [5],[6].
The estimate of the life time of the metastable MH phase relative to spontaneous quantum tunneling transition in the insulating phase is among the most important problems. This estimate cannot be made without consideration of the specific microscopic mechanism of the nucleation of $H_2$ molecules or $H_2^+$ ions in metallic phase. For the MH as a system in which the tendency to diatomically ordering exists [8], the calculations of interionic interactions potentials and elucidation of this tendency on the language of groups ion interaction potentials in configurational space have great interest. In the quantum kinetics of the new phase formation two characteristic times may be distinguished [10]. In the first place the time of transition through potential barrier (in our case the life time of the metallic phase relative to the nucleation of the $H_2$ molecule). In the second place the total time of the new phase formation. As a consequence of a significant difference between electron and proton masses during the process of molecular hydrogen phase homogeneous nucleation the characteristic time will be determined by slow ionic motion in potential relief created by nearest neighbouring ions group. Diatomically ordering in MH corresponds to the possibility of the drawing together of ions to the distance corresponding to the interatomic separation in molecule $H_2$. Inasmuch the direct interionic interaction corresponds to the Coulomb repulsion the possibility of drawing ions together may be ensure only by means of indirect ions interaction through surrounding electron gas.

The purpose of this paper is to consider pair- and three-ion interactions in metastable MH at $P=0$. The consideration is based on the many-particle Brovman and Kagan approach [3]-[6]. The peculiarities of the potential relief for ions group are discovered and interpreted from the point of view many-particle tunneling formation of the molecular hydrogen phase.

In sec. 2 expressions for many-particle potentials are received. In sec. 3 and sec. 4 results of calculations are shown.

2. Many-body interaction in metals

In the framework of many-particle theory of non-transition metals the energy of electron subsystem in the field of fixed ions in the adiabatic approximation may be written [3]:

$$ E_e = \varphi_0 + \sum_n \varphi_1(R_n) + \frac{1}{2!} \sum_{m \neq n} \varphi_2(R_n, R_m) + \frac{1}{3!} \sum_{m \neq n \neq l} \varphi_3(R_n, R_m, R_l) + \cdots (1) $$

where each term of the (1) series describes interaction of ion groups through the surrounding electron gas and can be represented as a power series in the EIP [3]. For example

$$ \varphi_2(R_1, R_2) = \sum_{i=2}^{\infty} \Phi_2^{(i)}(R_1, R_2), $$
$$ \varphi_3(R_1, R_2, R_3) = \sum_{i=3}^{\infty} \Phi_3^{(i)}(R_1, R_2, R_3), (2) $$

etc. The indirect interaction of two ions in second order perturbation theory in EIP is well known [11] and equal to

$$ \Phi_2^{(2)}(R) = \frac{1}{\pi^2} \int_0^{\infty} dq q^2 \Gamma^{(2)}(q)|V(q)|^2 \frac{\sin(qR)}{qR}, (3) $$
where $V(q) = -\frac{4\pi^2}{q^2}$ is the form factor of the EIP; $\Gamma^{(2)}(q)$ is the sum of two-pole diagrams.

In the third-order perturbation theory in EIP the indirect pair-ion interaction is defined by the expression

$$\Phi^{(3)}_2(R) = \frac{3}{4\pi^4} \int_0^{\infty} dq_1 q_1^2 \int_0^{\infty} dq_2 q_2^2 \int_{-1}^{1} dx V(q_1) V(q_2) V(q_3) \Gamma^{(3)}(q_1, q_2, q_3) \times$$

$$\times \frac{\sin(q_1 R)}{q_1 R},$$

(4)

where $\Gamma^{(3)}(q_1, q_2, q_3)$ is the sum of three-pole diagrams; $q_3 = (q_1^2 + q_2^2 + 2q_1q_2x)^{1/2}$.

The potential of indirect three-ion interaction after double integration may be written

$$\Phi^{(3)}_3(R_{12}, R_{23}, R_{13}) = \frac{3}{2\pi^4} \int_0^{\infty} dq_1 q_1^2 \int_0^{\infty} dq_2 q_2^2 \times$$

$$\times \int_{-1}^{1} dz V(q_1) V(q_2) V(q_3) \Gamma^{(3)}(q_1, q_2, q_3) \int_{0}^{1} dx \times$$

$$\times \cos \left( x \left( q_1 R_{12} + R_{23}^2 - R_{13}^2 \right) + q_2 R_{23} z^2 \right) \right) \times$$

$$\times J_0 \left( q_1 R_{12} \left( 1 - x^2 \right)^{1/2} \left( 1 - \frac{R_{12}^2 + R_{23}^2 - R_{13}^2}{4R_{12}^2 R_{23}^2} \right)^{1/2} \right) \times$$

$$\times J_0 \left( q_2 R_{23} \left( 1 - x^2 \right)^{1/2} \left( 1 - z^2 \right)^{1/2} \right),$$

(5)

where $J_0(x)$ is Bessel function of zeroth order; $z = \cos(q_1, q_2)$; $R_{12}$, $R_{23}$, $R_{13}$ - the distances between the vertices of a triangle formed by the protons.

The calculations of potentials were executed at the Wigner-Zeitz radius $r_S = 1.65$ which corresponds to zero pressure in the zeroth model of a metal. A permittivity function in the Heldart-Vosko form was employed. The collections of potential values were calculated on set with step equal to 1 Bohr radius for each dimension. In the drawings of graphs was used cubic-spline interpolation.

3. Results

Pair interionic potential in the third order has a form

$$\varphi^*(R) = \frac{e^2}{R} + \Phi^{(2)}_2(R) + \Phi^{(3)}_2(R),$$

(6)

where $e$ is the electron charge.

Figure 1 shows computed potential $\varphi^*(R)$ and its components. The curve 1 corresponds to contribution $\frac{e^2}{R} + \Phi^{(2)}_2(R)$, 2 - $\Phi^{(3)}_2(R)$, 3 - $\varphi^*(R)$. Pair interionic potential $\frac{e^2}{R} + \Phi^{(2)}_2(R)$ hasn’t deep potential well. Stevenson and Ashcroft have obtained pair interproton potential $\frac{e^2}{R} + \Phi^{(2)}_2(R)$ for MH at $r_S = 1.6$ analogous to
showed in Fig. 1 (curve 1). Indirect interionic interaction \( \Phi_2^{(3)}(R) \) has attractive nature and forms potential well for nearest neighbouring ion and minimum in the repulsive part of the potential \( \varphi^*(R) \). The decrease of the density leads to strong increase of the deep of minimum in the repulsive part of the potential \( \varphi^*(R) \). The curve 1 at the Fig. 2 corresponds to potential \( \varphi^*(R) \) at \( r_S = 1,72 \). At \( r_S < 1,65 \) the minimum in the repulsive part of \( \varphi^*(R) \) turns shallow and its position shifts towards smaller \( R \) and at \( r_S = 1,55 \) this minimum disappears (curve 2 in Fig. 2). The position of minimum in the repulsive part of \( \varphi^*(R) \) in the Fig. 1 corresponds to separation \( R = 1,6a_B \). It should be mentioned that the separation between nuclei in \( H_2 \) molecule is equal to \( 1,4a_B \) and binding length in \( H_2^+ \) ion is equal to \( 2a_B \) \[13\].

The results of calculation of the irreducible three-ion interaction potential \( \Phi_3^{(3)} \) for \( r_S = 1,65 \) are presented in Fig. 3 in form of the potential relief. The minimal interproton separation in metallic phase at \( P=0 \) equals to \( 2,04a_B \) \[14\]. Two ions are placed in ordinate axis on distance \( 2a_B \) and third ion is sited in plane XOX. For small distances the potential \( \Phi_3^{(3)}(2, R_{23}, R_{13}) \) has attractive character. The potential \( \Phi_3^{(3)}(2, R_{23}, R_{13}) \) has anisotropic form and its most rapidly changing takes place in OX direction. For large distances the potential \( \Phi_3^{(3)} \) has oscillatory character. Note that \( \Phi_3^{(3)}(0, 0, 0) \simeq -1 \text{ Ry} \).

Fig. 4 (geometry coincides with Fig. 3) shows potential relief for the 3-rd ion in the fields of two other ions with pair interactions taken into account, that is the potential \( \varphi^*(R_{23}) + \varphi^*(R_{13}) \). The minima B and D and a valley which connects them correspond to the possible positions of the nearest neighbouring ion in the field of two fixed ions (see Fig. 4). It should be noted that ion transition from minimum B to minimum D along the valley entails the crossing the potential barrier with height \( \sim 1200 \text{ K} \). This situation remains unchanged when irreducible three-proton interaction is taken into account because of the short-acting character of potential \( \Phi_3^{(3)} \). The quantum consideration of ion motion in the field of two fixed ions results to conclusion about splitting of energy level for ion which is the nearest neighbour for pair considered. The local minima A and C in Fig. 4 correspond to distances to ion 1 and 2 which are less than interionic average distance.

Fig. 5 shows the potential relief which is created ions pair and taking into account pair- and three-ion interactions. It is described by function \( \varphi^*(R_{23}) + \varphi^*(R_{13}) + \Phi_3^{(3)}(2, R_{23}, R_{13}) \). The change of local minima A,B,C,D positions as compared with Fig. 4 is unimportant. As a consequence of short-range and anisotropic character of potential \( \Phi_3^{(3)} \) the depth of minimum A changes markedly and the depth of minimum B increases a bit. The ion wave function in potential relief which is shown in Fig. 5 has nonzero value near local minima A and C. This means that ions have finite probability draw together to separation of the order of internuclei distances in \( H_2 \) or \( H_2^+ \). From comparison of Fig. 1 and Fig. 5 the conclusion follows that the presence of third ion essentially increases this probability.

Fig. 6 shows computed distribution of conditional probability density for ion positions in ions pair field with pair and three-ion interactions taken into account.
in Boltzmann approximation at temperature $T = 1000$ K. In this approximation distribution of the conditional probability density may be described in the form

$$F_1(R_1|R_2, R_3) \sim \exp \left( -(\varphi^*(R_{12}) + \varphi^*(R_{13}) + \Phi_3(3)(R_{12}, 2, R_{13}))/kT \right),$$  \hspace{1cm} (7)$$

where $k$ is Boltzmann constant. Local minima of the potential relief at Fig. 5 correspond to peaks of the function $F_1(R_1|R_2, R_3)$.

It is interesting to consider the potential relief which is created by group of ions. Fig. 7 shows potential relief which three ions forming equiangular triangle with side $2a_B$ and placing in XOY plane create in the same plane towards fourth ion. In Fig. 7 the pair-ion interaction is taken into account and potential relief assigns to function $\varphi^*(R_{14}) + \varphi^*(R_{24}) + \varphi^*(R_{34})$. It is easy to see two minima A and B and saddle point C in XOY plane.

Potential relief which is shown in Fig. 8 (the geometry is the same as in Fig. 7) and which is described by function

$$\varphi^*(R_{14}) + \varphi^*(R_{24}) + \varphi^*(R_{34}) + \Phi_3(3)(2, R_{24}, R_{14}) +$$

$$\Phi_3(3)(R_{24}, 2, R_{34}) + \Phi_3(3)(R_{14}, R_{34}, 2)$$  \hspace{1cm} (8)$$
takes into account three-ion interactions in the cluster of four ions. Three-ion interactions transform the saddle C into local minimum and minima A and B become deeper considerably. This means that an increase of the particles number in cluster lowers the potential barrier to diatomic ordering.

If three ions are situated so as is shown in Fig. 8 and the fourth ion is placed on Z-axis, the dependence of potential with pair- and three-ions interactions taken into account is shown in Fig. 9. The presence of deep minimum at $z = a_B$ is characteristic peculiarity of this dependency. Second minimum at $z = 3, 5a_B$ corresponds to equilibrium position of fourth ion.

The quantum description of ion motion in two-well potential of Fig. 9 yields the conclusion about a possibility of tunneling transition from well A to well B. The probability of ion transition per 1 s is equal to product of the ion oscillation frequency in well A and transmission coefficient through potential barrier. The transmission coefficient can be estimated in quasiclassical approach. The ion frequency of zero-oscillation in the well A is equal to $\nu = 3, 61 \cdot 10^{13}$ Hz. The transmission coefficient through potential barrier $D = 3, 85 \cdot 10^{-12}$. Then ion life time $\tau$ in well A is equal to $\tau = (D\nu)^{-1} = 0, 0072$ s. If ion transition into well B takes place the conditions for electrons localization on ion pairs will be created. Taking into consideration also small characteristic time of an electron subsystem it is possible to consider obtained time as characteristic time of the tunneling nucleation of $H_2$ molecule in MH at zero pressure. If the identity ions is taken into account it is possible to make a conclusion about manyionic tunneling mechanism for metallic hydrogen transition into molecular phase.

The quantum Monte-Carlo simulations of the molecular hydrogen \[14\] and calculations of the diatomic phase energy as function of the interproton separation \[8\] indicate that at chosen density the molecular unit interproton separation is somewhat less than the neutral molecule separation $1, 4a_B$. We calculated the potential
relief which is created by ions pair with interproton separation 1,5a_B (Fig. 10,11). Fig. 10 shows potential relief for the third ion in the field of two other ions with pair-ion interaction in third order perturbation theory (analogous to Fig. 4). Fig. 11 (geometry coincides with Fig. 10) shows potential relief for the third ion with pair and irreducible three-ion interactions taken into account, that is the potential \( \varphi^*(R_{12}) + \varphi^*(R_{23}) + \Phi_3^{(3)}(1.5, R_{13}, R_{23}) \). As is easily seen from Fig. 10,11, the irreducible three-ions interaction essentially deepens the potential well A (Fig. 11 is analogous to Fig. 5). The comparison of Fig. 5 and Fig. 11 yields the conclusion about strong dependence on the interproton separation \( R_{12} \) of the probability of triplet ions drawing together to the interproton separation as in molecule \( H_2 \). The time of the proton transition from well B into well A (Fig. 11) cannot be considered as characteristic time of the tunneling nucleation \( H_2 \) molecule in metallic phase since interproton separation \( R_{12} = 1.5a_B \) is less than minimal interproton separation in MH phase at \( P=0 \) which equals to 2,04a_B [1].

4. Discussion and conclusions

Our consideration is based on the assumption that metastable MH phase exists at \( P=0 \). The calculations show that irreducible three-ion indirect interactions have decisive influence on the local structure of the ionic subsystem. The calculations of the possible MH structures at \( P=0 \) show the tendency for MH to crystallize in triangular string with two-dimensional periodicity structure [1]. Our calculations of the potential relief which three ions create towards fourth ion confirm this conclusion and show that taking into account \( \Phi_3^{(3)} \) really leads to formation of the hexagonal structure in the plane of four ions arrangement. Taking into account \( \Phi_3^{(3)} \) leads to transformation of the saddle C (Fig. 7) in local minimum (Fig. 8). Minimum C is formed along direction which forms angle 60\(^\circ\) with OX axis (the curves on Fig. 7, 8 are drawn with a step 15\(^\circ\)).

It is possible to observe an interesting peculiarity of the potential relief which ion pair creates towards third ion (Fig. 4,5,6): local minima B and D and valley which connects them and has saddle point. To make transition from minimum B to D it is necessary to cross over the potential barrier. This means that energy levels of the third ion in field of two fixed ions are split. The quantum effect of energy levels splitting will be exercised at temperatures which are less than potential barrier height. It should be noted here that as a consequence of short-range character of potential \( \Phi_3^{(3)} \) it has weak influence on this effect (Fig. 4,5). It can be supposed that the existence of two-level subsystems in amorphous solids at low temperature is somehow the display of collective quantum oscillatory states of three particle groups.

In this study the peculiarities of the pair- and three-ion interactions are interpreted as the vestiges of the molecular phase in metastable MH. These peculiarities occur in metastable metallic phase and are absent at megabar pressure (Fig. 2). This means that electron-proton system possesses a self-organization effect of the ”preparing” a transition to the molecular phase. Such effect increases sharply with decreasing of the electron gas density.

The probability of ions drawing together to the interproton separation as in molecule \( H_2 \) depends essentially on the electron gas density. With a density decreasing the probability of the manyionic tunneling nucleation of the molecules \( H_2 \)
sharply increases. Therefore some interest has a study of the life time of metastable MH relative to the homogeneous nucleation of the molecular phase in pressure interval $0 < P < P_t$ ($P_t$ is the pressure of the molecular hydrogen transition in metallic phase).

The calculation of the life time of the MH as macroscopic system needs the consideration both the mechanism of homogeneous nucleation of molecular phase and kinetics of formation of the insulating phase droplets in the metastable metal. In this paper we did not consider a kinetic stage. Such consideration must include a search of volume and surface free energy minimum of heterogeneous system consisting of metastable metal and insulating droplets. In accordance with the classical and quantum theories of the new phase formation [10],[15],[16] calculated in this paper life time of metallic phase relatively tunneling nucleation of the $H_2$ molecule may differ from life time of MH as macroscopic system by a factor $\sim 3-5$. The new experimental data on structures and phase diagrams for molecular hydrogen and deuterium at megabar pressure [17], [18] may be very useful by consideration of the kinetic stage of the formation and growth of the insulating phase droplets in the metastable MH.

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**Figure captions**

Fig. 1. Potential $\varphi^*(R)$ and its components for $r_S = 1, 65$.

Fig. 2. Potential $\varphi^*(R)$ for $r_S = 1, 72$ and $r_S = 1, 55$.

Fig. 3. Irreducible three-ion interaction potential $\Phi_3^{(3)}(2, R_{13}, R_{23})$.

Fig. 4. Potential relief for the 3-rd ion in the field of two ions with pair interactions taken into account.

Fig. 5. Potential relief for the 3-rd ion in the field of two ions with pair- and three-ion interactions taken into account.

Fig. 6. Distribution of conditional probability density for ion positions in ions pair field.

Fig. 7. Potential relief which three ions create toward fourth ion (pair interactions taken into account).

Fig. 8. Potential relief which three ions create toward fourth ion (pair- and three-ion interactions taken into account).

Fig. 9. The dependence of potential $\Phi(z)$.

Fig. 10. Potential relief for the 3-rd ion in the field of two ions (interionic separation is equal to $1.5a_B$) with pair interactions taken into account.

Fig. 11. Potential relief for the 3-rd ion in the field of two ions (interionic separation is equal to $1.5a_B$) with pair- and three-ion interactions taken into account.