SOLVATION FREE ENERGY OF ISOLATED IMPURITY IN SIMPLE LIQUID METAL

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The "liquid metal + negative impurity" system is discussed. The generalized microscopic Anderson model in the Hartree—Fock (HF) approximation is used to describe the charge and magnetic states of an impurity. The scattering of conduction electrons by the charged impurity are included in the model Hamiltonian. The solvation free energy of the charged impurity is obtained through the connection with two-time Green's functions and the thermodynamical averages.

1. Introduction

Since the pioneering work of Anderson [1], the model of localized impurity atom has been applied to different systems [2], and the variety of solutions and methods have been reported. Notable among them are the solutions given by [3]. In our previous papers [4, 5] we presented the generalized Anderson model to describe the states of negative impurities in liquid metal. In those papers, a solution in terms of Green's functions was obtained in the HF approximation. The limits of the applicability of the proposed model to a description of real systems are considered in [6].

The main aim of the present paper is to find the analytical expression for the solvation free energy which determines the excess free energy associated with the insertion of an impurity atom in liquid metal. The ground-state energy for the Anderson model of a dilute alloy was derived in [8], and this analytical expression agrees with experimental results [9]. Since the work of Newns [7], the Anderson model has been applied to chemisorption theory, and this expression has been used to calculate the chemisorption energy as well [10].

The paper is organized as follows: in Section 1, we consider a model Hamiltonian and the main processes of scattering of conduction electrons. For the sake of clarity, in the next section, we repeat some of the results and equations of our previous paper [4]. The expressions for a Green's function was obtained in the self-consistent HF approximation in the quasi-crystalline case. In the final section, the solvation free energy is given in terms of an integral over the single-particle Green's function (GF) of a localized state following the scheme of [8].

2. Microscopic Model of the "Metallic Alloy + Gaseous Impurity" System

Let us consider a separate gaseous impurity dissolved in liquid alkaline metal. The liquid-metal phase will be described within the framework of the electron - ionic model which gives a satisfactory computational description of electronic and structural properties for such metals.

Let $\mathbf{R}_1, \ldots, \mathbf{R}_N$ be the coordinates of atoms of a metallic alloy which accept arbitrary values in a volume V. The impurity has a coordinate $\mathbf{R}_0$. We selected the following full model Hamiltonian in the coordinate representation:

$$\hat{H} = E_{\mathrm{cl}} + \hat{H}_{\mathrm{el-i}} + \hat{H}_{\mathrm{el-el}}. \tag{2.1}$$

The energy operator of the electron-ion interaction is written as follows:

$$\hat{H}_{\mathrm{el-i}} = -\frac{\hbar^2}{2m} \sum_{1 \leq i \leq N} \Delta_i + \sum_{1 \leq i \leq N} \sum_{1 \leq j \leq N} V(\mid \mathbf{r}_i - \mathbf{R}_j \mid) +$$

$$+ \sum_{1 \leq i \leq N_e} V_0(\mid \mathbf{r}_i - \mathbf{R}_0 \mid). \tag{2.2}$$

In this formula, $\mathbf{r}_1, \ldots, \mathbf{r}_N$ are the electron coordinates of the metallic subsystem, the amount of which coincides with the number of metal atoms due to the one-valence of alkaline elements. It is assumed that the electrons of the valence impurity shell remain localized on the impurity.

The pseudopotentials $V(|\mathbf{r}_i - \mathbf{R}_j|)$ and $V_0(|\mathbf{r}_i - \mathbf{R}_0|)$ describe the electron scattering on ions of the metal and the impurity, respectively.

The first term in formula (2.2) is the operator of kinetic energy of the free electron subsystem.

The last term in (2.1) describes the energy of the pairwise electron-electron interaction

$$\widehat{H}_{\mathrm{el-el}} = \frac{1}{2} \sum_{1 \leq i \neq j \leq N} \Phi(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{1}{2} \sum_{1 \leq i \neq j \leq N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

The non-operator part E_{cl} describes the energy of the classical ion-ion interaction.

In the representation of secondary quantization, operator (2.1) with regard for only a certain class of Coulomb electron-electron interactions has the following form [4]:

$$\widehat{H} = E_{\mathrm{cl}} + \sum_{\mathbf{k} \in \Lambda} \sum_{\sigma = \pm 1} E_k \, a_{\mathbf{k}\sigma}^+ \, a_{\mathbf{k}\sigma} +$$

$$+ \sum_{\sigma = \pm 1} E_0 \, d_{0\sigma}^+ \, d_{0\sigma} + \sum_{\sigma = \pm 1} U_0 \, \hat{n}_{0\sigma} \hat{n}_{0,\sigma'} +$$

$$+ \sum_{\mathbf{k} \in \Lambda} \sum_{\mathbf{q} \in \Lambda} \sum_{\sigma = \pm 1} \left(V_{\mathbf{q}} \, a_{\mathbf{k}\sigma}^+ \, a_{\mathbf{k-q},\sigma} + V_{\mathbf{q}}^{(0)} \, a_{\mathbf{k}\sigma}^+ \, a_{\mathbf{k-q},\sigma} \right) +$$

$$+ \sum_{\mathbf{k} \in \Lambda} \sum_{\sigma = \pm 1} \left(W_{\mathbf{k},0} \, a_{\mathbf{k}\sigma}^+ \, d_{0\sigma} + W_{\mathbf{k},0}^* \, d_{0\sigma}^+ \, a_{\mathbf{k}\sigma} \right) +$$

$$+ \sum_{\mathbf{k} \in \Lambda} \sum_{\sigma \neq \sigma'} \left(U_{\mathbf{k},0} \, \hat{n}_{\sigma'} \, a_{\mathbf{k}\sigma}^+ \, d_{0\sigma} + U_{\mathbf{k},0}^* \, d_{0\sigma}^+ \, a_{\mathbf{k}\sigma} \, \hat{n}_{0\sigma'} \right) +$$

$$+ \sum_{\mathbf{k} \in \Lambda} \sum_{\mathbf{q} \in \Lambda} \sum_{\sigma, \sigma' = \pm 1} P_{\mathbf{q},0} \, a_{\mathbf{k}\sigma}^+ \, a_{\mathbf{k-q},\sigma} \, \hat{n}_{0\sigma'}. \qquad (2.3)$$

Here, $a_{\mathbf{k}\sigma}(a_{\mathbf{k}\sigma}^+)$ and $d_{0,\sigma}(d_{0,\sigma}^+)$ are the annihilation (creation) Fermi-type operators for electrons in the states $\{\mathbf{k}, \sigma\}$ and $\{\mathbf{R}_0, \sigma\}$, where $\sigma = \pm 1$ is the quantum spin number which accepts two values according to two possible orientations of the electron spin relatively to the quantization axis. $E_k = \hbar^2 k^2 / 2m$ is the energy spectrum of electrons in the states $\varphi_{\mathbf{k}}(\mathbf{r})$, E_0 is the energy of the localized electron state $\psi_0(\mathbf{r})$, and $\hat{n}_\sigma = d_\sigma^+ d_\sigma$ is the spin-depended occupation number operator for a localized state.

The matrix elements V_q and $V_{0,q}$ characterize the processes of elastic scattering of electrons on ions of the metal and the impurity. Their explicit analytical forms are as follows:

$$V_q = \frac{1}{N} \sum_{1 \leq j \leq N} e^{-i\mathbf{q}\mathbf{R}_j} \, v(q), \quad V_{0,q} = e^{-i\mathbf{q}\mathbf{R}_0} \, v_0(q). \qquad (2.4)$$

The formfactors of scattering pseudopotentials

$$v(q) = \int_V V(|\mathbf{r}|) \, e^{-i\mathbf{q}\mathbf{r}} \, d\mathbf{r}, \quad v_0(q) = \frac{1}{V} \int_V V_0(|\mathbf{r}|) \, e^{-i\mathbf{q}\mathbf{r}} \, d\mathbf{r}$$

depend only on the modulus of the momentum transferred $\mathbf{q}$, due to the locality of the pseudopotentials $V(|\mathbf{r}|)$ and $V_0(|\mathbf{r}|)$. The modeling of the proper electron-ion interaction potential can be found in [6].

The processes of nonelastic scattering of electrons caused by their transition from the state localized on the impurity into the conduction band and vice versa are described by the matrix element $W_{\mathbf{k},0}$. The term $\sum_\sigma U_0 \, \hat{n}_\sigma \hat{n}_{-\sigma}$ in Hamiltonian (2.3) corresponds to the Coulomb interaction between electrons of opposite spins in the localized orbital, and the processes of elastic and nonelastic scatterings of electrons on the charged impurity are described by the matrix elements $P_{\mathbf{q},0}$ and $U_{\mathbf{q},0}$, respectively. Their analytical expressions were derived in [4]. Actually, in Hamiltonian (2.3), only the electrostatic effects including two electrons are taken into account, and the processes of exchange character are not considered.

3. Hartree—Fock Approximation

Following the Anderson's initial paper [1], the Hartree—Fock (HF) approximation was used to solve Hamiltonian (2.3). The HF approximation includes the perturbation U_0 only to the first order and should be valid for sufficiently small U_0. Moreover, the HF solution is exact when the hybridized terms in (2.3) are identically zero [11].

The HF Hamiltonian obtained from (2.3) in [4] may be written as

$$\widehat{H}^\sigma = H_{\mathrm{cl}} + \sum_{\mathbf{k}} E_k \, \hat{n}_{\mathbf{k}\sigma} + E_{0,\sigma} \, \hat{n}_{0\sigma} +$$

$$+ \sum_{\mathbf{k}} \sum_{\mathbf{q}} \left(V_{\mathbf{q}} \, a_{\mathbf{k}\sigma}^+ \, a_{\mathbf{k-q},\sigma} + V_{\mathbf{q}}^{(0)} \, a_{\mathbf{k}\sigma}^+ \, a_{\mathbf{k-q},\sigma} \right) +$$

$$+ \sum_{\mathbf{k}} \left(W_{\mathbf{k},0} \, a_{\mathbf{k}\sigma}^+ \, d_{0\sigma} + k.c. \right), \qquad (3.5)$$

where

$$E_{0,\sigma} = E_0 + U_0 \langle \hat{n}_{0,-\sigma} \rangle + \sum_{\mathbf{k},\mathbf{q}} \sum_{\sigma'} P_{\mathbf{q},0} \langle a_{\mathbf{k},\sigma'}^+ a_{\mathbf{k-q},\sigma'} \rangle +$$

$$+ \sum_{\mathbf{k}} \left[U_{\mathbf{k},0} \langle a_{\mathbf{k},-\sigma}^+ d_{0,-\sigma} \rangle + U_{\mathbf{k},0}^* \langle d_{0,-\sigma}^+ a_{\mathbf{k},-\sigma} \rangle \right]. \qquad (3.6)$$

The last expression defines the renormalized effective impurity level.

Now it is convenient to introduce a one-particle Green's function [12] defined by

$$G_{\mathbf{k},\mathbf{k}'}^{\sigma}(t) = -i\langle 0|T\, a_{\mathbf{k}\sigma}(t)a_{\mathbf{k}\sigma}^{+}(0)|0\rangle,$$

where $|0\rangle$ is the true ground state of the system. From the equation of motion for the operators $a_{\mathbf{k}\sigma}$, we get

$$\langle 0|a_{\mathbf{k}\sigma}^{+}[a_{\mathbf{k}\sigma},\widehat{H}]|0\rangle = \frac{d}{dt}G_{\mathbf{k},\mathbf{k}}^{\sigma}(t)|_{t=0}$$

or, by taking the Fourier transforms,

$$\langle 0|a_{\mathbf{k}\sigma}^{+}[a_{\mathbf{k}\sigma},\widehat{H}]|0\rangle = \frac{1}{2\pi i}\int_{C}\omega G_{\mathbf{k},\mathbf{k}}^{\sigma}(\omega)d\omega. \tag{3.7}$$

Here, C is the contour consisting of the real axis and a semicircle at infinity in the upper half-plane. Let's now consider the matrix of one-particle Green's functions:

$$\mathbf{G}(\omega) = \begin{pmatrix} G_{\mathbf{k},\mathbf{k}'}^{\sigma}(\omega) & M_{\mathbf{k},0}^{\sigma}(\omega) \\ M_{0,\mathbf{k}'}^{\sigma}(\omega) & L_{0,0}^{\sigma}(\omega) \end{pmatrix} \equiv$$

$$\equiv \begin{pmatrix} \langle\langle a_{\mathbf{k}\sigma}|a_{\mathbf{k}'\sigma}^{+}\rangle\rangle_{\omega} & \langle\langle a_{\mathbf{k}\sigma}|d_{0\sigma}^{+}\rangle\rangle_{\omega} \\ \langle\langle d_{0\sigma}|a_{\mathbf{k}'\sigma}^{+}\rangle\rangle_{\omega} & \langle\langle d_{0\sigma}|d_{0\sigma}^{+}\rangle\rangle_{\omega} \end{pmatrix}. \tag{3.8}$$

In the same manner, we get the relations

$$\langle 0|d_{0\sigma}^{+}[d_{0\sigma},\widehat{H}]|0\rangle = \frac{1}{2\pi i}\int_{C}\omega L_{0,0}^{\sigma}(\omega)d\omega, \tag{3.9}$$

$$\langle 0|n_{0\sigma}|0\rangle = \frac{1}{2\pi i}\int_{C}L_{0,0}^{\sigma}(\omega)d\omega, \tag{3.10}$$

$$\langle 0|d_{0\sigma}^{+}a_{\mathbf{k}\sigma}|0\rangle = \frac{1}{2\pi i}\int_{C}\omega M_{\mathbf{k},0}^{\sigma}(\omega)d\omega. \tag{3.11}$$

From the equations of motion, we get the system of equations for a Green's function in the quasi-crystalline approximation [4]. The equations for Green's functions [4] have been reduced to a closed form through the Green's function of localized electrons

$$L_{0,0}^{\sigma}(\omega) = [\omega - E_{\sigma} - S^{\sigma}(\omega)]^{-1}, \tag{3.12}$$

where $S^{\sigma}(\omega) = \sum_{\mathbf{k}}|\Omega_{k}^{\sigma}|^{2}/(\omega - E_{k} - \Lambda_{0})$. For the Green's function $M_{\mathbf{k},0}^{\sigma}(\omega)$, we get

$$M_{\mathbf{k},0}^{\sigma}(\omega) = \frac{\Omega_{\mathbf{k},0}^{\sigma}}{\omega - E_{k} - \Lambda_{0}}L_{0,0}^{\sigma}(\omega). \tag{3.13}$$

The one-particle Green's function of conduction electrons is as follows:

$$G_{\mathbf{k},\mathbf{k}'}^{\sigma}(\omega) = \frac{\delta_{\mathbf{k},\mathbf{k}'}}{\omega - E_{k} - \Lambda_{0}} + \frac{\Omega_{\mathbf{k},0}^{\sigma}L_{0,0}^{\sigma}(\omega)\Omega_{0,\mathbf{k}'}^{\sigma}}{(\omega - E_{k} - \Lambda_{0})(\omega - E_{k'} - \Lambda_{0})}, \tag{3.14}$$

where the effective pseudopotential

$$\Omega_{\mathbf{k},0}^{\sigma}(\omega) = U_{\mathbf{k},0}\langle\hat{n}_{0-\sigma}\rangle + W_{\mathbf{k},0}. \tag{3.15}$$

The constant $\Lambda_{0} = v(0) + v_{0}(0) - 2\pi\langle\hat{n}_{0}\rangle e^{2}r_{p}^{2}/V$.

Green's functions (3.26)–(3.14) are needed to obtain the average numbers $\langle n_{s\sigma}\rangle$ of s-electrons $\langle n_{0\sigma}\rangle$ of localized electrons per atom with spin σ and the mixed averages $\langle a_{\mathbf{k},-\sigma}^{+}d_{0,-\sigma}\rangle$, $\langle d_{0,-\sigma}^{+}a_{\mathbf{k},-\sigma}\rangle$.

The occupation number of the localized states at absolute zero for alkali metals can be found by integrating the density of states up to the Fermi energy:

$$\langle\hat{n}_{0\sigma}\rangle = \langle d_{0\sigma}^{+}d_{0\sigma}\rangle = \int_{-\infty}^{E_{\mathrm{F}}}\rho_{0}^{\sigma}(E)\,dE. \tag{3.16}$$

Here,

$$\rho_{0}^{\sigma}(E) = -\frac{1}{\pi}\mathrm{Im}\,L_{0,0}^{\sigma}(E + i\varepsilon), \quad \varepsilon \to 0, \tag{3.17}$$

is the density of localized electron states for spin σ.

The occupation number

$$\langle\hat{n}_{s\sigma}\rangle = \sum_{\mathbf{k}}\langle a_{\mathbf{k}\sigma}^{+}a_{\mathbf{k}\sigma}\rangle = \int_{-\infty}^{E_{\mathrm{F}}}\rho_{s}^{\sigma}(E)\,dE, \tag{3.18}$$

where

$$\rho_{s}^{\sigma}(E) = -\frac{1}{\pi N}\mathrm{Im}\sum_{\mathbf{k}}G_{\mathbf{k},\mathbf{k}}^{\sigma}(E + i\varepsilon), \quad \varepsilon \to 0, \tag{3.19}$$

is the density of collective electron states for spin σ. The mixed averages $\langle a_{\mathbf{k},-\sigma}^{+}d_{0,-\sigma}\rangle$ and $\langle d_{0,-\sigma}^{+}a_{\mathbf{k},-\sigma}\rangle$ are defined analogically in terms of the diagonal Green's function $M_{\mathbf{k},0}$.

To calculate the density of states $\rho_{0}^{\sigma}(E)$, we should find the sum over the wave vector $\mathbf{k}$. We use the relation

$$S^{\sigma}(E) = \lim_{\varepsilon\to 0}\sum_{\mathbf{k}}\frac{|\Omega_{k}^{\sigma}|^{2}}{E - E_{k} - \Lambda_{0} + i\varepsilon} =$$

$$= \mathcal{P}\sum_{\mathbf{k}}\frac{|\Omega_{k}^{\sigma}|^{2}}{E - E_{k} - \Lambda_{0}} - i\pi\sum_{\mathbf{k}}|\Omega_{k}^{\sigma}|^{2}\delta(E - E_{k} - \Lambda_{0}), \tag{3.20}$$

where the symbol $\mathcal{P}$ denotes the Cauchy principal value. For convenience, we introduce the notation

$$\Delta_{1}^{\sigma}(E) = \pi\sum_{\mathbf{k}}|\Omega_{k}^{\sigma}|^{2}\delta(E - E_{k} - \Lambda_{0}), \tag{3.21}$$

$$\Lambda_1^\sigma(E) = \mathcal{P} \sum_{\mathbf{k}} \frac{|\Omega_k^\sigma|^2}{E - E_k - \Lambda_0} = \frac{\mathcal{P}}{\pi} \int_{-\infty}^{+\infty} \frac{\Delta_1^\sigma(E')dE'}{E - E'}, \quad (3.22)$$

where $\Delta_1^\sigma(E)$ is the weighted density-of-states function with Λ_1^σ to be its Hilbert transform. Λ_1^σ can be neglected [1], since it primarily leads to an effective level shift which can be taken into account by the redefinition of E_0. This effect can be significant for the investigation of semiconductors or in systems with intermediate valency, where the localized level lies near the edge of the conduction band [13, 14]. The energy shift was investigated in [11]. The explicit expression for $\Lambda(E)$ was derived for a different form of the density of states $\rho_0(E)$ of the unperturbed conduction band. It was shown that $\Lambda(E)$ is negative in the lower half of the band and the ratio Λ/Δ must be less than $-\pi/2$.

Taking into account the structure of the effective pseudopotential (3.15),

$$\Delta_1^\sigma(E) = \Delta(E) + \beta(E)\langle n_{-\sigma}\rangle^2 + 2\gamma(E)\langle n_{-\sigma}\rangle, \quad (3.23)$$

where $\langle n_{-\sigma}\rangle \equiv \langle n_{0,-\sigma}\rangle$. The expressions

$$\beta(E) = \pi\langle U^2\rangle\rho_0(E), \quad \gamma(E) = \pi\langle UW\rangle\rho_0(E),$$

$$\Delta(E) = \pi\langle W^2\rangle\rho_0(E) \quad (3.24)$$

are slowly varying functions of E over the band, and they can be treated as parameters evaluated at the Fermi energy $E_{\rm F}$ [8, 11]. Now it is convenient to introduce the parameter $z = \langle U/W\rangle$ which characterized the intensity of the scattering on a charged impurity. Using the analytical expressions for the matrix elements W_k, U_k, and P_k as functions of the modulus of the momentum transferred $\mathbf{k}$, the parameters Δ, β, γ were evaluated in [4] at the Fermi energy.

Now the localized level width

$$\Delta_1^\sigma = \Delta(1 + z\langle\hat{n}_{-\sigma}\rangle)^2. \quad (3.25)$$

has a new term associated with the processes of nonelastic scattering of conduction electrons on the charged impurity, which leads to the broadening of a localized level. If $z = 0$, we have reproduced the Anderson's results.

Neglecting the energy shift Λ_1^σ, $L_{0,0}^\sigma(E)$ becomes

$$L_{0,0}^\sigma(E) = \frac{1}{E - E_\sigma + i\Delta_1^\sigma}. \quad (3.26)$$

The diagonal Green's function of the extended states (3.14) is

$$G_{\mathbf{k},\mathbf{k}}^\sigma(E) = G_{\mathbf{k},\mathbf{k}}^{\sigma}{}^{(0)} \left[1 + \frac{|\Omega_k^\sigma|^2 G_{\mathbf{k},\mathbf{k}}^{\sigma}{}^{(0)}}{(E - E_\sigma + i\Delta_1^\sigma)}\right], \quad (3.27)$$

where $G_{\mathbf{k},\mathbf{k}}^{\sigma}{}^{(0)} = 1/(E - E_k - \Lambda_0)$. The density of localized states (3.17) has the Lorentzian form

$$\rho_0^\sigma(E) = \frac{1}{\pi} \frac{\Delta_1^\sigma}{(E - E_\sigma)^2 + (\Delta_1^\sigma)^2}. \quad (3.28)$$

Now we will determine the density of extended states (3.19). We need to calculate the sum

$$\lim_{\varepsilon \to 0} \sum_{\mathbf{k}} \frac{|\Omega_k^\sigma|^2}{(E - E_k - \Lambda_0 + i\varepsilon)^2} = -\frac{d\Lambda_1^\sigma}{dE} - i\frac{d\Delta_1^\sigma}{dE}. \quad (3.29)$$

Using expression (3.27) for $G_{\mathbf{k},\mathbf{k}}^\sigma(E)$ and taking the sum over all $\mathbf{k}$, we get

$$\rho_s^\sigma(E) = \rho_0(E) + \frac{d\Delta_1^\sigma}{dE} \frac{E - E_\sigma}{(E - E_\sigma)^2 + (\Delta_1^\sigma)^2}. \quad (3.30)$$

In view of (3.16), the occupation number of a localized state with spin σ is

$$\langle\hat{n}_\sigma\rangle = \frac{1}{\pi}\text{arcctg}\left[\frac{E_\sigma - E_{\rm F}}{\Delta(1 + z\langle\hat{n}_{-\sigma}\rangle)^2}\right]. \quad (3.31)$$

In the quasi-crystalline approximation, expression (3.6) for the renormalized effective localized level becomes

$$E_\sigma = E_\sigma^0 + \Delta E^{\pm\sigma}, \quad (3.32)$$

where we denote

$$E_\sigma^0 = E_0 + U_0\langle\hat{n}_{-\sigma}\rangle,$$

$$\Delta E^{\pm\sigma} = \sum_{\mathbf{k}} \sum_{\sigma'} P_{\mathbf{q}=0} \langle a_{\mathbf{k},\sigma'}^+ a_{\mathbf{k},\sigma'}\rangle +$$

$$+ \sum_{\mathbf{k}} \left[U_{\mathbf{k},0} \langle a_{\mathbf{k},-\sigma}^+ d_{0,-\sigma}\rangle + U_{\mathbf{k},0}^* \langle d_{0,-\sigma}^+ a_{\mathbf{k},-\sigma}\rangle\right].$$

The contribution from the term [4]

$$\sum_{\mathbf{k}} \sum_{\sigma} P_{\mathbf{q}=0}\langle a_{\mathbf{k},-\sigma}^+ a_{\mathbf{k},-\sigma}\rangle = 2\pi e^2 r_p^2 N/V$$

describes the energy shift associated with a homogeneous distribution of electrons with the spin values opposite to σ.

Using the mixed averages [4], we get

$$\Delta E^{\pm\sigma} = -\frac{2}{\pi}\text{Im} \int_{-\infty}^{E_{\rm F}} \sum_{\mathbf{k}} \frac{U_k \Omega_k^{-\sigma}}{E - E_k - \Lambda_0} L_{0,0}^{-\sigma}(E)dE.$$

Relations (3.20) and (3.31) yield

$$\Delta E^{\pm\sigma} = -2\frac{\Delta_2^{\sigma}}{\pi}\ln|\sin(\pi\langle\hat{n}_{-\sigma}\rangle)|,$$

$$\Delta_2^{\sigma} = \beta\langle\hat{n}_{\sigma}\rangle + \gamma = z\Delta(1 + z\langle\hat{n}_{\sigma}\rangle).$$

So, the density of localized states (3.28) looks as

$$\rho_0^{\sigma}(E) = \frac{1}{\pi}\frac{\Delta(1+z\langle\hat{n}_{-\sigma}\rangle)^2}{(E-E_{\sigma}^0-\Delta E^{\pm\sigma})^2+\Delta^2(1+z\langle\hat{n}_{-\sigma}\rangle)^4}. \quad (3.33)$$

At least, the number of localized electrons with spin σ is

$$\langle\hat{n}_{\sigma}\rangle = \frac{1}{\pi}\text{arcctg}\left[\frac{E_0-E_{\mathrm{F}}+U_0\langle\hat{n}_{-\sigma}\rangle+\Delta E^{\pm\sigma}}{\Delta(1+z\langle\hat{n}_{-\sigma}\rangle)^2}\right]. \quad (3.34)$$

This equation generates two simultaneous equations for $\langle\hat{n}_{\sigma}\rangle$ and $\langle\hat{n}_{-\sigma}\rangle$: the self-consistent solutions correspond to the points of intersection of the curves. We note there must be solutions, for which $\langle\hat{n}_{\sigma}\rangle \neq \langle\hat{n}_{-\sigma}\rangle$.

We introduce the parameter $x=(E_{\mathrm{F}}-E_0)/U_0$. If $x=0$, then the empty localized state is right at the Fermi level. The condition $x=1$ puts $E_0 + U_0$ at the Fermi level, which means that two electrons can occupy the same localized state even at absolute zero, and we never have a magnetic moment. We also introduce the parameter $y=U_0/\Delta$ which measures the ratio of the Coulomb integral to the width of the virtual state (i.e. y compares the correlation between localized electrons with the interaction energy of the localized states with free electrons).

So, the self-consistent system of equations for finding the charged and magnetic impurity states is

$$n_{\pm}=\frac{1}{\pi}\text{arcctg}\left[\frac{y(n_{\mp}-x)-2z/\pi(1+zn_{\pm})\ln|\sin\pi n_{\mp}|}{(1+zn_{\mp})^2}\right],$$

where $n_+ \equiv \langle\hat{n}_{\sigma}\rangle$. The effective impurity charge is evaluated from the relation $q=|e|Z_{\mathrm{eff}}$, $Z_{\mathrm{eff}}=\langle n_++n_-\rangle$, and the magnetic moment is defined by $M=\mu_B m$, $m=\langle n_+-n_-\rangle$. The obtained system of transcendental equations has been solved in [4].

4. Solvation Free Energy

In order to present the ground-state energy for the "liquid metal + impurity" system via the integral over the single-particle locator Green's function $L_{0,0}^{\sigma}(\omega)$, we rewrite the Hamiltonian in terms of commutators [8] as

$$\widehat{H} = E_{\mathrm{cl}}+\sum_{\sigma=\pm1}\left[\sum_{\mathbf{k}}a_{\mathbf{k}\sigma}^+[a_{\mathbf{k}\sigma},\widehat{H}]+\frac{1}{2}d_{0\sigma}^+[d_{0\sigma},\widehat{H}]+\right.$$

$$\left.+\frac{1}{2}(E_0-\Delta E^{\pm\sigma})\hat{n}_{0\sigma}+\frac{1}{2}\sum_{\mathbf{k}}(\Omega_{\mathbf{k}0}^{\sigma})^*d_{0\sigma}^+a_{\mathbf{k}\sigma}\right].$$

Now we use the GFs in terms of commutators (3.7), (3.9 – 3.11). Then the ground-state energy of the "liquid metal + impurity" system is

$$E = \langle0|\widehat{H}|0\rangle = \frac{1}{2\pi i}\sum_{\sigma}\int_C\left[\sum_{\mathbf{k}}EG_{\mathbf{k},\mathbf{k}}^{\sigma}(E)+\right.$$

$$\left.+\frac{E+E_0-\Delta E^{\pm\sigma}+S^{\sigma}(E)}{2}L_{0,0}^{\sigma}(E)\right]dE.$$

For the "pure metal + isolated impurity" system infinitely separated, the ground-state energy is

$$E^{(0)} = \langle0|\widehat{H}^{(0)}|0\rangle = \frac{1}{2\pi i}\sum_{\sigma}\int_C\sum_{\mathbf{k}}EG_{\mathbf{k},\mathbf{k}}^{\sigma}{}^{(0)}(E)dE + E_0,$$

where $G_{\mathbf{k},\mathbf{k}}^{\sigma}{}^{(0)} = 1/(E-E_k)$.

Now we arrive at the following expression for the solvation free energy defined as $\Delta E=E-E^{(0)}$:

$$\Delta E=\frac{1}{2\pi i}\sum_{\sigma}\int_C\left[\frac{E+E_0-\Delta E^{\pm\sigma}+S^{\sigma}(E)}{2}L_{0,0}^{\sigma}(E)-\right.$$

$$\left.-L_{0,0}^{\sigma}(E)E\frac{\partial}{\partial E}S^{\sigma}(E)\right]dE - E_0,$$

where we have used the propagator GF $G_{\mathbf{k},\mathbf{k}}^{\sigma}(E)$.

Now let's introduce $L^0(E)^{-1}=E-E_0-S^{\sigma}(E)$ and define a proper Coulomb self-energy by the Dyson equation

$$L_{0,0}^{\sigma}(E) = L^0(E) + L^0(E)\Sigma^{\sigma}L_{0,0}^{\sigma}(E). \quad (4.35)$$

The self-energy from the Dyson equation

$$\Sigma^{\sigma} = U_0\langle\hat{n}_{-\sigma}\rangle + \Delta E^{\pm\sigma}$$

$$= U_0\langle\hat{n}_{-\sigma}\rangle - 2z\Delta/\pi(1 + z\langle\hat{n}_{\sigma}\rangle)\ln|\sin(\pi\langle\hat{n}_{-\sigma}\rangle)|. \quad (4.36)$$

Then

$$\Delta E=\frac{1}{2\pi i}\sum_{\sigma}\int_C\left[E-E\frac{\partial S^{\sigma}(E)}{\partial E}-\frac{\Sigma^{\sigma}+\Delta E^{\pm\sigma}}{2}\right]L_{0,0}^{\sigma}(E)dE-E_0.$$

The last expression can be rewritten as

$$\Delta E = \sum_{\sigma}\left[\Delta E_1^{\sigma}-\Delta E^{\pm\sigma}\langle\hat{n}_{\sigma}\rangle\right] - E_0-U_0\langle\hat{n}_{-\sigma}\rangle\langle\hat{n}_{\sigma}\rangle, \quad (4.37)$$
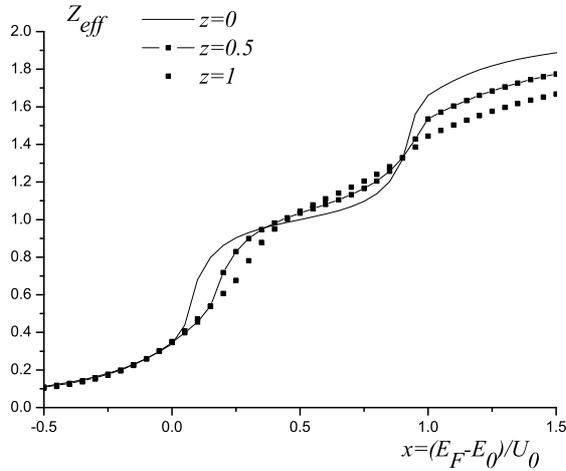
Fig. 1. Effective impurity charge $Z_{\text{eff}}=\langle n_+ + n_- \rangle$ vs $(E_{\text{F}} - E_0)/U_0$ $(y=10)$

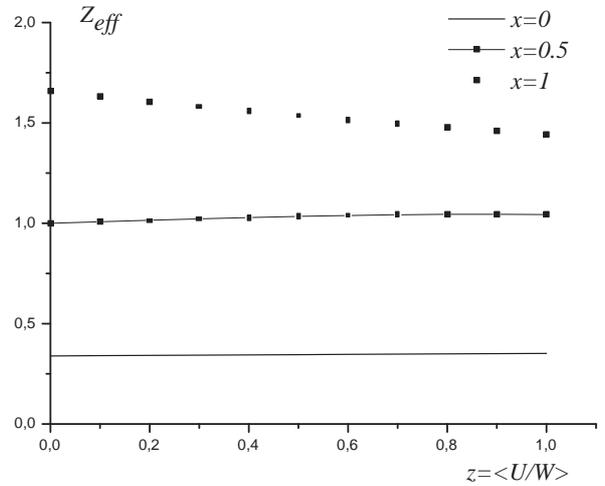Fig. 2. Solvation free energy $\Delta E/U_0$ vs $(E_{\text{F}} - E_0)/U_0$ $(y=10)$

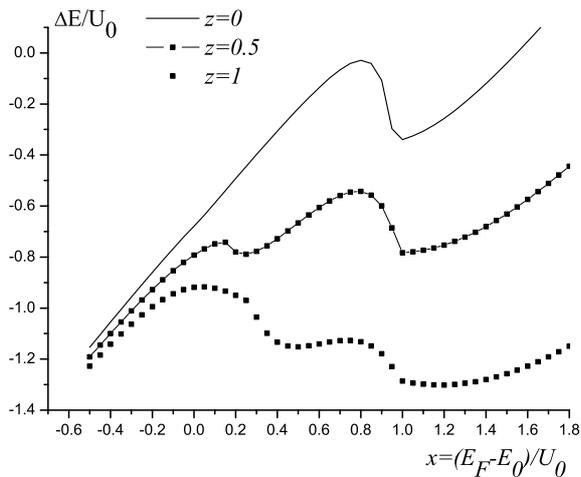Fig. 3. Effective impurity charge $Z_{\text{eff}}=\langle n_+ + n_- \rangle$ vs $z = \langle U/W \rangle$, $(y=10)$
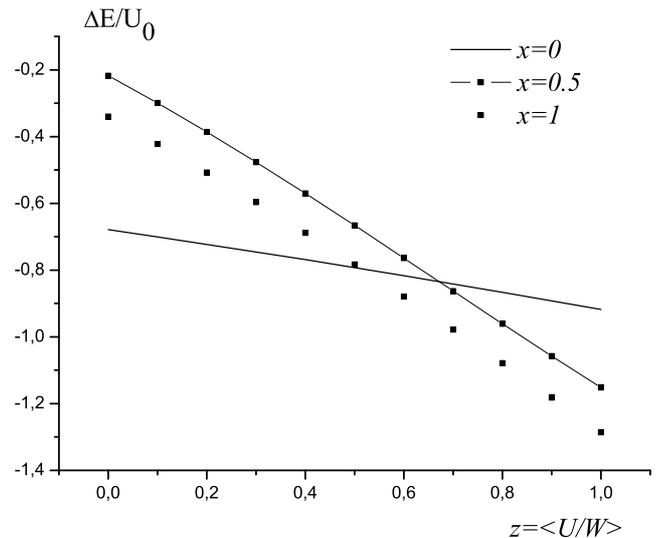

Fig. 4. Solvation free energy $\Delta E/U_0$ vs $z = \langle U/W \rangle$ $(y=10)$

where it is convenient to define a one-electron energy change ΔE_1^σ by

$$\Delta E_1^\sigma = \frac{1}{2\pi i} \int_C E \frac{d}{dE} \ln L_{0,0}^\sigma(E) dE.$$

The contour C is to enclose all the occupied eigenvalues. Integrating by parts [7], we get

$$\Delta E^{1\sigma} = \frac{1}{\pi} \int_{-\infty}^{E_{\text{F}}} \text{arctg} \left[\frac{\Delta(1 + z\langle \hat{n}_{-\sigma}\rangle)}{E - E_\sigma} \right] dE + E_{\text{F}},$$

where we have used (3.21), (3.22). The one-electron energy change ΔE_1^σ and the thermodynamic averages $\langle \hat{n}_\sigma \rangle$ depend explicitly on the metal eigenstates $|\mathbf{k}\rangle$ only through the function Δ_1^σ. The detailed structure of Δ_1^σ will have an important effect on the results. We have obtained the analytical expressions for the pseudopotential Ω_k^σ in [4] and estimate it at the Fermi energy. It may be shown from Eq. (4.37) that $\Delta E \to 0$ when $\Delta_1^\sigma \to 0$ (see [7]). ΔE is always less than or equal to zero.
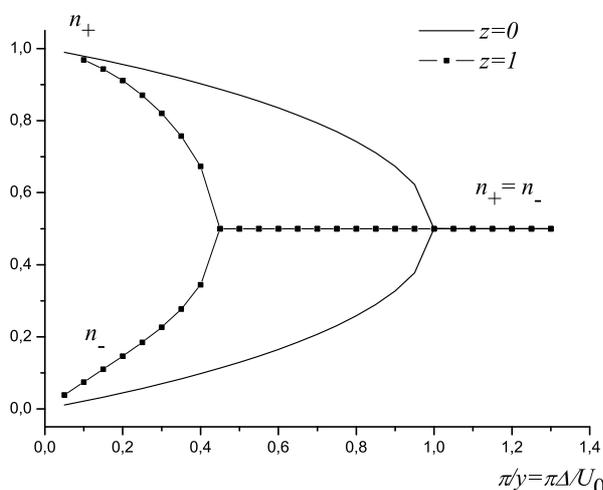
1300

Fig. 5. Occupation numbers n_+, n_- vs $\pi\Delta/U_0$

Fig. 6. Solvation free energy $\Delta E/U_0$ versus $\pi\Delta/U_0$

5.   Conclusions

Using the Green's function method, we have derioved the self-consistent equations describing the charged and spin-polarized impurity states. The effect of the scattering of conduction electrons on the charged impurity leads to the broadening of a localized level and to the renormalization of the effective pseudopotential. The solvation free energy of the charged impurity is obtained through the two-time Green's functions and the thermodynamical averages. The qualitative graphical dependence of the solvation free energy on the model parameters is given. This is only the electron part of the solvation free energy. In order to compare with experimental data, one must include the classical ion-ion interactions. A significant part of the solvation free energy arises from the required expulsion of solvent molecules from the region occupied by the harshly repulsive molecular core of the solute. The excess of solvation free energy associated with the insertion of a spherical cavity into the hard-sphere fluid has been calculated in [15].

The experimental measurements of ΔE referring to a dilute solution with the small oxygen concentration (from 0.0001 to 0.1%) in liquid metals are discussed in [16]. For 0.0001% of oxygen impurities in potassium, $\Delta E/n = -600$ kJ/mol$= -6.23$ eV. The parameters employed in our calculation were taken as follows. For an oxygen atom, $U_0 = 5e^2/8r_p \sim 10$ eV, $r_p = 1.2$ a.u., and $E_0 = -1.46$ eV relative to the vacuum level. The
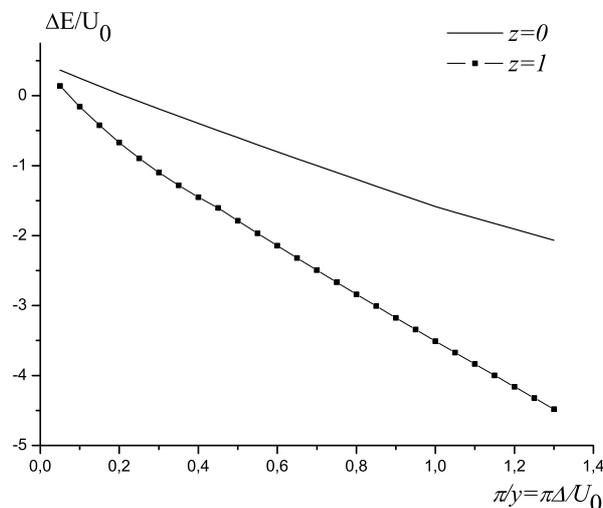
parameters Δ and $z = \langle U/W \rangle$ at the Fermi level for the gaseous impurities O, C, Cl, and F were estimated in [4].

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ВІЛЬНА ЕНЕРГІЯ
СОЛЬВАТАЦІЇ ІЗОЛЬОВАНОЇ
ДОМІШКИ В ПРОСТОМУ РІДКОМУ МЕТАЛІ

Ю.К. Рудавський, Г.В. Понеділок, М.І. Клапчук

Р е з ю м е

Розглянуто систему "рідкий метал + електронегативна домішка". Для опису зарядового та магнітного станів доміш-ки застосовано узагальнену мікроскопічну модель Андерсо-на в наближенні Хартрі—Фока. До модельного гамільтоніа-на включено процеси пружного і непружного розсіяння елек-тронів провідності на зарядженій домішці. Вільну енергію сольватації зарядженої домішки отримано через загальний зв'язок з двочасовими функціями Гріна та термодинамічними середніми.