

## ACCOUNT OF METAL STRUCTURE PERIODICITY IN DESCRIPTION OF SURFACE ELECTRON GAS PROPERTIES IN TERMS OF MULTIPARTICLE DENSITY FUNCTIONALS

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The electron gas spatial distribution near a metal surface is analyzed subject to the crystal lattice periodic structure. Within the formalism of multiparticle density functionals, an analytic expression for the two-particle density function of electron gas in a periodic potential is derived. These results can be used for calculating the electron gas characteristics in solids.

In the present paper we discuss the potentialities of the theory of multiparticle density functionals [1–3] for description of electron gas spatial structure in metals. The theory is based on describing nonrelativistic quantum systems with the aid of multiparticle density functions  $n_m(r_1, \dots, r_m)$ , i.e., the diagonal elements of spin-independent  $m$ -particle density matrices, for which the normalization condition was selected in the form similar to [1–3],

$$\int d^3r_1 \dots d^3r_m n_m(r_1, \dots, r_m) = C_N^m = \frac{N!}{(N-m)!m!},$$

where  $N$  is the number of particles in the system. The ground state energy  $E_0$  of a Fermi system is a unique functional of  $n_m(r_1, \dots, r_m)$  whose minimum is realized on a function which corresponds to the spatial distribution of particles in the ground state. Systems with pairwise interaction potentials are best described by two-particle density functions. Then the total energy of the ground state can be presented as

$$E_0 = E[n_2] = T[n_2] + \frac{1}{N-1} \int dr_1 dr_2 (V(r_1) + V(r_2)) n_2(r_1, r_2) + \int dr_1 dr_2 W(r_1, r_2) n_2(r_1, r_2), \quad (1)$$

where  $T[n_2]$  is the kinetic energy functional [3],

$$\begin{aligned} T[n_2] &= \int d^3r_1 d^3r_2 t[n_2](r_1, r_2), \\ t[n_2](r_1, r_2) &= \frac{1}{N-1} \text{Sp}_{\sigma\tau} \left\{ \frac{3}{10} (18\pi^4)^{1/3} (C(p_d))^{-4/3} n_2^{4/3}(r_1, r_2) - \frac{1}{960} (C(p_d))^{-1} ((\Delta_1 + \Delta_2) n_2(r_1, r_2)) \right. \\ &\quad \left. + \frac{5}{1152} (C(p_d))^{-1} \left( (\nabla_1 n_2(r_1, r_2))^2 + (\nabla_2 n_2(r_1, r_2))^2 \right) n_2^{-1}(r_1, r_2) \right\}; \end{aligned} \quad (2)$$

the constant  $C(p_d)$  is determined by the degeneracy factor  $p_d$  equal to the number of possible projections of discrete variables (spin, isospin) for the particles that constitute the system. In particular,  $p_d = 2$  for electrons,  $p_d = 4$  for nucleons, etc.;

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$$C(p_d) = \left\{ 1 - \frac{9}{2} \left( \frac{j_1 \left( \left( \frac{9\pi}{2p_d} \right)^{1/3} \right)}{\left( \frac{9\pi}{2p_d} \right)^{1/3}} \right)^2 \right\}.$$

Here  $j_1(x) = (\sin x - x \cos x)/x^2$  is the spherical Bessel function of the first order.

We used the adiabatic approximation assuming that the metal's electron gas is exposed to the external potential  $V(r) = V_0(r) + V_1(r)$ . The crystal lattice potential  $V(r)$  was treated as the sum of the uniform background potential  $V_0(r)$ , produced by a uniformly distributed positive charge of density

$$n_0^+(r) = n\Theta(-z),$$

$$\Theta(x) = \begin{cases} 0 & \text{for } x < 0, \\ 1 & \text{for } x > 0 \end{cases}$$

(the  $Oz$  axis is directed into vacuum normal to the metal surface), and the potential  $V_1(r)$  produced by a positive charge periodic distribution with density  $n_1^+(r)$ . The potential  $V_1(r)$  can be regarded as a perturbation because the basic parameters of the electron gas in a metal are quite accurately described by the jelly model [2]. The interaction between electrons was assumed to be purely Coulombian,  $W(r_1, r_2) = |r_1 - r_2|^{-1}$ .

Substituting into the Euler-Lagrange equation,

$$\frac{\delta}{\delta n_2(r_1, r_2)} \left( E[n_2] - \mu_2 \int dr_1 dr_2 n_2(r_1, r_2) \right) = 0, \quad (3)$$

the expansions of  $E[n_2]$ ,  $n_2(r_1, r_2)$ , and the Lagrange constant  $\mu_2$  into the perturbation theory series and retaining the first two orders, we obtain

$$\frac{1}{N-1} (V_0(r_1) + V_0(r_2)) + W(r_1, r_2) + \frac{\delta T[n_2]}{\delta n_2(r_1, r_2)} \Big|_{n_2=n_2^{(0)}} = \mu_2^{(0)},$$

$$\frac{1}{N-1} (V_1(r_1) + V_1(r_2)) + \frac{1}{2} \int dr'_1 dr'_2 n_2^{(1)}(r'_1, r'_2) \frac{\delta^2 T[n_2]}{\delta n_2(r_1, r_2) \delta n_2(r'_1, r'_2)} \Big|_{n_2=n_2^{(0)}} = \mu_2^{(1)}, \quad (4)$$

where  $\mu_2^{(1)}$  and  $n_2^{(1)}(r_1, r_2)$  are the first-order corrections to the Lagrange constant  $\mu_2^{(0)}$  and the two-particle density function  $n_2^{(0)}(r_1, r_2)$  of the nonperturbed system for which the results of [2] were used.

In the case of a cubic lattice with period  $a$ , it is convenient to present  $n_1^+(r)$  as

$$n_1^+(r) = A \cos kx \cdot \cos ky \cdot \cos k(z + a/2)\Theta(-z) \quad (k = 2\pi/a), \quad (5)$$

aligning the coordinate axes with atom chains in the lattice. This choice of parametrization for  $n_1^+(r)$  automatically ensures electric neutrality of the metal as a whole, and also allows easy application of obtained results to description of any cubic lattice. Then the potential  $V_1(r)$  defined as

$$V_1(r) = - \int d^3r' \frac{n_1^+(r')}{|r - r'|}$$

can analytically be presented as

$$V_1(r) = -A \frac{\pi}{3k^2} \cos kx \cdot \cos ky \left\{ 2 \cos 2kz \cdot \exp(-k\sqrt{2}|z|) + [4 \cos kz - 2\sqrt{2} \sin kz] \Theta(-z) \right\}. \quad (6)$$

Retaining in (4) only the first order of gradient expansion (2) for the spatial density of kinetic energy  $t[n_2](r_1, r_2)$ , we can pass on to the algebraic equation in  $n_2^{(0)}(r_1, r_2)$ ,

$$\frac{1}{N-1} (V_1(r_1) + V_1(r_2)) + \frac{1}{N-1} \cdot \frac{2}{5} (18\pi^4)^{1/3} (C(p_d))^{-4/3} \left( n_2^{(0)}(r_1, r_2) \right)^{-2/3} n_2^{(1)}(r_1, r_2) = \mu_2^{(1)},$$

which can be analytically solved with respect to  $n_2^{(1)}(r_1, r_2)$ ,

$$n_2^{(1)}(r_1, r_2) = \frac{5}{2} (18\pi^4)^{-1/3} (C(p_d))^{4/3} \left( n_2^{(0)}(r_1, r_2) \right)^{2/3} \left\{ \mu_2^{(1)} - (V_1(r_1) + V_1(r_2)) \right\}.$$

The requirement of invariable normalization of  $n_2(r_1, r_2)$  makes the correction  $\mu_2^{(1)}$  to vanish, and, finally,

$$n_2^{(1)}(r_1, r_2) = -\frac{5}{2} (18\pi^4)^{-1/3} (C(p_d))^{4/3} \left( n_2^{(0)}(r_1, r_2) \right)^{2/3} (V_1(r_1) + V_1(r_2)),$$

where the potential  $V_1(r)$  is given by (6), and  $n_2^{(0)}(r_1, r_2)$  may be found based on the results of [2–4]. The oscillation amplitude  $A$  of the lattice ions positive charge density can be estimated using the crystal lattice periodic potentials which have been proved adequate in the scattering theory, and the Poisson equation  $\Delta V(r) = -4\pi n^+(r)$ . Under this approach,

$$n_1^+(r) = -\frac{1}{4\pi} (\Delta V(r) - n_0^+(r)),$$

where  $V(r)$  is the crystal lattice periodic potential (the Ashcroft potential [5], the screened Coulomb potential, etc.).

The results obtained in this work can be used for studying the periodic spatial structure of electron gas in solids with cubic (including face- and body-centered) crystal lattice because for such lattices the correction  $n_1^+(r)$  to the background charge density can be presented as a sum of terms of the form (5). The potential  $V_1(r)$  which is a linear function of  $n_1^+(r)$  can be also presented as a sum of contributions of the form (6).

The proposed approach allows one to avoid the otherwise inevitable (for single-particle approaches) replacement of the system's actual Hamiltonian with a model one being of a sum of single-particle operators. Such a replacement usually means that additional, not necessarily justified assumptions are introduced into the physical model. Thus, the approach discussed above is especially useful for describing the electron gas in metals [5, 6].

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