# Some corrections to the Thomas–Fermi theory

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(Received 12 November 2012; revised manuscript received 3 January 2013)

In the presented model the wave function describing the electron is a superposition of contributions from individual components of the system, in the case of metals — lattice ions and in this sense refers not to a single electron, but rather to the system as a whole. An unconventional approach to the Schrödinger equation can provide a simple analytical relationship between the total energy of the electron and the wave number. This expression can directly determine the basic parameters such as Fermi radius, the screening radius or work function and also produce a graphical interpretation of the Fermi surface.

**Keywords:** screening parameter, convolution, Fermi surface

**PACS:** 71.10.Ca, 71.15.Nc, 71.18.+y, 73.30.+y **DOI:** 10.1088/1674-1056/22/8/087101

## 1. Introduction

The basic problem in the theory of metals which has to be solved is how to deal mathematically with the interaction of a large number of particles. The full Hamiltonian should contain complete information about the Coulomb interaction between all electrons and ions of the system. It is obvious that all attempts to find the eigenvalues and the eigenfunctions to this Hamiltonian involve more or less approximations.

Hartree–Fock theory is one of the simplest approximate theories for solving the many-body Hamiltonian. It is based on a straightforward approximation to the true many-body wave function, that is, the wave function is given by a single Slater determinant of spin-orbitals

$$\Psi(\boldsymbol{r}_1\sigma_1,\boldsymbol{r}_2\sigma_2,\ldots,\boldsymbol{r}_N\sigma_N) = \begin{bmatrix} \psi_1(\boldsymbol{r}_1\sigma_1) & \psi_1(\boldsymbol{r}_2\sigma_2) & \cdots & \psi_1(\boldsymbol{r}_N\sigma_N) \\ \psi_2(\boldsymbol{r}_1\sigma_1) & \psi_2(\boldsymbol{r}_2\sigma_2) & \cdots & \psi_2(\boldsymbol{r}_N\sigma_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\boldsymbol{r}_1\sigma_1) & \psi_N(\boldsymbol{r}_2\sigma_2) & \cdots & \psi_N(\boldsymbol{r}_N\sigma_N) \end{bmatrix}. \quad (1)$$

This form of a wave function results from Pauli principle, because a simple product of $N$ orthonormal one-electron levels $\Psi_i(\boldsymbol{r}_i,\sigma_i)$:

$$\Psi(\boldsymbol{r}_1\sigma_1,\boldsymbol{r}_2\sigma_2,\ldots,\boldsymbol{r}_N\sigma_N) = \Psi_1(\boldsymbol{r}_1,\sigma_1)\Psi_2(\boldsymbol{r}_2,\sigma_2),\cdots,\Psi_N(\boldsymbol{r}_N,\sigma_N) \quad (2)$$

does not fulfil the antisymmetry condition.

The unknown Hartree–Fock orbitals can be written as a linear expansion in $N$ known basis functions. Some not very complicated transformations lead to a set of matrix equations for the expansion coefficients. In consequence the problem of solving Hartree–Fock equations is reduced to a linear algebra problem, which may be solved by techniques such as iterative diagonalisation.[1,2] Hartree–Fock equations can be solved numerically (exact Hartree–Fock), or they can be solved in the space spanned by a set of basis functions (Hartree–Fock–Roothan equations). In either case the solutions depend on the orbitals. Hence, we need to guess some initial orbitals and then refine our guesses iteratively. For this reason, Hartree–Fock is called a self-consistent-field (SCF) approach.

In practice, a basis of plane waves in periodic systems or localized Gaussians in finite systems, is commonly used. The basis set expansion represents an additional limitation of the techniques: unless the basis set expansion has sufficient freedom to encompass the exact solutions for the Hartree–Fock orbitals, and a compromise solution with a higher Hartree–Fock energy will be found. In practical applications, convergence of the basis set must be studied to verify that the expansion is sufficiently complete.

The idea of replacing the wave function with the charge density was proposed in the so-called Thomas–Fermi approach (TFA) to electronic theory.[3,4] Although the TFA failed to produce any quantitatively impressive results, the basic idea — using the electron density turned out to be very promising and was elaborated in density functional theory (DFT) formulated by Hohenberg and Kohn.[5,6] The fundamental assumption of DFT states that the ground state expectation value of any observable is a unique functional of the exact ground state density $n(\boldsymbol{r})$. So in consequence a ground state of the total energy $E$ of a system can always and unambiguously be written as

$$E[n] = T[n] + \frac{1}{2}\int \mathrm{d}^3r\,\mathrm{d}^3r' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{\mathrm{xc}}[n] + \int \mathrm{d}^3r V_{\mathrm{ext}}(\boldsymbol{r})n(\boldsymbol{r}), \quad (3)$$

where the first term on the right-hand side $T[n]$ is the kinetic energy of a non-interacting electron gas, the second term means the classical Coulomb interaction, $E_{\mathrm{xc}}[n]$ the exchange and correlation energy, and $V_{\mathrm{ext}}(\boldsymbol{r})$ the external potential.

In order to calculate the ground state charge density, and total energy we need to know both $T[n]$ and $E_{\mathrm{xc}}[n]$. In prac-

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tice it is a very complex task, all the more so because the exchange and correlation energy retains all difficulties of the many-particle problem. The difficulties are significant enough to make the use of the total energy expression directly in the variational procedure impossible and one works around the problem with the help of the Kohn–Sham (KS) scheme. The basic idea of the KS scheme is to map the many-particle problem onto a system of non-interacting particles with the same ground state density $n(\boldsymbol{r})$. In consequence we can obtain the following expression for the total energy:

$$E = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int \mathrm{d}^3 r \mathrm{d}^3 r' \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \int \mathrm{d}^3 r V_{\mathrm{xc}}[n] n(\boldsymbol{r}) + E_{\mathrm{xc}}[n], \tag{4}$$

where $\varepsilon_i$ are the Kohn–Sham eigenvalues obtained from Schrödinger-like equations:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\mathrm{eff}}(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r}). \tag{5}$$

The effective potential in the last equation

$$V_{\mathrm{eff}}(\boldsymbol{r}) = V_{\mathrm{xc}} + V_{\mathrm{ext}} + \int \mathrm{d}^3 r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{5a}$$

transforms the many-particle problem to a single particle formulation and the exchange–correlation potential $V_{\mathrm{xc}}$ is defined as follows:

$$V_{\mathrm{xc}} = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n[\boldsymbol{r}]}. \tag{6}$$

It is usually assumed that KS equations are simple to solve[7,8] compared with other traditional methods, such as Hartree–Fock (HF). Nevertheless any DFT-based computer program has several thousand lines and hundreds of input options.[9–12] In consequence, the line between physical and virtual reality created by sophisticated software is blurred; one cannot be sure whether the better and better results arise from using a more suitable theory or it is just an effect of simplification introduced by a computer specialist.

Therefore, any attempts to present these complex issues in a more lucid form should be interesting especially if it leads to interesting results.

## 2. New potential operator

In dealing with a many-body system such as electrons in an atom it was pointed out by Hartree[13] that the mean field experienced by any single electron is due to the nucleus and the mean charge distribution of all the other electrons. Thus the wave function for a single electron, which describes its spatial distribution, also determines the average charge distribution which contributes to the determination of itself, i.e., there must be self-consistency between the one-particle wave function and the average field acting on it by the other particles.

In consequence, the wave function describing the state of the electron placed in a point $\boldsymbol{r}$ depends not on the electron, but on the system in which it is located. So the wave function must contain the information about all elements of the system interacting with the electron. Since elements of the system also interact with one another, one can expect that the wave function is entangled. In this sense, the wave function describing the behavior of the electron can be treated as the wave function of the whole system. Now we assume that the wave function $\Psi(\boldsymbol{r})$ is a superposition of components originating from individual elements of the system (notice that from this point $N$ is the number of ions):

$$\Psi(\boldsymbol{r}) = \sum_{i=1}^{N} \Psi(\boldsymbol{r}_i). \tag{7}$$

It seems obvious that in the case of metal the elements of a system are the ions in a crystal lattice. In contrast to other methods for example linear combination of atomic orbitals (LCAO),[14] the wave function of the system is not a linear combination of wave functions of individual atoms, but a natural superposition of wave functions from the individual atoms within the structure of the system.

It is a fundamental difference because the wave function of a single atom in the LCAO refers to the wave function obtained from solution of the Schrödinger equation for an isolated atom.[14,15] However, in macroscopic systems, individual system components interact with each other and therefore a contribution to the system wave function coming from the atom is essentially different from the wave function of the same atom but remaining in isolation.

The normalization condition: $\int \Psi^*(\boldsymbol{r}) \Psi(\boldsymbol{r}) \mathrm{d}^3 r = 1$, clearly emphasizes the difference between the wave function of a single element and the wave function contributed by this element in the case of a complex system.

The total potential acting on an electron placed at point $\boldsymbol{r}$ equals

$$V(\boldsymbol{r}) = \sum_{i=1}^{N} V(\boldsymbol{r}-\boldsymbol{r}_i), \tag{8}$$

where $V(\boldsymbol{r}-\boldsymbol{r}_i)$ means simple Coulomb potential between electron and ion positioned in point $\boldsymbol{r}_i$.

In order to take into account the influence of other electrons we can exchange the simple Coulomb potential for a screened Coulomb potential:

$$V(\boldsymbol{r}-\boldsymbol{r}_i) \to V_{\mathrm{sc}}(\boldsymbol{r}-\boldsymbol{r}_i) = -\frac{Ze^2}{|\boldsymbol{r}-\boldsymbol{r}_i|} \exp(-k_{\mathrm{s}}|\boldsymbol{r}-\boldsymbol{r}_i|), \tag{9}$$

which describes the electrical field of the $i$-th ion in the presence of all the remaining electrons. In the above equation, $k_{\mathrm{s}}$ means the screening parameter while $Z$ the valence. Consequently, the effect of the potential operator interaction on the wave function takes the following form:

$$\hat{V}\Psi(\boldsymbol{r}) = \sum_i V_{\mathrm{sc}}(\boldsymbol{r}-\boldsymbol{r}_i) \sum_j \Psi(\boldsymbol{r}_j) \tag{10}$$

and can be rewritten in the form of $N$-dimensional matrix:

$$V(\boldsymbol{r})\Psi(\boldsymbol{r}) = \begin{bmatrix} V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_1})\Psi(\boldsymbol{r_1}) & \cdots & V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_1})\Psi(\boldsymbol{r_N}) & V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_1})\Psi(\boldsymbol{r_2}) \\ V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_2})\Psi(\boldsymbol{r_1}) & V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_2})\Psi(\boldsymbol{r_2}) & \cdots & V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_2})\Psi(\boldsymbol{r_N}) \\ \vdots & \vdots & \ddots & \vdots \\ V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_N})\Psi(\boldsymbol{r_1}) & V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_N})\Psi(\boldsymbol{r_2}) & \cdots & V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_N})\Psi(\boldsymbol{r_N}) \end{bmatrix}. \tag{11}$$

Due to the screening effect, we can assume that the main contribution will come from the diagonal elements (below we prove that the contribution coming from the elements outside the main diagonal can be omitted), so the action of the potential operator on the wave function takes on the form:

$$\hat{V}\Psi(\boldsymbol{r}) = \sum_i V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_i})\Psi(\boldsymbol{r_i}). \tag{12}$$

If $n_i(\boldsymbol{r_i})$ denotes the local ion density and the volume of a single ion is $\Delta\boldsymbol{r}_i$ we can rewrite the last relation as follows:

$$\hat{V}\Psi(\boldsymbol{r}) = \sum_i n_i(\boldsymbol{r_i})V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r_i})\Psi(\boldsymbol{r_i})\Delta\boldsymbol{r}_i. \tag{13}$$

Since for each metal $\Delta\boldsymbol{r}_i$ is very small, we can replace the last sum by the integral, obtaining in result,

$$\hat{V}\Psi(\boldsymbol{r}) = \int n_i(\boldsymbol{r}')\Psi(\boldsymbol{r}')V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}')\,{\rm d}^3r', \tag{14}$$

which allows to transform the stationary Schrödinger equation into

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\boldsymbol{r}) + \int n_i(\boldsymbol{r}')\Psi(\boldsymbol{r}')V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}')\,{\rm d}^3r' = E\Psi(\boldsymbol{r}). \tag{15}$$

Note that if we assume that $n_i(\boldsymbol{r}) = \delta(\boldsymbol{r})$ which corresponds to a single atom, we come back to the classical Schrödinger equation, since in this case $\Psi(\boldsymbol{r}) = \Psi(0)$; traditionally we analyze the arrangement in the reference frame associated with the ion. On the other hand, it is worth paying attention to the nonlocality of the potential operator with integrate operator of a similar form we meet in the HF equations: exchange potential.[16,17]

For a regular crystal lattice, when we do not include the size effects, we can assume a constant density of ions, i.e., $n_i(\boldsymbol{r}') = n_i = {\rm const}$. Passing now directly to the domain transforms and using the theorem of convolution,[18] we obtain the following relationship:

$$\frac{\hbar^2k^2}{2m} + n_i\tilde{V}_{\rm sc}(\boldsymbol{k}) = E(\boldsymbol{k}), \tag{16}$$

where $\tilde{V}_{\rm sc}(\boldsymbol{k})$ means the well-known Fourier transform of screened Coulomb potential:

$$\tilde{V}_{\rm sc}(\boldsymbol{k}) = -\frac{Z4\pi e^2}{k^2+k_{\rm s}^2}, \tag{17}$$

so in result we have

$$\frac{\hbar^2k^2}{2m} - n_i\frac{Z4\pi e^2}{k^2+k_{\rm s}^2} = E(\boldsymbol{k}). \tag{18}$$

Noting that $Zn_i$ is equal to the electron density $n$, we have

$$\frac{\hbar^2k^2}{2m} - \frac{4\pi ne^2}{k^2+k_{\rm s}^2} = E(\boldsymbol{k}). \tag{19}$$

This is an important equation showing the relationship between the total energy of the electron and the wave number and electron density, despite the fact that the relation between $E$ and $n$ seems not so simple because the screening parameter is also a function of electron density (see below).

To show the effect of the other elements, we consider the matrix elements lying just above and under the main diagonal, that is, elements of the form

$$\begin{aligned} \Psi(\boldsymbol{r}_i)V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}_{i+1}) &= \Psi(\boldsymbol{r}_i)V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}_i-R), \\ \Psi(\boldsymbol{r}_i)V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}_{i-1}) &= \Psi(\boldsymbol{r}_i)V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}_i+R), \end{aligned} \tag{20}$$

where $\boldsymbol{R} = \boldsymbol{r}_{i+1} - \boldsymbol{r}_i$ is a vector generating a Bravais lattice[16] with primitive vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, and expressed as

$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3. \tag{21}$$

Both elements give a total contribution to the potential operator in the form of integrals:

$$\int n_i(\boldsymbol{r}')\Psi(\boldsymbol{r}')V_{\rm sc}(\boldsymbol{r}-\boldsymbol{r}'\mp R)\,{\rm d}^3r'. \tag{22}$$

With regard to the shift theorem[18] ( in the case of metal the displacement does not affect the symmetry of the system), after passing to the transforms domain we obtain conditions under which all these components equal zero, i.e.,

$$\cos(\boldsymbol{k}\cdot\boldsymbol{R}) = 0. \tag{23}$$

If we present the wave vector in the system related to the primitive cell of a Bravais lattice

$$\begin{aligned} &\boldsymbol{k} = k_1\boldsymbol{\alpha} + k_2\boldsymbol{\beta} + k_3\boldsymbol{\gamma}, \\ &\boldsymbol{a_1} = \boldsymbol{\alpha}a_1,\ \boldsymbol{a_2} = \boldsymbol{\beta}a_2,\ \boldsymbol{a_3} = \boldsymbol{\gamma}a_3, \end{aligned} \tag{24}$$

condition (23) transforms into

$$k_i = \frac{(2n_j+1)\pi}{2n_qa_i}, \quad i = 1,\ 2,\ 3, \tag{25}$$

which corresponds to the Born–Karman[16] conditions for free electrons.

In an analogous way we can prove the disappearance of the remaining matrix elements (11) beyond the main diagonal.

Thus, due to wave vector components satisfying condition (25), matrix (11) restricts itself to diagonal elements and consequently, the action of the potential operator on wave function comes down to the convolution integral (14).

## 3. Comparisons and correction

We may now determine the screening parameter $k_{\rm s}$ and the radius $k_0$, on the assumption that they correspond to surfaces of constant energy $E = C_1 = {\rm const.}$, and that the group

velocity of electron located on these surfaces equals zero. Because energy is determined with an accuracy of an additive constant, for simplicity we assume $C_1 = 0$.

Thus solving a simple set of equations:

$$E = 0, \quad V_g = \frac{1}{\hbar}\nabla_k E(k) = 0, \tag{26}$$

we obtain

$$k_0 = (-1)^{\alpha}[(-1)^{\beta} + \mathrm{i}]\frac{\sqrt{e}m^{1/4}n^{1/4}(2\pi)^{1/4}}{\sqrt{\hbar}}, \ \alpha\beta \in \{1,2\}, \tag{27}$$

and for each $k_1$ the two parameters

$$k_{\mathrm{s}} \pm \sqrt{2}k_0, \tag{28}$$

this means that both parameters are complex numbers whose modules are as follows:

$$\mathrm{Abs}[k_0] = \frac{2^{3/4}\sqrt{e}m^{1/4}n^{1/4}\pi^{1/4}}{\sqrt{\hbar}}, \tag{29}$$

and

$$\mathrm{Abs}[k_{\mathrm{s}}] = \frac{2\sqrt{e}m^{1/4}n^{1/4}(2\pi)^{1/4}}{\sqrt{\hbar}}. \tag{30}$$

The figure below (Fig. 1) shows the values of both parameters for all metals.

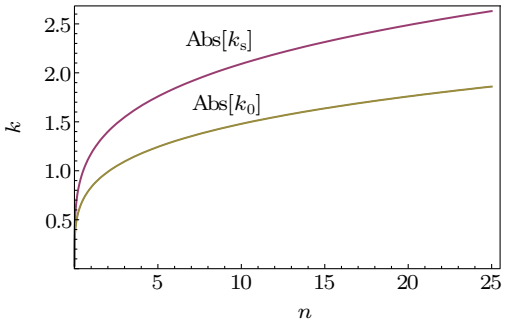



**Fig. 1.** (color online) Values $k_0$ and $k_{\mathrm{s}}$ for all metals versus $n$, $k = k \times 10^8$ cm$^{-1}$, $n = n \times 10^{22}$ cm$^{-3}$.

A closer analysis shows that $k_0$ corresponds to the Fermi radius $k_{\mathrm{F}}$ for a given metal. The difference between the two parameters for any metal does not exceed a few percent (Fig. 2).

Screening parameter determines the characteristic distance at which effective damping occurs. Therefore it provides important information required to obtain a correct shape of the potential. Generally known formula for the screening parameter (Thomas–Fermi (TF) theory of screening) shows that it is comparable to the Fermi radius for the metal.[16,17] This is confirmed in the present work, except that now $k_{\mathrm{s}}$ is visibly smaller than $k_{\mathrm{TF}}$, which means that the screening occurs at a longer distance than it results from the TF theory.

Figure 3 shows the dependences of total and potential energy of the electron on wave number $k$ for the example of Na.

According to the theory electrons occupy all states for which $k \leqslant k_{\mathrm{F}}$. It is worth noting that the potential energy of the electron on the Fermi surface $V$ ($k_{\mathrm{F}} \approx k_0$) is about 2.8 eV and the work function for Na equals 2.75 eV.

It allows to give a new and effective interpretation to the work function; namely the potential energy of an electron on the Fermi surface is

$$W = \frac{4\pi n e^2}{k_{\mathrm{F}}^2 + k_{\mathrm{s}}^2}, \tag{31}$$

which even in the simplest approximations[19,20] leads to analytical equations that allow to calculate the work functions for most metals, with an accuracy of a few percent (Fig. (4)).

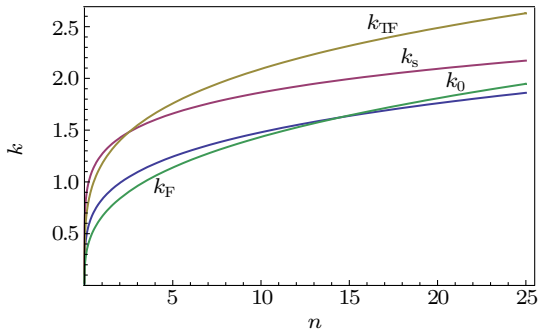



**Fig. 2.** (color online) Comparisons of the Fermi radius $k_{\mathrm{F}}$, Thomas–Fermi screening parameter $k_{\mathrm{TF}}$ with parameters $k_0$, $k_{\mathrm{s}}$, $k = k \times 10^8$ cm$^{-1}$, $n = n \times 10^{22}$ cm$^{-3}$.

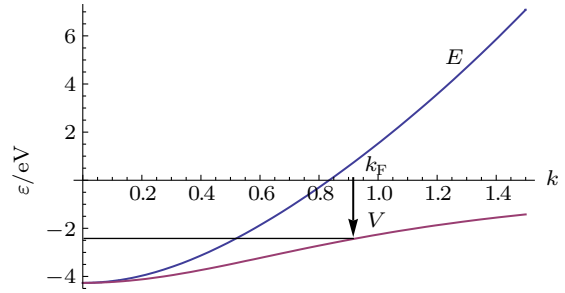



**Fig. 3.** (color online) Dependences of the total and the potential energy on wave number for Na, $k = k \times 10^8$ cm$^{-1}$.

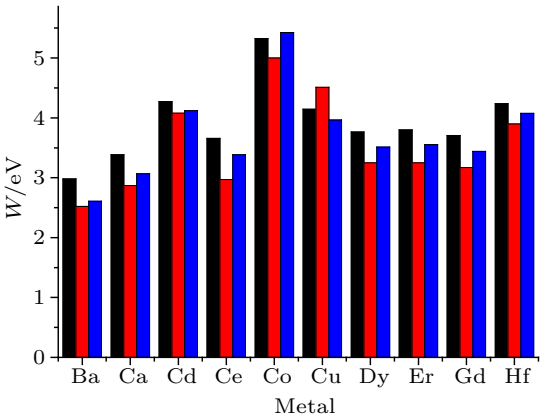



**Fig. 4.** (color online) Work function values for selected metals calculated directly from Eq. (31) (in cgs units), left column[20] is for $k_{\mathrm{s}} = k_{\mathrm{F}}$ from free electron approximation, the central column for the experimental values, the right column[19] for $k_{\mathrm{s}} = \mathrm{Re}[k_{\mathrm{s}}]$ from Eq. (30) and $k_{\mathrm{F}}$ from free electron approximation.

In the Hartree–Fock approximation the total electron energy is the sum of the kinetic energy $\hbar^2k^2/2m$, and a component describing the electron interaction effects, i.e.,

$$E(\boldsymbol{k}) = \frac{\hbar^2k^2}{2m} - \frac{2e^2}{\pi}k_{\mathrm{F}}F\left(\frac{k}{k_{\mathrm{F}}}\right), \tag{32}$$

where

$$F\left(\frac{k}{k_{\mathrm{F}}}\right) \approx \frac{1}{2} + \frac{1-(k/k_{\mathrm{F}})^2}{4k/k_{\mathrm{F}}} \ln\left|\frac{1+k/k_{\mathrm{F}}}{1-k/k_{\mathrm{F}}}\right|. \qquad (33)$$

Inclusion of the interaction between electrons causes a significant reduction of energy in comparison to the free electrons theory, and also increases the distance between the bottom of the conduction band and Fermi-level $\Delta E_{\mathrm{HF}}$ which is not confirmed in the experiment (observation of soft X-ray emission and photoemission). In the proposed model, this problem does not arise because it is clear from Eq. (19) that in this case, $\Delta E_1$ is much smaller (Fig. 5).

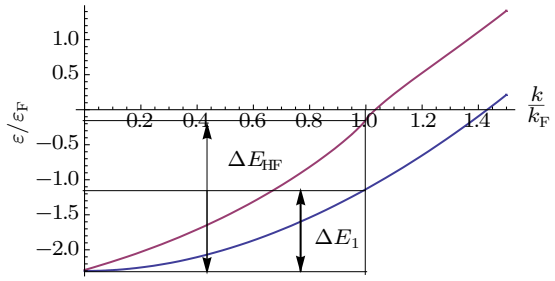



**Fig. 5.** (color online) Dependences of the relative value electron energy on the relative wave number for Na.

## 4. Determination of the Fermi surface

Determination of the Fermi surface is one of the main tasks of physics of metals. The shape of Fermi surface is closely related to the kinetic coefficients of the metal as well as its thermal, electrical, magnetic, and optical properties. Up to now, a number of experimental methods have been proposed to determine the shapes of the Fermi surfaces in metals. These methods are based on studies of magnetic, galvanomagnetic, and resonance phenomena. Electronic Fermi surfaces have been measured through the observation of the oscillation of transport properties in magnetic field $H$, for example the de Haas-van Alphen effect (dHvA) and the Shubnikov–de Haas effect (SdH).[16,17] The former is an oscillation in magnetic susceptibility and the latter in resistivity. The oscillations are periodic versus $1/H$ and occur because of the quantization of energy levels in the plane perpendicular to a magnetic field, a phenomenon first predicted by Landau.[21] Thus the determination of the periods of oscillation for various applied field directions allows mapping of the Fermi surface.

However, so far as the author knows there are no commonly known equations in the literature which allow to describe the shape of the Fermi surface for any metal. All the more it needs to be emphasized that equation (19) allows to outline the shape of the Fermi surface for any metal using simple commercial mathematical programs.

The three-dimensional figure presented below (Fig. 6) shows the shape of the Fermi surface for Na, obtained directly from Eq. (19).

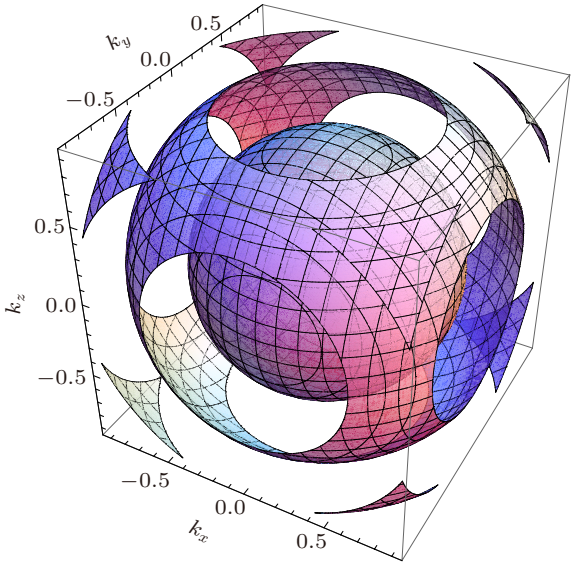



**Fig. 6.** (color online) Spatial dependence of the electron energy on the coordinates of the wave vector for Na. Each coordinate of the wave vector $\boldsymbol{k}$ takes values in the range $(-k_{\mathrm{F}}, k_{\mathrm{F}})$, while the screening parameter $k_{\mathrm{s}}$ is determined directly from Eq. (28).

From the above figure you can see that the Fermi surface for sodium in the ground state (0 K) is the sphere (the inner part). However we can observe the apparent deformations of the surface shape for $k$ greater slightly than the Fermi radius (Fig. 7). This explains to some extent the complicated shape of the Fermi surface for metal which we obtain as a result of experiments. So we should keep in mind that the experiments are carried out at temperatures higher than 0 K, and applied magnetic fields disrupt the state of the system. So in consequence we have not the Fermi surface in the ground state, but in conditions generated by the experiment. Observation of the dHvA and SdH oscillations requires magnetic fields to be large enough so that the circumference of the cyclotron orbit is smaller than a mean free path.

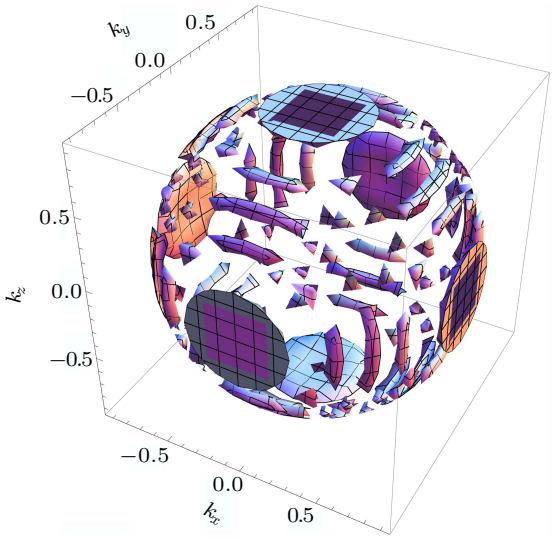



**Fig. 7.** (color online) Spatial dependence of the electron energy on the coordinates of the wave vector in a narrow range of variation $k$: $k_{\mathrm{F}}^2 \leqslant k_x^2 + k_y^2 + k_z^2 \leqslant (k_{\mathrm{F}} + \Delta k)^2$, $\Delta k \approx 0.1 k_{\mathrm{F}}$.

## 5. Conclusions

In the present work, a new original approach to solving the Schrödinger equation for a macroscopic system is proposed.

Because we do not know, and unfortunately we cannot determine the effective potential acting on the electron, located at a given point $\boldsymbol{r}$, we consider the interaction of an electron with each ion of the crystal lattice, which is described by the well-known Coulomb potential obtained as a result of the total potential in the form of Eq. (8). Interaction of the said electron with other electrons is taken into account by including screening.

As a result, the action of the potential operator on the wave function can be represented in the form of a matrix (11) but as shown only diagonal elements are important.

This allows to present the action of the potential operator on the wave function in the form of convolution, and then easily pass to the domain transforms, thereby obtaining a simple analytic relationship between the total electron energy and the wave number, Eq. (19), where the only additional parameter is the screening parameter $k_{\mathrm{s}}$.

If we impose the appropriate conditions on the total energy (26), we obtain a set of equations in which the variables are the screening parameter $k_{\mathrm{s}}$ and the wave vector values $k_0$ for which the electron total energy is constant.

It is worth emphasizing that the $k_0$ values obtained in this way are practically identical with the values of basic parameter in the theory of metals, i.e., the values of Fermi radius $k_{\mathrm{F}}$, while the $k_{\mathrm{s}}$ differs from the known Thomas–Fermi screening parameter $k_{\mathrm{TF}}$, $k_{\mathrm{s}} < k_{\mathrm{TF}}$, showing that screening has a much greater range than that from the TF theory.

The most important equation in the present paper (19), much better than the corresponding equation in the Hartree–Fock theory, allows to determine the band width of the electron energy and to give the electronic work function an analytical formula that even in the simplest approximation leads to results which are in good agreement with experimental results for many metals.

No less important advantage of this equation is the possibility to present the essential features of the Fermi surface in three-dimensional space.

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