The perturbation of the condensed medium in the Thomas–Fermi model

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Abstract. The research presented in this work is the continuation of the previous studies, which gave a qualitative estimating solution of the problem. The aim of this work is the calculation of static perturbation of condensed medium in the Thomas–Fermi approximation.

The research presented in this work is the continuation of the studies started in [1], which gave a qualitative estimating solution of the problem.

Theory of density functional as theoretical justification of approximate methods is widely used in the development of approximate theories of atomic interactions in molecules [2,3], intermetallic compounds and chemisorption [4].

Despite the large number of approximate methods of calculation of atoms and ions characteristics, allowing receiving some parameters with high accuracy, the statistical model continues to evolve and is used in many applications. General issues of density functional theory, and particularly the Thomas–Fermi method, are discussed in monographs [5–7]. Successful development of the theory of an inhomogeneous electron gas and its applications in various fields of physics, chemistry and technology leave no doubt of its effectiveness and relevance.

In some cases, the one-particle approximation for calculating the polarizability is insufficient due to the importance of many-body effects. This occurs, for example, for atoms with filled shells. It is necessary to use methods of many-body perturbation theory. It was found out that the decisive contribution to the dipole polarizability of noble gas atoms is given by the virtual transitions of the outer shell in the d-states of the continuous spectrum [8]. The contribution of transitions in the discrete spectrum is 10–20%.

The necessity to consider the electronic distribution, taking into account the shell structure of the atom, such as the Hartree–Fock electron densities, is quite obvious. The most well-known approach, linking the electron density and the interaction potential is based on the Thomas–Fermi model. Taking into account the exchange interaction and the amendments to the correlation, as well as the gradient corrections to the electron gas heterogeneity, quite a big number of models for calculating the polarizability of condensed matter can be created.

Recently, the Thomas–Fermi statistical approach has been improved and generalized to the high temperature and pressure region using a cellular model at finite temperatures [9–13]. The possibility of its use has been expanded for nano-sized (nanoscale) objects, for example. The improvement of the Thomas–Fermi model allows one to solve successfully enough the problems of incorrect motion of the semiclassical electron density near the nucleus and on the asymptotics, as well as shell effects to take into account.
The accuracy of the density functional theory in the local approximation is usually no better than 1%, and proposed clarification by the present time can not radically change the situation. If a more accurate calculation is required, it is necessary to calculate the many-electron wave function directly using the variational principle of Rayleigh–Ritz or any other scheme. However, these calculations are only possible for systems containing only a few electrons, while the density functional theory can be applied without difficulty to systems containing a large number of electrons.

The aim of this work is the calculation of static perturbation in condensed medium in the approximation of the Thomas–Fermi. In [1] the need to solve this problem has arisen in the calculation of the polarizability of the atoms, namely, when choosing a test function in the variational approach. Selecting the perturbed electron density in [1] was based on the use of the results obtained in the framework of quantum-mechanical perturbation theory [14], and quantum electrodynamics [15]. A similar approach can not be unambiguously considered as going beyond the scope of the Thomas–Fermi method as the minimization of the Ritz energy functional involves a wide arbitrariness in the choice of test functions.

In this paper, the electronic distribution of the unperturbed system is assumed to be preset. In particular, if we talk about atoms of inert gases, then we use electron densities [16], which are an approximation of the Hartree–Fock densities, taking into account kinetic and exchange energies and having an oscillatory character. From the point of view of improved models it is analogous to the inclusion of exchange and oscillation corrections. We take the expression for the electron density in the following form (where all the parameters are in atomic units):

$$D(r) = 4\pi r^2 \rho_0 = N r \left[ \sum_{i=1}^{2} \gamma_i^0 (\lambda_i^0)^2 \exp(-\lambda_i^0 r) + \sum_j \gamma_j^b \lambda_j^b (\lambda_j^b r - 2) \exp(-\lambda_j^b r) \right],$$

where $\rho_0$ is the electron density of the unperturbed atom, $N$ is the number of electrons in the atom, $r$ is the distance to the nucleus, and $\gamma, \lambda$ are parameters different for each atom. The form of $D(r)$ is shown in figure 1.

Thomas–Fermi equation reads

$$\Delta \varphi_0(r) = (8\sqrt{2}/3\pi) \varphi_0(r)^{3/2},$$

where $\varphi_0$—unperturbed potential.

**Figure 1.** Dependence of the electron density on the distance to the nucleus for Kr.
In this case, the unperturbed potential is related to the unperturbed electron density as follows:

\[ \varphi_0 = \frac{(3\pi^2 \rho_0)^{2/3}}{2}. \]

In addition, the correlation correction can be self-consistently taken into account by varying the electron density parameters in the same way as it was presented in [17] to refine the value of the total ionization energy of atoms and calculation of the pair potentials.

Let the result of some process in the system has changed the electron density and potential:

\[ \rho(r) = \rho_0(r) + \delta\rho(r), \quad \varphi(r) = \varphi_0(r) + \delta\varphi(r). \]

We consider small perturbations.

From the equation of Thomas–Fermi for the perturbed electron density we obtain

\[ \Delta \delta\varphi(r) = \frac{4\sqrt{2}}{\pi} \varphi_0(r)^{1/2} \delta\varphi. \] (2)

Considering

\[ k^2 = \frac{4\sqrt{2}}{\pi} \varphi_0(r)^{1/2} = \text{const}, \]

i.e. linearizing equation (2) and taking into account the spherical symmetry of the task, we get

\[ \frac{d^2\delta\varphi}{dr^2} + \frac{2\delta\varphi}{r} = k^2 \delta\varphi. \] (3)

By making the substitution

\[ \delta\varphi(r) = \frac{R(r)}{\sqrt{r}} \]

and the change of variables \( r = x/k, \ y(kr) = R(r) \) we obtain the modified differential equation of Bessel:

\[ \frac{d^2y}{dx^2} + \frac{1}{x} \frac{dy}{dx} \left[ 1 + \frac{1/4}{x^2} \right] y = 0. \] (4)

The General solution of (4) has the form

\[ y = C_1 J_{1/2}(x) + C_2 K_{1/2}(x), \]

where \( J_{1/2}(x), \ K_{1/2}(x) \)—Bessel and MacDonald functions, \( C_1, \ C_2 \)—some constants. Consider that the desired function is limited when \( r \to \infty \), consequently \( C_1 = 0 \). Finally, we get

\[ y = BK_{1/2}(x) = B \sqrt{\frac{\pi}{2x}} \exp(-x) = B \sqrt{\frac{\pi}{2kr}} \exp(-kr). \] (5)

Given that \( \varphi_0 \sim 1/r \) and \( k \sim \frac{1}{\varphi_0^{1/4}} \) we obtain

\[ \delta\varphi \approx \varphi_0^{3/4} \exp(-\varphi_0^{-3/4}), \] (6)

which corresponds to the results shown in [1]:

\[ \delta\varphi = A \varphi_0 \exp\left(-\frac{C_0 r^2}{r^\beta \varphi_0(r)}\right), \] (7)

where \( A, \ C_0, \ \beta \)—some real numbers. In [1] for simplicity we have chosen \( A = 1, \ C_0 = 6, \ \beta = 0 \). Here it is taken into account that the coefficient \( A \) does not affect the results in the calculation.
of the polarizability, $\beta$ is chosen from considerations of dimensionality. For atoms of noble gases, a change in $C_0$ in the range from 1 to 10 gives a change in $\alpha$ of less than 7%. Wherein

$$\varphi^{1/2} = \varphi_0^{1/2} \exp\left(-\frac{2\tau^2}{\varphi_0(r)}\right). \quad (8)$$

The integrand in [18] contains $\delta \rho \sim \rho_0^{1/3} \sim \varphi_0^{1/2} \sim \delta \varphi^{1/2}$, and the value of $C_0$ in [8] was chosen from the best agreement of the results for the helium atom.

Our results on electron density and potential are shown in figures 2 and 3.

Calculation results of polarizability of atoms of noble gases helium, neon, argon, krypton, and alkali metal atoms: lithium, sodium and potassium, halogen atoms: fluorine, chlorine and bromine, as well as the quadrupole and octupole polarizability of inert gases in this model are presented in [18, 19].
The exact implementation of the proposed model in this paper is only slightly complicates the calculation process. We are talking about functional model of Thomas–Fermi. Refinement of the energy the functional problem will eventually lead to the Kohn–Sham, so the connection between the study of the energy functional accuracy and calculated polarizability is a separate non-trivial task, which is far from solution.

Physically, a substantial part can be understood by analyzing the behavior of the function $\delta \varphi$. At $r \to 0$, $r^n \delta \varphi \to 0$ ($n \geq 1$) (it is in this form that this function enters the integrand for the polarizability of the atom), that eliminates the features arising in models based on the use of the quasi-classical approximation (statistical models), close to the nucleus. Next, the function increases rapidly enough forming a wide area further, weakly depending on $r$. The function $\delta \varphi$ then rapidly approaches zero. This excludes any significant impact of electronic “tails” on the change in energy of the atom in an external field.

At distances $R \approx 4–5$ atomic units, i.e. of the order of the dimensions of the Wigner–Seitz cell, the potential $\delta \varphi(r)$ and its derivative tend to zero, ensuring the fulfillment of the boundary conditions of the generalized Thomas–Fermi theory [9].

This dependence of the function $\delta \varphi$ leads to the following consequences. First and for most, the results of calculations in the model are in good agreement with the experimental values for the static polarizability of any multipole atom with closed electron shells. Second, the emergence of this function, as shown above, is physically quite reasonable, and due to the fact that the main contribution to the change in the energy of an atom in an external static electric field is associated with the transitions in the continuous spectrum.

In general, the results obtained in the formula for calculating the polarizability does not contain, in general, any atomic characteristics. Therefore, they are well suited for determining the polarizability of any condensed matter, including nanoparticles the electron distribution (or potentials) of which are known.

The analysis proves a high accuracy of the model [18, 19]. The simplicity and transparency of the physical clarification as well as the lack of computational problems are emphasized as one of its advantages.

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