Static polarizability of condensed particles

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Abstract. Within the inhomogeneous electron gas theory, a model is considered for calculations of static polarizability of matter. The analysis confirms the high accuracy of the new model. Among the main advantages of the model are its simplicity and physical transparency, as well as lack of computational problems.

One of the consequences of exposure of dielectrics to laser light is polarization of matter. Modeling and simulations of this process belong to the most relevant current problems in modern physics.

The purpose of this paper is to construct a new model providing a high-accuracy assessment of the polarizability of matter without considerable mathematical complications.

The paper proposes a new model for static dipole polarizability of spherically symmetric condensed particles, whose electron density (or potential) is known. The results obtained show that the model is credible as applied to atoms of inert gases, alkalis and halogens. As an initial approximation, we use the Thomas–Fermi statistical atomic model and account for the contribution from transitions in a continuous spectrum.

Development of a self-consistent quantum-statistical electron gas model accounting for contributions to the long-range part of the interatomic potential expands our understanding of the structure and mechanisms of interaction in condensed matter and allows us to use the results in many applications, including the studies of nano-dimensional physical objects that are so popular today.

Despite the fact that the most popular models of polarizability of condensed matter in recent years include those employing differential equations for the perturbed electron density, no significant progress has been made in this area.

It should be noted that of fundamental significance for such simulations is which particular initial statistical model is used. The results obtained in the framework of the Thomas–Fermi and Thomas–Fermi–Dirac dipole polarizability models, although different, are shown to be far enough from the experiment. However, in the Thomas–Fermi model, the values of multipole polarizabilities of atoms are infinite, while in the Thomas–Fermi–Dirac model they are finite. This is quite clear bearing in mind that the polarizability of the \( \mu \)-th multipole is proportional to \( r_0^{2\mu+1} \), where \( r_0 \) is the boundary radius of the atom, which is infinite in the first model and finite in the second.

For the static case, calculations of dispersion forces resolve themselves into the following. When the atom falls into an external electric field, its electron shell gets deformed, and the energy levels change. The shift of the energy levels is determined by the corresponding matrix elements of the perturbation:

\[
V = -\bar{d} \varepsilon = -\varepsilon d_z.
\]
The diagonal matrix elements of the dipole moment are zero, so splitting of levels in the electric field is a second-order effect with respect to the field. The shift \( \Delta E_n \) of the level \( E_n \) is given by the formula

\[
\Delta E_n = -\frac{1}{2} \alpha_{ij}^{(n)} \varepsilon_i \varepsilon_j,
\]

where the tensor \( \alpha_{ij}^{(n)} \) represents the polarizability of the atom in the external electric field.

Within the framework of the statistical theory [1] for the dipole polarizability of the atom, the following simple formula was obtained:

\[
\alpha = K^2(r_0) \left( 2 \int_0^{r_0} K(r)(\rho(r))^{1/3} r dr + \frac{5\chi k}{6\pi e^2} K(r_0) \right)^{-1},
\]

(1)

where

\[
K(r) = \int_0^r \left[ \rho(r') \right]^{1/3} r'^4 dr',
\]

and \( r_0 \) is the boundary radius of the atom. Formula (1) is obtained without the exchange, correlation and quantum corrections, which is quite admissible in this case because their contribution is insignificant for finite-radius atoms. This formula can be obtained in different ways, for example, by the standard perturbation atom energy minimization procedure. Here, the perturbed electron density was chosen in the following form [1]:

\[
\rho' = \rho(1 + \lambda \frac{\nu_s - \nu_0}{V_s - V_0}), \quad V_0 = \int \nu_s \rho^{1/3} dV / \int \rho^{1/3} dV,
\]

where \( \lambda \) is a variational parameter, \( V_s \) is the electron-nuclear potential, \( V_0 \) is the Lagrange multiplier.

In the framework of the inhomogeneous electron gas theory, numerous attempts have been made to improve formula (1) for the dipole polarizability.

A significant drawback of standard statistical models is the appearance of unphysical infinities in the vicinity of the nucleus. This feature causes a systematic understatement of the total energy of atoms and ions. Corrections to the total energy to eliminate the influence of the neighborhood of the nucleus were studied in a number of papers [2].

However, while all of the proposed ways to correct the behavior of the electron density near the nucleus (directly within the framework of the inhomogeneous electron gas theory) fail to succeed in calculations of polarizability, which is highly sensitive to the behavior of the electron density.

In some cases, the single-particle approximation for calculating the polarizability is insufficient because of the significance of multiparticle effects. This occurs, for example, for atoms with filled shells. Here it is necessary to use the methods of the multiparticle perturbation theory. One of the main problems of the theory of small oscillations relative to the ground state is the choice of the ground state. In the Thomas–Fermi model, the scale invariance holds; however, the electron density of the atoms in the ground state does not reflect their shell structure.

In view of these shortcomings, it becomes evident that we should use electronic distributions, accounting for the shell structure of the atom, such as the electronic density of the Hartree-Fock approximation.

The most well-known approximations linking the electron density and the interaction potential are based on the Thomas–Fermi model. Taking into account the exchange interaction and the correlation corrections, as well as gradient corrections for the heterogeneity of the electron gas, one can create a sufficiently large number of models to calculate the polarizability of condensed matter.
The most consistent way to determine the polarizability within the statistical model seems to be that accounting for the external field in the initial equations of the model. This approach was first used as early as in [1], but for the perturbed electron density a test function was employed that was expressed in terms of the unperturbed density and one variational parameter.

As we will further need an expression for \( \varphi(r) \), we write it explicitly. To do this, we use the electronic densities of atoms in the ground state from [3]:

\[
D(r) = 4\pi r^2 \rho(r) = Nr \left[ \sum_{i=1}^{2} \gamma_i^a \lambda_i^2 \exp(-a \lambda_i r) + \sum_{j=1}^{3} b_j^b \lambda_j (b \lambda_j r - 2) \exp(-b \lambda_j r) \right].
\]

From the Poisson equation, given the spherical symmetry of the electron distribution

\[
\triangle \varphi_0 = 4\pi e \rho(r),
\]

we obtain

\[
\varphi_0 = N \left\{ \frac{1}{r} \sum_{i} a_i \gamma_i \exp(-a \lambda_i r) + \sum_{j} b_j \exp(-b \lambda_j r) \right\}.
\]

In the Thomas–Fermi approximation, the electron density and the potential interactions are related by:

\[
\rho_0(r) = \gamma \varphi_0^{3/2}.
\]

In this paper, which is a continuation of [4], we confine ourselves to the Thomas–Fermi approximation. The computational procedure is standard, using the variational approach. The variational parameter is determined from the condition of minimum energy.

In the dipole approximation, the perturbing potential has the following form:

\[
\delta \varphi_1 = -\left| \vec{E} \right| r \cos \theta.
\]

This scheme for calculating the polarizability of the atom in all the approximations (the Thomas–Fermi and Thomas–Fermi–Dirac models, Thomas–Fermi–Dirac with correlation correction) was used before by a number of authors. The following conclusions were drawn:

(i) The models give overestimated values of the dipole polarizability, and in the case of multipole polarizabilities, the integrals diverge at all for Hartree–Fock-type electron densities.

(ii) We identified the need to specify the expression for the perturbed electron density.

In this paper, special attention should be paid to the case where the total potential energy of the system in an external field can be considered as the perturbation [5]. The unperturbed Schrödinger equation is then the equation of free motion of the particle

\[
\triangle \psi^{(0)} + k^2 \psi^{(0)} = 0, \quad k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{p}{\hbar}
\]

and has plane waves as solutions. The energy spectrum of free motion is continuous, so we are dealing with a special case of the perturbation theory in a continuous spectrum. It is easier to solve the problem without resorting to the general formulas of the perturbation theory.

The equation for the first-order correction \( \psi^{(1)} \) to the wave function is:

\[
\triangle \psi^{(1)} + k^2 \psi^{(1)} = \frac{2mU}{\hbar^2} \psi^{(0)},
\]
where \( U \) is the potential energy. The solution of this equation can be written in the form of “retarded potentials”:

\[
\psi^{(1)}(x, y, z) = -\frac{m}{2\pi \hbar^2} \int \psi^{(0)} U(x', y', z') e^{ikr} dV'.
\] (2)

Given that the weak external electric field removes the spherical symmetry and makes the task of finding the response function for the expression (2) two-dimensional, we consider a model problem: to determine the level of energy in a small-depth two-dimensional potential well \( U(r) \) (\( r \) is the polar coordinate in the plane).

For the Schrödinger equation near the well we ignore \( E \) and obtain the equation

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{d\psi}{dr} \right) = \frac{2m}{\hbar^2} U.
\] (3)

Integrating it over \( dr \) from zero to \( r_1 \) (where \( a \ll r_1 \ll 1/\chi \)), we have

\[
\frac{d\psi}{dr} \bigg|_{r=r_1} = \frac{2m}{\hbar^2 r_1} \int_0^{r_1} rU(r)dr.
\]

Away from the well, the equation of two-dimensional free motion is:

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{d\psi}{dr} \right) + \frac{2m}{\hbar^2} E\psi = 0,
\]

\[
\psi = \psi_0 S.
\] (4)

The general solution to the problem depends on the specific form of the potential energy, but in our case, there is no need to find the exact solution. Assuming that the function \( S \) can be considered almost constant near the well, we have:

\[
S \propto A \exp \left[ -\frac{\hbar^2}{m} \left( \int_0^{r_1} Ur'dr' \right)^{-1} \right].
\]

Equation (4) allows us to determine the perturbed electron density of the atom in the form of

\[
\rho(r) = \rho_0(r) S_0(r), \quad S_0(r) = A \exp \left( -\frac{C_0 r^2}{r^\beta \varphi_0(r)} \right),
\]

where \( A, C_0, \beta \) are some real numbers. Given the law of conservation of charge, the following condition must be satisfied:

\[
\int_0^\infty D(r) S_0(r) dr = N.
\]

In this paper, for simplicity, we choose \( A = 1, C_0 = 6, \beta = 0. \)

In our case,

\[
\varphi^{1/2} = \varphi_0^{1/2} \exp \left( -\frac{2r^2}{\varphi_0(r)} \right).
\]

The formula for the dipole polarizability (1) after the integration of the original expression becomes quite simple:

\[
\alpha_1 = \frac{\varepsilon_1}{\varepsilon_0 + \frac{\eta_1}{2} \int_0^\infty r\varphi^{1/2} \eta_1(r) dr}.
\]
\[ \xi_1 = \frac{3\pi}{4\sqrt{2}}, \quad \eta_{01} = \eta_1(\infty) = \int_0^\infty \varphi^{1/2}(r) r^4 dr. \]

The obvious advantage of the new model is its simplicity in terms of the complexity of the calculations. The simplest implementation of the model provides (as the most difficult procedure) for calculations of the double integral of a sufficiently smooth function.

Formula (5) converts to (1) if we take \( S = 1 \) and insert the Thomas–Fermi electron density instead of the Hartree–Fock distribution that minimizes the energy functional in the local approximation [2, 3].

The exact implementation of the proposed model in this paper only slightly complicates the calculations. Of course, here we are talking about the model implementation based on the Thomas–Fermi functional. Specification of the energy functional will eventually lead to the Kohn–Sham task, so studying the relationship between the accuracy of the energy functional and the calculated polarizability is a separate non-trivial task, which is still far from being solved.

If we proceed from the Schrödinger equation, we must understand that its exact solution can be found only in a relatively small number of simple cases, because most of the problems in quantum mechanics lead to very complicated equations. However, problem statements often appear to contain quantities of different orders of magnitude; among them one can find negligibly small quantities, ignoring which may simplify the problem to the extent that the problem can be solved exactly. In this case, the first step in solving the problem is the exact solution of the simplified problem, and the second, approximate calculations of the corrections associated with the small terms discarded in the simplified task. Basically, we used the general method for calculating these corrections, the perturbation theory method, to determine the response function in a weak external electric field.

The main problem is that the functional relationship between the density of the ground state of the coupled system of interacting electrons and the potential \( \varphi(\vec{r}) \) is unknown. This has been discussed in detail by Kohn [6]. The question is whether any positive function \( n(\vec{r}) \) with regular behavior, the integral of which is a positive integer \( N \), can represent the density of the ground state corresponding to any potential \( \varphi(\vec{r}) \).

Although there is still no exact answer, the practical use of the density functional theory is relevant in all areas of condensed matter physics.

The fundamental basis here is the theorem proved by Hohenberg and Kohn [7]: the energy of the ground state of a system of identical spinless fermions with arbitrary interaction in the scalar local static potential is a single-valued density functional of the particle number

\[ E = E \{ n(\vec{r}) \}. \]

For a fixed particle number, i.e. provided

\[ \int d\vec{r} n(\vec{r}) = N, \]

the functional attains its minimum value with respect to the density variation when the density coincides with the exact value for the ground state of the system.

\[ \frac{\delta E(n)}{\delta n} \bigg|_{n=n_0(\vec{r})} = 0. \]

The Hohenberg–Kohn theorem has been further extended to the case of spin particles, the relativistic case, the case of finite temperatures, etc.
Table 1. Dipole polarizability $\alpha_1$ of atoms of inert gases $[a_0^3]$.

|                  | He  | Ne  | Ar  | Kr  |
|------------------|-----|-----|-----|-----|
| Variational statistics |    | 37.0| 44.8| 54.0|
| Quantum mechanics  |    |  2.4| 10.1| 24.8|
| Hartree–Fock with relativistic corrections|  2.4| 10.8| 16.5|
| Present work      | 1.14| 2.28|  9.9| 16.2|
| Experiment        | 1.36–1.37| 2.63–2.65| 10.9–11.2| 16.6–16.9|

Table 2. Dipole polarizability of atoms of alkali metals $[a_0^3]$.

|     | Li  | Na  | K   |
|-----|-----|-----|-----|
| Present work | 158.3| 166.7| 298.7|
| Experiment   | 162.0 (B) | 162.0 (B) | 286.8 (B) |

The essence of this approach is that the environment of the atom in the condensed system is characterized by the electron density distribution around the atom. At the same time, the analysis of large systems with lower symmetry is simplified significantly, as there is no need in a quantum-mechanical analysis of the whole system. But the question of how well the density functional theory performs and how to use it has many aspects, and today they are still far from being resolved. For this reason, as the initial approximation one often uses the statistical Thomas–Fermi model of the atom, which is an effective method for calculating the atomic characteristics, especially in the case of many-electron atoms and ions, when calculations by the Hartree–Fock method are very cumbersome [8]. The results obtained using the statistical method are generally less accurate; anyway, it is extremely difficult to determine the criteria of accuracy. However, the Thomas–Fermi method enables qualitative and illustrative analysis of the basic properties and characteristics depending on the charge of the nucleus and the number of electrons in the atomic system.

This can be illustrated for some atoms.

Polarizabilities of the atoms of helium, neon, argon and krypton calculated by this model are summarized in table 1. It is clear that the accuracy of the model is comparable to that of quantum-mechanical calculations, and the maximum error (for He) is about 16%, which can be explained quite easily considering the essentially statistical nature of the Thomas–Fermi model. It is appropriate to note here that the statistical models available today do not provide quantitative agreement with experiment for all atoms; there is only qualitative agreement—for example, a definite power law of polarizability versus nuclear charge and number of electrons in the atom or ion. As a rule, the models employ artificial parameters, whose physical credibility is far from evident. We are referring, for example, to the “boundary radius” of the atom, which actually does not occur in ab-initio calculations, and is rather introduced artificially to set bounds to the integration domain.

We also calculated the polarizabilities of atoms of alkali metals, such as lithium, sodium and potassium (table 2) and halogens, such as fluorine, chlorine and bromine (table 3).

The experimental error B is 1–3%; C is 3–10%; D is > 10%.

The physically meaningful part can be understood by analyzing the behavior of the function...
**Table 3.** Dipole polarizability of atoms of halogens $[\alpha_0^3]$.  

|       | F     | Cl    | Br    |
|-------|-------|-------|-------|
| Present work | 3.81  | 15.5  | 27.6  |
| Experiment  | 3.76 (B) | 15.0 (C) | 26.0 (D) |

$S(r)$. At $r \to 0$, $S(r) \to 0$, which excludes the features that arise in the models based on the quasi-classical approximation (statistical models) near the nucleus. Next, the function grows quickly enough to form a wide region of weak function on $r$. Then ($\varphi(r) \leq r^2$) the function $S(r)$ sharply approaches zero. This eliminates quite a significant impact of electronic “tails” on the variation of the energy of the atom in the external field.

Such a dependence of the function $S(r)$ has the following consequences. Firstly, and this is absolutely important, the results of the calculations by this model are in good agreement with the experimental values for the static dipole polarizability of atoms with closed electron shells. Secondly, the emergence of this function is physically quite reasonable and is due to the fact that the main contribution to the change in the energy of the atom in the external static electric field is associated with the transition to the continuous spectrum.

Perhaps the use of the quantum-mechanical approach leads the model beyond the density functional theory, but the following can be noted in response: as of today, the inhomogeneous electron gas theory is insufficiently good in describing the transitions in the continuous spectrum, and the spectrum of excited states in general.

The polarizability formulas obtained in this work, generally speaking, contain no specifically atomic characteristics. Therefore, they are well suited for the determination of the polarizability of any condensed matter, the electronic distribution (or potentials) of which is known.

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