Static polarizability in a combined model

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Abstract.   In the framework of the theory of inhomogeneous electron gas, we consider a model to calculate the static multipole polarizability. The analysis shows the possibility of the specific dependence of the electron density perturbation (potential) of an atom in a weak external electrostatic field.

General questions of density functional theory (DFT), one of the implementations of which is the Thomas–Fermi model, are addressed in monographs [1, 2]. The successful development of the inhomogeneous electron gas theory or DFT and numerous applications in various fields of physics, chemistry and technology leave no doubt that it is effective and relevant.

The aim of this work is to study a combined Thomas–Fermi model. The proposed model is combined in the sense that it uses Hartree–Fock electronic distributions of atoms approximated by Slater functions as the unperturbed electron density. In a broad sense, this does not go beyond the scope of the model, or more precisely, beyond the DFT, because accounting for all the corrections brings it to the quantum theory. Neglecting all the contributions to the energy, except kinetic and potential, cannot influence the result significantly, as these contributions have the same sign in static polarizability calculations; consequently, the others, being an order of magnitude smaller and having different signs, can be ignored. The choice of the perturbed electron density in the present model is based largely on the use of the results obtained in the framework of the quantum-mechanical perturbation theory [3] and quantum electrodynamics [4]. However, that choice of perturbed potential cannot be simply regarded as going beyond the scope of the Thomas–Fermi method, as the minimization of the energy functional by the Ritz method involves fairly wide arbitrariness of the choice of trial functions, which of course does not exclude the need for a physically clear rationale for this choice. Even the functional relationship between the density of the ground state of the coupled system of interacting electrons and the potential $\varphi_0(\vec{r})$ is not precisely known. However, Hohenberg and Kohn [1] showed that all the properties of the electronic structure of a system in the non-degenerate ground state are determined entirely by its electron density.

Poisson's equation (in atomic units):

$$\triangle \varphi_0(r) = -4\pi \rho(r). \tag{1}$$

In the Thomas–Fermi approximation:

$$\rho_0(r) = \gamma \varphi_0^{3/2}, \tag{2}$$

where $\gamma = 2^{3/2}/3\pi^2$.

Accordingly, from (1)–(2) we obtain the Thomas–Fermi equation:

$$\triangle\varphi_0(r) = \frac{8\sqrt{2}}{3\pi}\varphi_0(r)^{3/2}. \tag{3}$$

In (1)–(3), ρ_0, φ_0 are the unperturbed electron density and the potential.
Suppose that as a result of some process, the electron density changes is

$$\rho(r) = \rho_0(r) + \delta\rho(r), \tag{4}$$

and the potential equals to

$$\varphi(r) = \varphi_0(r) + \delta\varphi(r). \tag{5}$$

We assume that the perturbations are small:

$$\delta\rho(r) \ll \rho_0(r), \quad \delta\varphi(r) \ll \varphi_0(r). \tag{6}$$

From the Thomas–Fermi equation for the perturbed electron density (potential) we obtain:

$$\triangle\delta\varphi(r) = \frac{4\sqrt{2}}{\pi}\varphi_0(r)^{1/2}\delta\varphi. \tag{7}$$

Assuming $\delta\varphi \propto \varphi_0$ [2] and linearizing (4), we obtain an equation [1,5,6] similar to the Mott equation for test charge screening in a metal [1]:

$$\nabla^2 V = q^2 V, \tag{8}$$

where $q^2 = 4k_f/\pi a_0$, $V = -\varphi$, $V_0 = -(Z/r)$, k_f is the Fermi momentum, a_0 is the Bohr radius.
The solution to the Mott equation is

$$V(r) = -(Z/r)\exp(-qr) = V_0\exp(-\beta/V_0), \tag{9}$$

$\beta = Zq$, Z is the nuclear charge.
Accordingly, for $\delta\rho(r)$, we obtain:

$$\delta\rho(r) \propto \lambda\varphi_0\exp\left(-\frac{\beta}{\varphi_0}\right). \tag{10}$$

The dependence of the perturbed potential on the unperturbed one (6) is often the case when such problems are solved without using the standard perturbation theory. Note, for example, that the radiative correction to the Coulomb law associated with vacuum polarization by a point charge [4] has the form:

$$\delta\varphi(r) = C\varphi_0(r)\exp(-2r)/r^{3/2}, \quad r \gg 1/m, \tag{11}$$

where m is the electron mass.
Given that $\varphi_0 = e/r$, it is obvious that

$$\delta\varphi(r) \propto \exp(-2/\varphi_0). \tag{12}$$

In addition, within the framework of quantum mechanics, when the total potential energy of a particle in an external field is viewed as a perturbation [3], the following expression was obtained for the energy in the two-dimensional potential well:

$$|E| \propto \exp\left[-\left|\int_0^\infty \varphi_0 r\,dr\right|^{-1}\right]. \tag{13}$$

The exact calculation of the response function in the general case is not possible [1]. However, based on the above, the main conclusion for us will be the characteristic dependence of $\delta\varphi(r)$ on φ_0.

Thus, in the proposed model, the perturbed part of the potential is chosen in the form of

$$\delta\varphi_n = \nu_n \varphi_0 \exp\left(-\frac{\sigma}{\varphi_0(r)}\right), \tag{14}$$

where

$$\nu_n = -\mu_n \left|\frac{\partial^n E_Z}{\partial Z^n}\right| r^{n+1} P_{n+1}(\cos\theta), \tag{15}$$

$P_n(\cos\theta)$ are the Legendre polynomials, μ_n is the variational parameter, E_Z is the projection of the Z axis of the strength of a weak external static electric field, $\sigma = 3/\pi^2$.

From [7]:

$$\varphi_0 = N\left\{\frac{1}{r}\sum_i {}^a\gamma_i \exp(-{}^a\lambda_i r) + \sum_j {}^b\gamma_j \exp(-{}^b\lambda_j r)\right\}. \tag{16}$$

Here N is the number of electrons in the atom, ${}^a\gamma_i$, ${}^b\gamma_j$, ${}^a\lambda_i$, ${}^b\lambda_j$ are the parameters interpolating the atomic electron distribution in the ground state.

In this paper, we restrict ourselves to the Thomas–Fermi approximation. We use the same calculation procedure within the variational approach. The perturbation energy in the first and second approximation has the following form:

$$\delta E^{(1)} = -\int \delta\varphi\rho(\vec{r})d\vec{r}, \tag{17}$$

$$\delta E^{(2)} = -U_S + U_P + U_K, \tag{18}$$

where

$$U_S = \int \delta\varphi\delta(\vec{r})d\vec{r}, \tag{19}$$

$$U_K = \frac{5\chi_k}{9}\int \frac{(\delta\rho(r))^2}{\rho^{1/3}}d\vec{r}, \tag{20}$$

$$U_P = -\frac{1}{2}\int \delta V_e \delta\rho d\vec{r} = \frac{1}{2}\int\int \frac{\delta\rho(\vec{r})\delta\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}', \tag{21}$$

U_S, U_P is the energy of Coulomb interaction of the atomic nucleus with electrons and electrons with each other, U_K is the kinetic energy of the electron gas, $\chi_k = 0.3(3\pi^2)^{2/3}$.

The variational parameter is determined from the condition of minimum energy. We introduce the following notation:

$$W_S = U_S/\mu, \quad W_P = U_P/\mu^2, \quad W_K = U_K/\mu^2. \tag{22}$$

Then, the variational parameter is

$$\mu = -\frac{W_S^2}{2(W_P - W_K)}, \tag{23}$$

and, accordingly, the energy is

$$\delta E^{(2)} = -\frac{W_S^2}{4(W_P + W_K)}. \tag{24}$$

On the other hand, the displacement of $\triangle E_n$ of the level E_n is expressed as

$$\delta E^{(n)} = -\frac{1}{2}\alpha_{ij}^{(n)} E_i E_j, \tag{25}$$

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

The formula for multipole polarizability after integration over the angles of the original expression becomes rather simple:

$$\alpha_n = \frac{\eta_{0n}^2}{\xi_n \eta_{0n} + 2\int_0^\infty r\varphi^{1/2}\eta_n(r)dr}, \tag{26}$$

where

$$\xi_n = \frac{(2n+1)\pi}{4\sqrt{2}}, \tag{27}$$

$$\eta_{0n} = \eta_n(\infty) = \int\limits_0^\infty \varphi^{1/2}(r)r^{2n+2}dr, \tag{28}$$

$$\varphi_n = \varphi_0 \exp\left(-\frac{\sigma}{\varphi_0(r)}\right). \tag{29}$$

Application of any type of density functional theory based on the concept of the homogeneous electron gas to calculations of atomic properties represents a very hard test for it [1].

In this work, which is a follow-up of [8, 9], we restrict ourselves to the Thomas–Fermi approximation. The results of polarizability calculations for the atoms of helium, neon, argon and krypton, atoms of alkali metals (lithium, sodium and potassium), and halogen atoms (fluorine, chlorine and bromine) within this model are reported in [8, 9]. The calculations of the static multipole polarizability of atoms with closed electron shells demonstrate good accuracy of the model. The obvious advantage of the new model is its simplicity in terms of the amount of calculations. The simplest implementation provides for (as the most difficult procedure) the calculation of the double integral of a sufficiently smooth function.

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