

Computational analysis of electronic polarizabilities in Thomas-Fermi theory of atoms.

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Abstract

The electric polarizability, α , of a molecule is a measure of its ability to respond to an electric field and acquire an electric dipole moment, μ . The electric polarizability, α has been calculated for several ions and atoms by obtaining the perturbation of wave functions by an external field from a numerical solution of differential equation satisfied by perturbation. For helium-like ions an analytic solution was obtained by using the wave functions of Lowdin. In this paper the statistical Thomas-Fermi theory of atomic structure was used to describe the polarizabilities of atoms and ions with closed electronic shells.

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1.0 Introduction.

London dispersion forces occur between atoms or molecules of nonpolar substances. Monoatomic atoms (noble gases, diatomic molecules (H_2 , N_2 , O_3 , F_2 , Cl_2) and nonpolar compounds (CH_4 , CCl_4 , BF_3 , BeH_2) to mention a few are all characterized by a symmetric sharing of electrons in the atom or molecule. These compounds do not have a permanent dipole as in heteronuclear diatomic molecules (HCl , HBr , HI and so on.) and polar compounds (SO_2 , H_2S , NCl_3 and so on.). [1]

If we take a "snapshot" of the electron distribution we would generally see, a symmetric distribution of the electron density. However, occasionally we see, but not very often, an unequal sharing of the electrons. A "snapshot" an instant later would reveal a return to an equal distribution of the electrons every once and a while we observe that the electrons are usually distributed around the nuclei. When this occurs there is a very small charge separation created which gives rise to instantaneous dipole will also be affected causing a shift of its electron distribution resulting in a small dipole around it. When this occurs, even for an instant there is a small attraction between the two molecules. The strength of the London dispersion forces depends on how easily the electron could be distorted or polarized.

The larger the molecule, the farther the electrons are from the nucleus and the easier the electron could be polarized. So the magnitude of the dispersion forces increases whether they are polar or nonpolar.

It has been shown that the force of attraction between two nonpolar molecules is inversely proportional to the seventh power of the distance and directly proportional to a property of each molecule called *polarizability*. Polarizability of an atom or a molecule is a measure of the ease with which the electron occupies a large volume of space, which occurs in an atom or molecule with many electrons, the polarizability of the substance is large.

The unit on polarizability is larger for a particular atom or molecule the magnitude of the instantaneous dipole can be large with the result producing a stronger attraction between particles. The electrons which are the most easily displaced in an atom or molecule are the valence electrons these are the furthest from the nucleus. So valence electrons make the greatest contribution to the polarizability. The force acting on the valence electrons depends on their distance from the nucleus and on the core charge. For any group in the periodic table the core charge remains constant, so we expect the polarizability to increase as the atomic size increases. So the polarizability of HI is greater than the polarizability of HF .

In molecules with large numbers of atoms the polarizability will be larger compared to smaller molecules. The polarizability of a molecule increases with both increasing size and increasing numbers of atoms in the molecule. So we expect the magnitude of the instantaneous dipoles, and therefore the strength of the London forces, to be greater the number of atoms in a molecule and the larger the atoms.

The polarization of N_2 is greater than H_2 , and that of CCl_4 greater than CH_4 , and CO_2 greater than that of CO . the strength of the intermolecular attractive forces is affected in the boiling points of the substances.

2.0 Theoretical background.

There are quite a number of atoms and ions that experiments have been able to provide their polarizabilities. These values of atoms and ions polarizabilities have been of great importance in the worlds of material science. Their discoveries have greatly improve the precision of the electrical properties in these elements. These polarizabilities values are however too small to cope with the challenges of today's industrial dynamics. Hence the need to provide theoretical values which are consistent with the experimental values. The statistical Thomas-Fermi theory of atomic structure is used to validate the existing experimental data on polarizabilities of atoms with closed electrons shells. We also desire to predict theoretically the various of polarizabilities that are yet to be obtained experimentally.

Atomic electrons in statistical model are considered as a degenerate non uniform Fermi as. The electron density $\rho(r)$ and potential $\Phi_o(r)$ inside the atom satisfy the equations

$$\nabla^2 \Phi(r) = 4\pi\rho \quad (2.1)$$

$$\frac{1}{2} \left(3\pi^2 \rho(r) \right)^{2/3} - \Phi(r) = E_F \quad (2.2)$$

where r is the distance from the nucleus, and E_F is the Fermi energy. These equations (in atomic units) are valid both for an isolated atom and an atom placed into an external field. The potential $\Phi_o(r)$ and the electron density $\rho_o(r)$ of an isolated atom are the spherically symmetrical solutions of equations (1) and (2) with $E_r = -Z/r_o$, r_o being atomic radius, Z , nuclear charge, and N the number of electrons (for neutral atom $Z = N$). If the atom is put into the uniform external field the electron density and the potential will suffer small deviations:

$$\Phi(r) = \Phi_o(r) + \Phi_1(r), \rho(r) = \rho_o(r) + \rho_1(r) \quad (2.3)$$

The equations for the induced potential $\Phi_1(r)$ and density $\rho_1(r)$ are obtained by putting (2.3) into (2.1) and (2.2) and keeping the terms of the first order [2] & [3]:

$$\rho_1(r) = \frac{\sqrt{2}}{\pi^2} \left(\Phi_o(r) - \frac{Z}{r_o} \right)^{1/2} \Phi_1(r), \quad r < r_o \quad (2.4)$$

$$\nabla^2 \Phi_1(r) = \frac{4\sqrt{2}}{\pi} \left(\Phi_o(r) - \frac{Z}{r_o} \right)^{1/2} \Phi_1(r), \quad r < r_o \quad (2.5)$$

The Thomas-Fermi (TF) energy functional taken into account the effect of exchange energy is:

$$E[\rho] = k \int \rho_1^{5/3}(r) d^3r + \int \Phi_1(r) \rho_1(r) d^3r + \frac{1}{2} \iint \frac{\rho_1(r) \rho_1(r^1) d^3r d^3r^1}{|r - r^1|} \quad (2.6)$$

$$\rho_1(r) = \left(\frac{3}{5k}\right)^{3/2} \left(\frac{Z}{r} - \int \frac{\rho_1(r^1)d^3r^1}{|r-r^1|}\right)^{3/2}, r \neq r^1 \neq 0 \quad (2.7)$$

where $k = (3/10)(3\pi^2)^{3/2}$, a constant. The constraint on $\rho_1(r)$ is $\rho_1(r) \geq 0$ and $\int \rho_1(r)d^3r = N$ Nothing particularly that equation (2.7) has been obtained by minimizing the TF energy and density functional equation (2.6) (in atomic units) [3]. Outside the atom, $\Phi_1(r)$ is the sum of potential of the external field and the induced atomic dipole:

$$\Phi_1(r) = -(\mathcal{E} \bullet r) + \alpha \frac{(\mathcal{E} \bullet r)}{r^3}, r > r_o \quad (2.8)$$

where α is atomic polarizability. The latter may be matching at the edge of atom $r > r_o$, the potential $\Phi_1(r)$ inside the atom (solution of (2.4)) with potential outside the atom given by (2.7) One obtains [5]:

$$\frac{\alpha}{r_o^3} = \frac{1-a}{1+a/r_o}, a = \frac{\Phi_1(r)}{\Phi_1^1(r)} \Big|_{r=r_o}, \Phi_1^1(r) = \frac{d\Phi_1(r)}{dr} \quad (2.9)$$

where $\Phi_1(r)$ is defined so that $\Phi_1(r) = \Phi_1(r) \cos(\mathcal{E}r)$ is the regular solution of equation of (2.4) and $\Phi_1^1(r)$ is the derivative of $\Phi_1(r)$ with respect to r at $r = r_o$ respectively.

3.0 Results and discussions.

Formulae (2.4) and (2.5) show that the density, $\rho_1(r)$ and the potential $\Phi_1(r)$ of atomic charge induced by the external field are solutions of a self-consistence problem and cannot be expressed algebraically in terms of the non-perturbed TF density $\rho_0(r)$.

Figures 1 and 2 are the plots of $\rho_1(r)$ versus r and $n(r) = r^2\rho_1(r)$ versus r respectively obtained by the solution of equation (2.6). The effect of interaction or exchange energy has been included.

Figure 3 shows the dependence of polarizability per unit volume, $\frac{\alpha}{r^3}$ on the scaled atomic radius,

$X_o = r_o Z^{1/3} / 0.885$ obtained by numerical solution of equation (2.4). The value of atomic radius, r_o were taken from Thomas-Fermi-Dirac calculation as in equation (2.4). For heavier atoms and ions then argon there is agreement between the experimental and the theoretical values.

4.0 Conclusion

The graph of figure 3 shows that the theoretical polarizability output values agree will with the experimental values. This fact gives hope that the graph of Figure 3 can also be used for evaluation of polarizabilities of atoms and ions for which the experimental data are obtained yet.

An analytical expression for polarization of atomic electrons just slightly screens the external field.

One may write $\Phi_1(r) = -\frac{Z}{r^3}$, $\Phi_o(r) = -(\mathcal{E} \bullet r)$. Hence $\alpha = -\frac{1}{\mathcal{E}} \int r\rho_1(r)d^3r \approx \frac{63}{16Z^{4/3}}$.

This last expression agrees with the $\alpha \approx Z^{-4/3}$ obtained for atom with all closed shells from exact quantum theory [6].

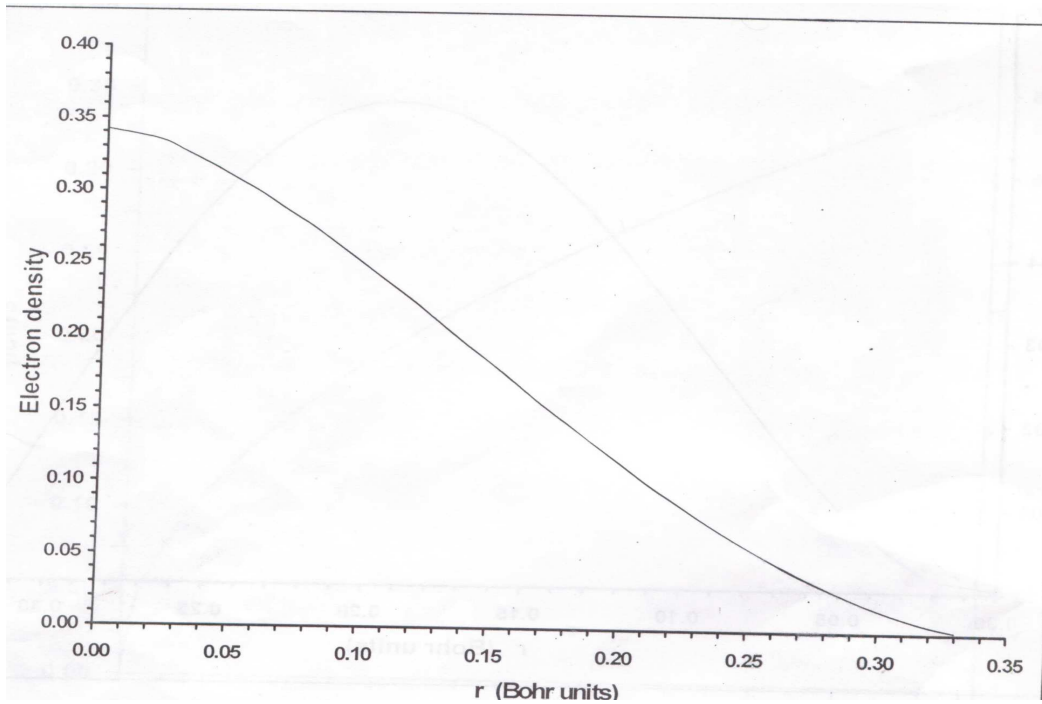


Figure 1: Electron density $\rho_1(r)$ versus radial distance, r (Bohr units) for $z = 90$.

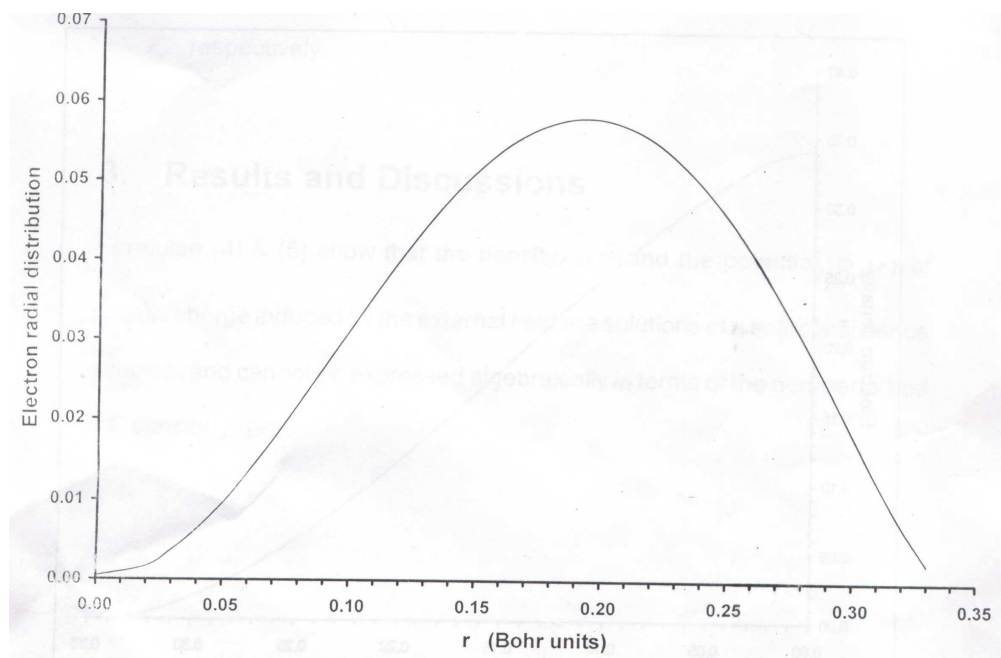


Figure 2: Electron radial distribution, $n(r) = r^2 \rho_1(r)$ versus radial distance r (Both units), $z = 90$

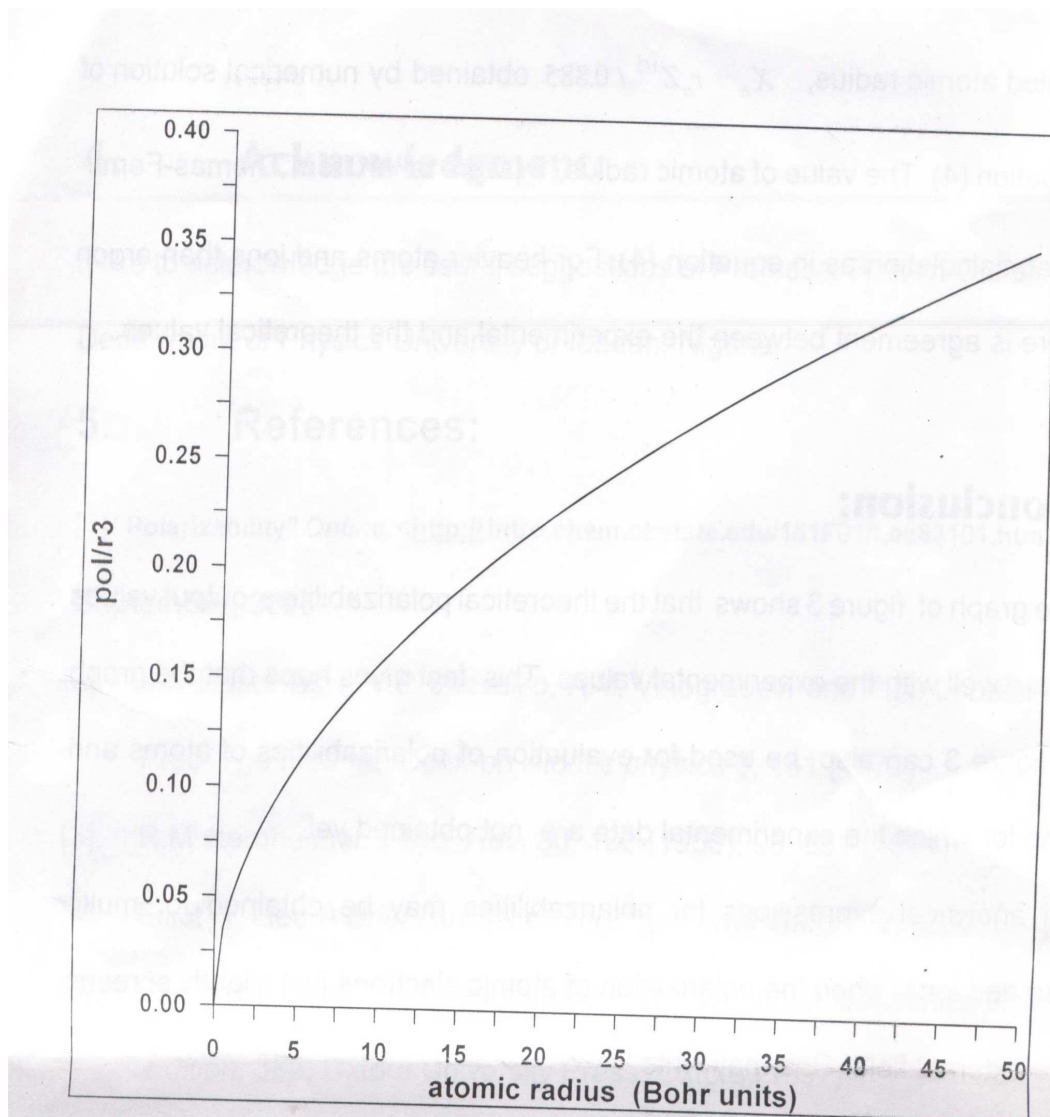


Figure 2: The plot of $\frac{a}{r^3}$ versus $X_o = r_o Z^{1/3} / 0.885$

4.0 Acknowledgement

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