ELECTRON POLARIZABILITY AND DIAMAGNETIC SUSCEPTIBILITY OF NEUTRAL ATOMS IN THE THOMAS-FERMI MODEL

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The Latter potential is employed to calculate the following quantities for a free neutral atom: the field at the atomic nucleus due to the variation of density, the total induced quadrupole moment, and the change in the gradient of the electric field at the nucleus produced by an external charge. These quantities turn out to be finite, in contrast to the result obtained on the basis of the usual statistical theory of the atom. Also the diamagnetic susceptibility of atoms is calculated according to the Thomas-Fermi model corresponding to the effective charge distribution of Latter and Byatt.

IT is well known[1] that in the statistical theory of Thomas and Fermi[2] (T.F.) for a free neutral atom the field at the nucleus, the total induced quadrupole moment, and also the gradient of the electric field at the atomic nucleus due to the external charge cannot be evaluated since these quantities all diverge in this theory. In this paper we shall show that if we assume for the potential of a free neutral atom the Latter potential,[3] then all the quantities enumerated above become finite.

We assume that the electric field is due to a single charge +e situated at a large distance R from the nucleus along the positive X axis. If R is measured in units of the Bohr radius a_0, then the dipole part of the potential energy (in Rydberg units) is given by the expression

$$H_1 = -2R^{-2}r\cos\vartheta, \tag{1}$$

where ϑ is the angle between the X axis and the radius vector **r** directed from the nucleus to an electron of the filled shell. The momentum p of an electron in the presence of the external charge +e at the point X = R is given in the case of the Latter potential by the expression

$$\begin{aligned} \frac{p^2}{2m} &= \frac{Ze^2}{r}\varphi(x) + \frac{e^2 r\cos\vartheta}{R^2} \quad \text{for} \quad \frac{Ze^2}{r}\varphi(x) \geqslant \frac{e^2}{r}, \\ \frac{p^2}{2m} &= 0 + \frac{e^2 r\cos\vartheta}{R^2} \quad \text{for} \quad \frac{Ze^2}{r}\varphi(x) < \frac{e^2}{r}. \end{aligned} \tag{2}$$

Here $\varphi(x)$ is the T. F. function for a free neutral atom, while the dimensionless variable x is related to r in the following manner:[2]

$$x = 2Z^{1/3}r\,(3\pi/4)^{-2/3}a_H^{-1}. \tag{3}$$

If we denote by p_0 the momentum of the electron in the absence of the external charge, then we have for $\Delta p = p - p_0$

$$p_0\Delta p = me^2 rR^{-2}\cos\vartheta, \tag{4}$$

where

$$\begin{aligned} p_0 &= (2mZ\varphi e^2/r)^{1/2} \quad \text{for} \quad Z\varphi(x) \geqslant 1, \\ p_0 &= 0 \quad \text{for} \quad Z\varphi(x) < 1. \end{aligned} \tag{5}$$

The change in density $\Delta\rho$ corresponding to Δp has the form

$$\Delta\rho = 8\pi p_0^2\Delta p/h^3. \tag{6}$$

By utilizing formulas (4) — (6) we find in the case of the Latter potential for the field at the nucleus produced by the increment $\Delta\rho$ the expression

$$E_i(0) = \frac{e}{2R^2}\int_0^{x_0} [x\varphi(x)]^{1/2}dx. \tag{7}$$

To obtain a rough estimate of the momentum induced in the filled shells of the T.F. theory we shall express the momentum p corresponding to the maximum energy E = 0 in terms of the nuclear quadrupole moment Q:

$$\begin{aligned} \frac{p^2}{2m} &= \frac{Ze^2}{r}\varphi(x) + \frac{e^2Q(3\cos^2\vartheta - 1)}{4r^2} \quad \text{for} \quad \frac{Ze^2}{r}\varphi(x) > \frac{e^2}{r}, \\ \frac{p^2}{2m} &= 0 + \frac{e^2Q(3\cos^2\vartheta - 1)}{4r^2} \quad \text{for} \quad \frac{Ze^2}{r}\varphi(x) < \frac{e^2}{r}. \end{aligned} \tag{8}$$

Here $\varphi(x)$ is the T.F. function at the point x of the electron cloud, r is the length of the vector from the nucleus to this point, ϑ is the angle between r and the symmetry axis of Q. Since the electron density is $\rho = 8\pi p^3/3h^3$, then the density $\Delta\rho$ due to the second term in (8) is given by relation (6),

while the change in the momentum Δp associated with the term containing Q is equal to

$$(p_0 \Delta p)/m = e^2 Q (3 \cos^2 \vartheta - 1)/4r^3 \quad (9)$$

(p_0 is the maximum momentum p for Q = 0).

On taking (6), (8), and (9) into account we obtain for $\Delta\rho$ the expression

$$\Delta\rho = \pi (2me^2/h^2r^2)^{3/2} (Z\varphi/r)^{1/2} Q (3 \cos^2 \vartheta - 1). \quad (10)$$

The potential due to this $\Delta\rho$ corresponds to the quadrupole moment induced by the nuclear quadrupole moment Q. The total induced quadrupole moment Q will be obtained from (10) by integration over the angles and over r. In the case of the Latter potential we obtain

$$Q_i = \frac{3}{10} Q \int_0^{x_0} [\varphi(x)]^{1/2} dx, \quad (11)$$

where the sign of Q_i is such that the nuclear moment q is screened. It can be concluded from (11) that the gradient of the electric field at the nucleus due to the external charge is altered by an amount

$$\Delta\left(\frac{\partial E_x}{\partial x}\right) = \frac{2e}{R^3} \cdot \frac{3}{10} \int_0^{x_0} [x\varphi(x)]^{1/2} dx. \quad (12)$$

It can be seen from (7), (11), and (12) that in the case of the Latter potential the quantities E_i, Q_i and $\Delta(\partial E_x/\partial x)$ exist. The upper limit of integration x_0 in the aforementioned formulas is obtained from the relation $Z\varphi(x_0) = 1$.

Table I. The values of $R^2e^{-1}E_i(0)$ obtained in the present work and by Sternheimer[1] for the case of the T.F. D. model for different values of the slope at x = 0

Z	Sternheimer		Present work	
	x_0	$R^2e^{-1}E_i(0)$	x_0	$R^2e^{-1}E_i(0)$
18	7.25 6.66 5.46	2.98 2.73 2.22	6.2558	1.96
57	9.66 3.81	3.50 1.47	11.8352	3.36

In Table I we compare our results for $E_i(0)$ with those obtained by Sternheimer[1] for Z = 18 and Z = 57. We obtain the integral of $[\varphi(x)x]^{1/2}$ numerically by utilizing the tables of the T.F. functions due to Taima and Kobayashi [4]. The Thomas-Fermi-Dirac (T.F.D.) solutions with a smaller negative slope at x = 0 have a minimum at large x corresponding to a neutral atom; they were cut off at a distance x_0. The smallest value for $(R^2/e)E_i(0)$ is the best one. It can be seen from Table I that our results agree with Sternheimer's results.

Table II. Effect of the induced quadrupole moment*

Element	Z	$Q, 10^{-24}$ cm^2	Sternheimer $Q_c, 10^{-24}$ cm^2	Present work $Q_c, 10^{-24}$ cm^2
Lu	71	5.9[a] 7,0[b]	6,7[a] 8.0[b]	8.1[a] 9.2[b]
Eu	63	1.2[c] 2,5[d]	2,0[c] 4.2[d]	3.3[c] 4.1[d]

*The indices correspond to the different isotopes: a – Lu^{175}, b – Lu^{176}, c – Eu^{151}, d – Eu^{153}.

In Table II we compare our numerical results for the corrected nuclear quadrupole moment $Q_c = Q + Q_i$ with Sternheimer's quantum mechanical calculations.[5] It can be seen from Table II that the agreement is only rough.

We now go on to consider the diamagnetic susceptibility according to the T. F. model in the case of the Latter potential. It is well known that the original T. F. model cannot explain the molar diamagnetic susceptibility of free neutral atoms because of the excessive smearing out of the electron cloud in this model.

For the diamagnetic susceptibility of a gram-atom of the substance χ_d one obtains the dependence of χ_d on Z in the form $\chi_d = \text{const} \cdot Z^{1/3}$. The constant in this formula gives according to the T.F. model excessively large values of χ. For this reason this formula has been corrected in different ways with the best agreement being obtained in the case of a free neutral atom if one evaluates χ_d according to a modified T.F. model, viz., according to the Fermi-Amaldi model. The T.F.D. model usually does not lead to any better results than the Fermi-Amaldi model.

In this paper we evaluate χ_d by utilizing the Latter potential and also by assuming Byatt's expression[6] for the effective charge $Z_p(r)$. The susceptibility per gram atom is given by the formula

$$\chi_d = -(7.923 \cdot 10^{-7}) a_0^{-2} \left(0 \left| \sum_j r_j^2 \right| 0\right), \quad (13)$$

where r_j is the distance of the j-th electron from the nucleus, a_0 is the Bohr radius, and 0 denotes the ground state of the atom. For a spherically symmetric atom we have

$$\left(0 \left| \sum_j r_j^2 \right| 0\right) = 6 \int_0^{\infty} Z_p(r)\, r\, dr, \quad (14)$$

where $Z_p(r)$ is the effective charge. In the T.F. model the charge Z_p is related to the T.F. function for the free neutral atom $\varphi_0(x)$ by the expression $Z_p = Z\varphi_0(x)$. Here Z is the atomic

Table III. Numerical values of the constants c_i and b_i in (19)

Element	c_1	c_2	c_3	b_1	b_2	b_3	Element	c_1	c_2	c_3	b_1	b_2	b_3
He	1.25	—0.25	0.0	1.75	3.845	0.0	O	1.25	—0.35	0.1	0.991	1.63	18.3
Ne	1.0	0.0	0.0	0.978	0.0	0.0	Fe	0.25	0.56	0.19	0.335	0.828	3.76
Ar	0.659	0.341	0.0	0.574	2.77	0.0	As	0.295	0.705	0.0	0.387	1.295	0.0
Kr	0.415	0.51	0.075	0.378	1.48	7.0	Hg	0.19	0.56	0.25	0.257	0.779	3.16
C	1.25	—0.44	0.19	0.828	1.41	4.29							

Table IV. Values of the quantity $-10^6 \chi_d$ obtained according to the different models

Element	He	Ne	Ar	Kr	Xe
T. F. model (uncorrected)	—	67.0	81.0	10.20	11.70
Fermi-Amaldi model	—	12.62	21.67	37.34	49.53
T. F. D. model	—	14.33	22.15	35.51	45.96
Hartree-Fock model	—	8.06	—	31.10	—
According to formula (18)	—	14.21	24.60	42.15	64.0
According to formula (20)	1.73	8.39	19.97	38.61	—
Experimental	—	6.8	19.5	28.0	42.4

Table V. Gram-atom susceptibility $-10^6 \chi_d$

Element	C	O	Fe	As	Hg
According to formula (18)	6.71	12.50	33.34	61.60	75.11
According to formula (20)	8.38	6.55	31.90	28.57	61.40
Experimental	6.2[8]	4.6[8]	—	23.2[9]	38.1[9]

number, $x = r/\mu$, where $\mu = 0.88534\, a_0 Z^{-1/3}$. In the case of the Latter potential Z_p, as is well known, is given by the formula

$$Z_p = Z\varphi_0(x), \quad \text{if} \quad Z\varphi_0(x) \geqslant 1,$$
$$Z_p = 0, \quad \text{if} \quad Z\varphi_0(x) < 1. \tag{15}$$

On taking this into account we write (14) for the case of the Latter potential:

$$\left(0 \left| \sum_j r_j^2 \right| 0\right) = 6 \int_0^{r_0} Z\varphi_0(x)\, r dr. \tag{16}$$

The upper limit of integration r_0 is given by the equation $Z\varphi_0(x_0) = Z\varphi_0(r_0/\mu) = 1$. By utilizing the expression obtained earlier[7]

$$\varphi_0(x) = (1 + bx + cx^2)^{-3/2}, \tag{17}$$

where b = 0.7105, c = 0.03919, we obtain in accordance with (13), (16) and (17) the expression for χ_d:

$$-10^6 \chi_d = 21.411\, Z^{1/3} \left[\frac{2 + bx_0}{\sqrt{1 + bx_0 + cx_0^2}} - 2 \right], \tag{18}$$

with $Z\varphi_0(x_0) = 1$. The function $\varphi_0(x)$ of the form (17) gives a very good approximation to the exact values of $\varphi_0(x)$ in the interval from x = 0 to x = 1000. The maximum error in this case amounts to less than 3%.

Ruark was the first to propose (cf. reference 6) that the following expression should be utilized for the effective charge Z_p

$$Z_p = Z\,[c_1 e^{-b_1 r/\mu} + c_2 e^{-b_2 r/\mu} + c_3 e^{-b_3 r/\mu}]. \tag{19}$$

The constants c_i and b_i in the last formula depend on Z. Byatt has calculated these constants with great accuracy for several values of Z. In Table III are given numerical values of c_i and b_i as functions of Z.

By utilizing (19), (16), and (13), we obtain for χ_d the expression

$$-10^6 \chi_d = 3.7260 Z^{1/3} [c_1 b_1^{-2} + c_2 b_2^{-2} + c_3 b_3^{-2}]. \tag{20}$$

In Table IV the values of χ_d evaluated by us in accordance with expressions (18) and (20) are compared with numerical values obtained in the original T.F. model (cf. reference 2), in the modified Fermi-Amaldi model, in the T.F.D. and the Hartree-Fock models, and also with experimental data. It may be seen from Table IV that expression (18) gives better results than the original T.F. model, although they are still too large in comparison with experiment. Formula (20) gives better results than (18), and this means that the charge Z_p obtained from (19) is very close to the true Hartree-Fock effective charge distribution.

In Table V we give values of χ_d, obtained from (20) and (18) for a number of substances which are not listed in Table 4; experimental data[8,9] are also shown there. As is well known, these data are not very definite, since it is difficult to find experimentally the diamagnetic susceptibility for atoms other than those shown in Table IV.

It can be seen from Tables IV and V that formula (19) for Z_p can be utilized for the description of the problem of interest to us.

From the present work it follows that the quantities $E_i(0)$, Q_i and $\Delta(\partial E_x/\partial x)$ [formulas (7), (11) and (12)], obtained with the aid of the Latter potential have finite values. Numerically they agree with the experimental data only very roughly. In order to obtain better agreement it is necessary to carry out a quantum mechanical averaging. Table II shows that Q_i evaluated with the aid of the Latter potential gives a somewhat worse result than the more elaborate T.F.D. model. It can be seen from Table IV that the diamagnetic susceptibility obtained with the aid of the Latter potential gives better results than the uncorrected T.F. theory. The results of Table IV provide evidence that the Latter potential, in principle, leads to values comparable to those obtained in the T.F.D. and the Fermi-Amaldi models.[10]

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