

Atomic diamagnetic susceptibilities from the statistical Thomas-Fermi-Amaldi theory

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Abstract. We report the calculation of atomic diamagnetic susceptibilities from the statistical Thomas-Fermi-Amaldi theory. The importance of the Fermi-Amaldi correction for the Thomas-Fermi theory is examined. The calculated values are compared with those obtained from self-consistent-field wave functions as well as with respect to available experimental data. Several general trends are pointed out and the advantages of the statistical procedure are stressed.

Keywords. Atomic diamagnetic susceptibilities; Thomas-Fermi theory; Fermi-Amaldi correction.

1. Introduction

Within the context of the Thomas-Fermi (TF) theory (Gombás 1949) a given electron interacts with itself in addition to the natural interactions with the remaining electrons. Clearly, this represents a serious shortcoming of the theory and the Fermi-Amaldi (FA) correction (Keller 1980) represents a valid attempt to withdraw this spurious self-interaction. In three recent papers (Csavinszky 1979; Donnamaría *et al* 1982a, b) the quantitative importance of the FA correction for the TF theory of atoms and ions was analyzed for an analytical trial electron density. The energy expression for this particular function was minimized by the Ritz variational method, and then the optimum electron densities were used to calculate the diamagnetic susceptibilities. Numerical results showed that, when dealing in a proper and complete fashion, the FA correction represents a significant quantitative improvement over the TF theory. Furthermore, a satisfactory estimation of diamagnetic susceptibilities was obtained in relation to the available experimental data (Mulay 1966). Regarding neutral atoms, a very small set was chosen to perform the calculations viz. the closed shell atoms of Ne, Ar, Kr, Xe and Rn.

The present paper attempts to extend the calculations to a wider class of atoms. We report the computations of diamagnetic susceptibilities in the case of most of the elements found in the periodic table ($Z=2$ to $Z=86$). Dehn and Mulay (1968) have compared the experimental diamagnetic susceptibilities of atoms with values calculated by using approximate atomic wave functions. The agreement among results emerging from these different sources is discussed and several general trends

are pointed out. Finally, the necessity of introducing the FA correction within the TF theory of atoms is stressed on the basis of the foregoing results.

2. Method

Since the method has already been reported (Donnataria *et al* 1982a, b), we confine ourselves to presenting the most important formulas. The Thomas-Fermi-Amaldi (TFA) energy relationship in atomic units is

$$E_{\text{TFA}} = K_k \int P^{5/3} dv - \int V_k P dv + \frac{N-1}{2N} \int V_e^{\text{TF}} P dv, \quad (1)$$

where the first term on the right side is the kinetic energy of the electron gas, the second term represents the interaction energy of the electron gas with the atomic nucleus and the third term denotes the self-energy resulting from the interaction of the electron gas. Besides, $K_k = 2.871\ 234$ and $V_k = Z/r$. The electron-electron potential energy V_e^{TF} is determined from the Poisson's equation by integrating it twice with the limiting condition

$$\lim_{r \rightarrow \infty} V_e^{\text{TF}} = -N/r. \quad (2)$$

When the trial density function (Jensen 1932)

$$P = N A^{-1} e^{-x} x^{-3} (1 + c^0 x)^3, \quad (3)$$

is used, the energy formula is (Csavinszky 1979)

$$E_{\text{TFA}} = \{0.063\ 243 p^2 L_1 L_0^{-5/3} - [0.5 L_2 L_0^{-1} - 0.25 (L_2 - M) L_0^{-1} (N-1) N^{-1}] p\} Z^{7/3}, \quad (4)$$

where L_i ($i=0, 1, 2$) and M are polynomials depending on c^0 , whose explicit formulas were given by Csavinszky (1979),

$$x = Z^{1/6} p^{1/2} r^{1/2} \quad (5)$$

c^0 and p are variational parameters which are computed from the minimization of the energy equation, and A is a constant determined from the normalization condition

$$\int P dv = N \quad (6)$$

The diamagnetic susceptibility D is calculated from the relation

$$D = -N_A (6 c^0)^{-1} \langle r^2 \rangle, \quad (7)$$

where N_A is the Avogadro's number, c is the velocity of light, and $\langle r^2 \rangle$ is given by

$$\langle r^2 \rangle = \int P r^2 dv. \quad (8)$$

3. Results and discussion

We have chosen the same neutral atoms as those reported by Dehn and Mulay (1968). First, we have minimized in a complete manner the TFA energy expression (4) associated to the 41 atoms and obtained optimum values for the parameters p and c^0 , according to a minimum energy criterion. Then, with each pair [$p_{\text{opt}}(Z)$, $c_{\text{opt}}^0(Z)$] the atomic diamagnetic susceptibilities were computed.

In table 1 we display the optimum values for the variational parameters p and c^0 ,

Table 1. Optimum values for the variational parameters, r^2 values (in units of 10^{-18} cm²) and diamagnetic susceptibilities ($-D \times 10^6$ cm³/molecule).

Atom	c_{TFA}^0 (a)	$p_{\text{TFA}}^{(b)}$	r_{TFA}^2	$D^{(c)}$	$D^{(d)}$	$D^{(e)}$ experimental
Li	0.379	15.036	3.03	13.579	8.535	para
Be	0.350	14.014	3.70	14.945	10.435	9.00
B	0.335	13.424	4.25	16.059	11.979	6.70
C	0.324	13.023	4.72	17.108	13.310	6.00
N	0.316	12.732	5.14	18.010	14.479	6.00
O	0.309	12.484	5.53	18.830	15.569	para
F	0.305	12.335	5.85	19.584	16.479	—
Na	0.298	12.083	6.44	20.938	18.147	para
Mg	0.295	11.977	6.71	21.555	18.914	para
Al	0.293	11.904	6.96	22.137	19.597	para
Si	0.291	11.833	7.19	22.691	20.259	3.90
P	0.289	11.763	7.42	23.219	20.902	20.8
S	0.288	11.725	7.62	23.724	21.459	15.5
Cl	0.286	11.657	7.83	24.208	22.071	20.75
Cu	0.278	11.368	9.70	28.925	27.324	6.16
Zn	0.277	11.336	9.85	29.254	27.740	11.4
Ga	0.277	11.334	9.96	29.576	28.055	21.6
Ge	0.276	11.302	10.10	29.980	28.461	76.84
As	0.276	11.300	10.21	30.199	28.764	23.7
Se	0.276	11.298	10.32	30.501	29.061	25.0
Br	0.275	11.266	10.45	30.792	29.452	56.4
Ag	0.273	11.192	11.65	33.977	32.801	24.0
Ca	0.273	11.191	11.73	34.126	33.037	19.8
In	0.273	11.190	11.81	34.452	33.270	64.0
Sn	0.272	11.160	11.93	34.685	33.614	37.0
Sb	0.272	11.159	12.01	34.914	33.842	99.0
Te	0.272	11.158	12.09	35.141	34.066	39.5
I	0.272	11.157	12.17	35.365	34.287	88.7
Au	0.270	11.085	14.03	40.398	39.524	34.0
Hg	0.270	11.085	14.09	40.567	39.693	33.4
Tl	0.270	11.085	14.15	40.736	39.860	50.9
Pb	0.270	11.084	14.21	40.903	40.025	23.0
Bi	0.269	11.054	14.31	41.068	40.329	10.5
Po	0.269	11.054	14.37	41.233	40.492	—
At	0.269	11.054	14.43	41.396	40.654	—

(a) $c_{\text{TFA}}^0 = 0.265$ for any atom; (b) $p_{\text{TFA}} = 10.911$ for any atom; (c) D_{TF} ; (d) D_{TFA} ; (e) Dehn and Mulay (1968).

and the average values $\langle r^2 \rangle$ and D results. Table 1 shows that, far from remaining constant, c^0 changes significantly with Z . However, when Z increases, c^0 tends to the TF value 0.265 (Jensen 1932), in agreement with previous discussions (Csavinszky 1979). A similar comment applies for the parameter p , which decreases with Z , tending to the TF value 10.911. Furthermore, it is noteworthy that the marked contraction of the electron cloud of an atom upon the FA correction, because in all cases $\langle r^2 \rangle_{\text{TF}} > \langle r^2 \rangle_{\text{TFA}}$, although their difference decreases as N increases. This fact is also expected, since as mentioned earlier (Donnataria 1982 a,b) $V_{\text{e}}^{\text{TFA}} \rightarrow V_{\text{e}}^{\text{TF}}$ as $(N-1)/N \rightarrow 1$. The comparison of results for D in table 1 and those reported by Dehn and Mulay (1968), shows the existence of a similar accuracy between the TFA results and those given by Clementi's SCF wave functions, and the superior quality of the statistical values with respect to the remaining wave functions. To appreciate properly these differences, it is important to consider that a considerable effort is involved in computing the SCF wave functions while the statistical procedure is simple, direct and fast. The comparison of statistical results for D shows that $|D_{\text{TF}}| > |D_{\text{TFA}}|$, and the TFA values are in a better agreement with the experimental values than the corresponding TF ones. The improvement of the TFA values over the TF results is considerable for the lighter elements, while it is only moderate for the heavier atoms.

It is important to point out that, in judging the parallelism between theoretical and experimental susceptibilities, the experimental data are not the results of true measurements on particular atoms, but they are determined from measurements on compounds and resorting to somewhat indirect considerations.

We may then conclude that the FA correction represents a significant improvement over the TF theory and that results obtained from the TFA model are of a similar quality as those computed from the best SCF wave functions.

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