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Z VARIABLE CALCULATION WITH THE STATISTICAL THOMAS - FERMI , THOMAS - FERMI - AMALDI , THOMAS - FERMI - DIRAC AND THOMAS - FERMI - AMALDI - DIRAC METHODS FOR IONS

María C. Donnamaría, Mario D. Glossman, Eduardo A. Castro and Francisco M. Fernández

INIFTA, Sección Química Teórica, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

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SUMMARY

A Z variation is introduced in the Thomas- Fermi, Thomas-Fermi- Amaldi, Thomas-Fermi-Amaldi-Dirac and Thomas-Fermi-Dirac methods. The procedure is simple, direct and easy to apply. It is based on the concept of effective nuclear charge Z, which is modified through an energy criterion. Atomic diamagnetic susceptibilities are calculated and the analysis of numerical data reveals the existence of a marked improvement when Z is varied.

INTRODUCTION

Since its presentation by Thomas /1/ and Fermi /2/, and subsequent modification by Dirac /3/, the Thomas- Fermi model (TFM) has been useful in the study of atoms, molecules and solids. The model supposes a degenerate free electron gas for the atom /4/. The electron gas is under the influence of a mean potential. The electron interaction is ignored, except for the

mean screening effect of the electron cloud. The exchange /3/ and correlation /5/ electronic energies are neglected. The statistical model works well in those cases in which one is not interested in the details of the electronic structure but rather in some integrated-quantities behaviour such as form factors, certain moments of electron density distribution, diamagnetic susceptibilities, polarizabilities and total energy density of electrons of an atom /6/. However, the TFM for atoms and ions has two important shortcomings : a) Close to the nucleus the electron density P(r) varies as $r^{-3/2}$, and becomes infinite as $Z \longrightarrow \infty$(r being the distance from the nucleus), giving an infinite density in this limit. b) At large distances, the electron density varies as r^{-6} decreasing rather exponentially /7/ (Hartree's approximation). Another error in the TFM, is that electrons interact with themselves, in addition to the natural interelectronic interaction. In order to tackle this, Fermi and Amaldi /8/ (FA) simply multiplied the charge distribution that each electron sees by a correction factor (N - 1)/ N, N being the atomic number. Recently, several attempts have been made /9 -13/ to test the efficacy of introducing the FA and Fermi-Amaldi -Dirac (FAD) modifications within statistical theories for atoms and ions. This is achieved by taking the quantum mechanical form for the electron density close to the nucleus and matching it with the statistical variational density corresponding to the trial function (Jensen's function /14/) at some $r = r_o$. This procedure usually yields improved electron densities, and recent results /9-13/ for diamagnetic susceptibilities showed a satisfactory agreement with experimental and SCF values. How-

ever, a very disturbing aspect of this kind of calculation scheme arises when one analyses the energy expressions. The TFM leads to total electronic energies which are too large , and subsequent introduction of correction terms makes things worse /15/. In a very recent paper /16/,we examined the possibility of improving total electronic energies calculated from the TFM and TFAM with the simple Jensen's trial function, through the consideration of the Z-variation for neutral atoms. We also performed a similar calculation from the Thomas-Fermi-Dirac (TFDM) and Thomas-Fermi-Amaldi-Dirac methods (TFADM) /17/. The comparison of numerical results to other previous theoretical values and experimental data for atomic diamagnetic susceptibilities allowed us to verify the existence of marked improvements.

The purpose of the present work is to extend the examination of the procedure by applying it to the TFM, TFAM, TFDM and TFADM, respectively, for several ions.

After fitting the necessary parameters associated with the trial electronic density function in respect to the non-relativistic total energy for the TF like methods, we test their values with regard to another independent atomic property :the atomic diamagnetic susceptibility.

RESULTS AND DISCUSSION

The atomic total energy in the TFM is given by /18/(in what follows, atomic units were used).

$$E_{TF} = 2.8712\int P(r)^{5/3}dv + \int P(r)V_N dv + \frac{1}{2}\iint \frac{P(r)P(r')}{|r - r'|}dv\,dv' \qquad (1)$$

P(r) being the electronic density function and V_N the electron nuclear interaction, which in an atom or ion with charge Z on the nucleus is simply (- Z/r). P(r) may be determined from the numerical solution of the TF equation

$$\frac{d^2 \phi}{d x^2} = \phi^{3/2} x^{-1/2} \qquad (2)$$

where

$$r = bx \; ; \; b = 0.8853 \; Z^{-1/3} \qquad (3)$$

$$V(r) - E_f = - Z/r \qquad (4)$$

$$E_f = p_f^2 + V(r) \qquad (5)$$

p_f is the maximum or Fermi momentum at the position r /19/, V(r) is the self-consistent potential energy.

It is of considerable importance to note that the density energy relationship (1) of the statistical theory follows from the variational principle for the total energy /19/. In fact, the TF equation (2) follows from equation (1) by minimizing E_{TF} with respect to variations in the density P(r), and it is subject only to the normalization condition :

$$\int P(r) \, dv = N \qquad (6)$$

N being the total number of electrons in the atom.
This second alternative gives us the possibility of using a relatively simple trial density function with the appropriate number of ajustable parameters instead of being involved with

the awkward management of the exact P(r) in numerical form.

We deem it necessary to point out that this variational principle is not the same as that for the ground state energy in terms of a trial wave function. In particular, the approximations that underlie the TFM are of a semiclassical nature so there is no assurance that the energy will be an upper bound to the true ground state energy. In addition, the TFM yields a lower energy than the true ground state values. Dirac's improvement /3/ consists of including within the energy functional (1) the exchange energy. The exchange functional K_o is approximated by that corresponding to a free electron gas and is expressed by:

$$K_o = \left(\frac{3}{4}\right)\left(\frac{3}{\pi}\right)^{1/2} \int P(r)^{4/3} dv \qquad (7)$$

The FA correction removes the self-electronic interaction via the introduction of the correction factor (N-1)/N in the last term of the relationship in Eq.(1). Then, the TFD, the TFA, and the TFAD energy formulas are respectively:

$$E_{TFD} = 2.8712 \int P(r)^{5/3} dv - \int Z \frac{P(r)}{r} dv + \frac{1}{2} \iint \frac{P(r)P(r')dv\, dv'}{|r - r'|} - 0.7386 \int P(r)^{4/3} dv \qquad (8)$$

$$E_{TFA} = 2.8712 \int P(r)^{5/3} dv - Z \int \frac{P(r)}{r} dv + \frac{(N-1)}{2N} \iint \frac{P(r)P(r')dv\, dv'}{|r - r'|} \qquad (9)$$

$$E_{TFAD} = E_{TFA} - 0.7386 \int P(r)^{4/3} dv \qquad (10)$$

We choose the trial density function proposed by Jensen /14/

$$P = N A^{-1} e^{-x} x^{-3} (1 + tx)^{3}, \qquad (11)$$

$$x = Z^{1/6} p^{1/2} r^{1/2} ,$$

t and p are variational parameters to be calculated from the minimization of the energy equation, A being the normalization constant.

When an atom loses one (or more) electron(s), then the resulting ion density, as we know from quantum mechanics,still decreases exponentially at large distances from the nucleus /20/. Furthermore,it seems reasonable to assume that, apart from very low Z atoms, the parameters describing the electron density distribution in a moderately ionized atom cannot differ drastically from the parameters describing the same in the neutral atom. If one performs an identical calculation of E_{TFA}, E_{TFD} and E_{TFAD} for ions, on the basis of the variational electron density (11), the energy formulas become the same as for neutral atoms (which is a particular case for N = Z). The energy relationships for the trial density (11) were given recently in two papers /13,17/ for neutral atoms, so that we consider it redundant to repeat them here again.

The habitual procedure consists in minimizing the energy formulas by variation of the parameters t and p, keeping constant the atomic number Z. This method gives very poor results for the total electronic energy and the introduction of corrections to the primitive TFM worsens them. In order to surmount

this difficulty, we have already used a procedure to introduce the Z-variation in the TF, TFA, TFD, and TFAD energy densities /16/,/17/ for neutral atoms. Here we extend it to ions in the following way:

a) An optimum Z value is determined from the condition

$$E_{TF} (Z_{op}, N_{op}) = E_{HF} (Z,N) \qquad (12)$$

where

$$N_{op} = Z_{op} \pm I$$

$I = 1,2$ according to the ionization degree

and E_{HF} denotes the self-consistent-field-energy values for the non-relativistic total electron energy /21/.

b) The Z_{op} value is employed for the trial density function (11) and new t and p optimum values are sought from the variational procedure. As we have already pointed out for neutral atoms /16/, since the consideration of the additional condition (12) in a certain manner forces a better agreement between statistical and SCF electronic energies, it is necessary to consider other independent properties to judge properly the merits of the procedure. Atomic diamagnetic susceptibility S is a convenient alternative, because it depends on $\langle r^2 \rangle$ /5/

$$S = - N_A \langle r^2 \rangle / (6 c^2) \qquad (13)$$

N_A is the Avogadro's number, c the velocity of light and the

TABLE 1. NON-RELATIVISTIC TOTAL ELECTRONIC ENERGIES FOR IONS (in a.u.)

ION	TF # $-E(Z,N)_{op}$	TF $-E(Z,N)$	TFD $-E(Z,N)_{op}$	TFD $-E(Z,N)$	TFA $-E(Z,N)_{op}$	TFA $-E(Z,N)$	TFAD $-E(Z,N)_{op}$	TFAD $-E(Z,N)$
Mg^{++}	198.8333	252.8495	210.3943	264.9911	205.6587	260.6512	217.6265	274.8957
Na^{+}	161.6965	206.7322	172.0097	218.6865	167.7183	213.6363	178.4426	326.3903
F^{-}	99.46626	128.8897	107.2424	137.9394	103.8584	133.9819	112.0632	143.7468
O^{--}	74.79457	97.19313	81.28396	104.1067	78.35145	101.3545	85.29633	109.6140
Ca^{++}	676.1904	834.0500	704.4943	865.2231	689.6856	849.2341	718.6100	882.8382
K^{+}	599.0369	740.0690	625.4563	770.4009	611.5422	754.1570	638.5868	785.5515
Cl^{-}	459.6374	569.6201	482.2549	595.5806	470.1456	581.5010	493.4036	608.4645
Rb^{+}	2938.357	3503.925	3020.698	3596.763	2968.991	3537.794	3050.357	3632.201
Br^{-}	2572.698	3074.415	2648.790	3160.268	2600.749	3105.501	2677.885	3192.863
I^{-}	6918.120	8097.594	7071.420	8268.463	6967.423	8151.626	7422.144	8324.390

$-E^{TF}(Z,N)_{op} = -E_{HF}$

average value $\langle r^2 \rangle$ is given by

$$\langle r^2 \rangle = \int P(r)\, r^2\, dv \qquad (14)$$

We present in TABLE 1 total electronic energies for a set of singly and doubly charged ions. In TABLES 2 and 3 we give the results of the optimum values for the parameters of the trial density function, comparing them with those referring to the inert gas of the isoelectronic series /8/. Calculated and experimental atomic diamagnetic susceptibilities for ions are displayed in TABLE 4.

All of the ions here considered have a closed-shell electron configuration and consequently a spherically symmetric electron density as assumed in the TFM.

The comparison of results in TABLE 1 shows clearly the existence of a very poor agreement between statistical and HF energy values. Furthermore, we can verify that the introduction of the FA correction worsens the TFD results even more. When an optimum Z-value is introduced within the energy formulas (1), (8), (9), and (10), results improve markedly. Notwithstanding, this better concordance cannot be considered as conclusive evidence of the effectiveness of the method , because of the particular criterion used to determine Z_{op} via equation (12).

The analysis of results in TABLES 2 and 3 reveals that, within each isoelectronic series, there are noticeable differences between $|t(Z) - t(Z_{op})|$ and $|p(Z) - p(Z_{op})|$; they tend to be null for higher Z while the differences $Z - Z_{op}$ and $N - N_{op}$ continue to be significant. The key role played

TABLE 2.OPTIMUM VALUES FOR THE t PARAMETERS ASSOCIATED WITH THE TRIAL DENSITY FUNCTION

ATOM	N	N_{op}	Z	Z_{op}	TF t(Z)	TF $t(Z_{op})$	TFA t(Z)	TFA $t(Z_{op})$	TFD t(Z)	TFD $t(Z_{op})$	TFAD t(Z)	TFAD $t(Z_{op})$
Mg^{++}		8.829	12	10.829	0.324	0.330	0.351	0.360	0.245	0.365	0.384	0.395
Na^{+}		8.901	11	9.901	0.298	0.301	0.329	0.335	0.278	0.341	0.365	0.374
Ne	10	8.976	10	8.976	0.265	0.265	0.301	0.305	0.308	0.311	0.342	0.349
F^{-}		9.056	9	8.056	0.221	0.216	0.265	0.265	0.336	0.273	0.313	0.317
O^{--}		9.156	8	7.156	0.154	1.134	0.216	0.209	0.360	0.220	0.275	0.274
Ca^{++}		16.281	20	18.281	0.301	0.304	0.318	0.323	0.262	0.331	0.343	0.349
K^{+}		16.354	19	17.354	0.284	0.286	0.303	0.306	0.279	0.315	0.329	0.334
Ar	18	16.430	18	16.430	0.265	0.265	0.285	0.287	0.294	0.296	0.314	0.317
Cl^{-}		16.508	17	15.508	0.243	0.240	0.265	0.265	0.309	0.275	0.296	0.299
Rb^{+}		33.311	37	34.311	0.275	0.276	0.285	0.286	0.276	0.295	0.302	0.305
Kr	36	33.368	36	33.368	0.265	0.265	0.275	0.276	0.284	0.285	0.294	0.295
Br^{-}		33.428	35	32.428	0.254	0.253	0.265	0.265	0.291	0.274	0.284	0.285
Xe	54	50.483	54	50.483	0.265	0.265	0.272	0.272	0.279	0.280	0.286	0.287
I^{-}		50.543	53	49.543	0.258	0.257	0.265	0.265	0.284	0.273	0.280	0.290

TABLE 3. OPTIMUM VALUES FOR THE p PARAMETERS ASSOCIATED WITH THE TRIAL DENSITY FUNCTION

ATOM	N	N_{op}	Z	Z_{op}	TF p(Z)	TF $p(Z_{op})$	TFA p(Z)	TFA $p(Z_{op})$	TFD p(Z)	TFD $p(Z_{op})$	TFAD p(Z)	TFAD $p(Z_{op})$
Mg^{++}		8.829	12	10.829	14.706	15.172	15.825	16.435	12.277	16.778	17.332	18.061
Na^{+}		8.901	11	9.901	12.875	13.051	14.071	14.417	12.585	14.790	15.616	16.100
Ne	10	8.976	10	8.976	10.911	10.911	12.192	12.335	12.572	12.691	13.816	14.082
F^{-}		9.056	9	8.056	8.756	8.631	10.171	10.092	12.276	10.480	11.900	11.852
O^{--}		9.156	8	7.156	6.225	5.619	7.947	7.627	11.660	8.052	9.830	9.660
Ca^{++}		16.281	20	18.281	13.079	13.289	13.739	14.030	12.036	14.435	14.802	15.151
K^{+}		16.354	19	17.354	12.010	12.125	12.713	12.873	12.095	13.298	13.780	14.024
Ar	18	16.430	18	16.430	10.911	10.911	11.621	11.691	12.026	12.102	12.746	12.865
Cl^{-}		16.508	17	15.508	9.760	9.632	10.503	10.466	11.894	10.890	11.469	11.711
Rb^{+}		33.311	37	34.311	11.471	11.523	11.832	11.888	11.653	12.266	12.508	12.636
Kr	36	33.368	36	33.368	10.911	10.911	11.265	11.299	11.633	11.671	11.991	13.034
Br^{-}		33.428	35	32.428	10.331	10.282	10.708	10.692	11.566	11.056	11.421	11.442
Xe	54	50.485	54	50.585	10.911	10.911	11.160	11.159	11.446	11.481	11.694	11.732
I^{-}		50.543	53	49.543	10.533	10.492	10.776	10.760	11.416	11.084	11.336	11.333

TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL DIAMAGNETIC SUSCEPTIBILITIES FOR IONS

(- $Sx10^{-6}$ cm^3/ mol)

ION	TF $S(Z)$	TF $S(Z_{op})$	TFA $S(Z)$	TFA $S(Z_{op})$	TFD $S(Z)$	TFD $S(Z_{op})$	TFAD $S(Z)$	TFAD $S(Z_{op})$	a) S_{CS}	b) S_{SS}	c) S_{exp}
Mg^{++}	10.96	9.82	9.84	8.73	13.65	8.45	8.58	7.57	9.79	12.50	3
Na^{+}	14.52	13.49	12.78	11.03	14.72	11.28	10.94	9.94	14.20	19.20	5
F^{-}	30.61	31.05	25.04	24.80	19.46	23.45	20.00	19.79	21.60	---	11
O^{--}	53.28	59.52	39.68	41.71	24.11	38.66	29.67	30.26	31.60	-----	12
Ca^{++}	17.10	15.99	15.93	14.78	18.85	14.19	15.79	13.21	16.00	16.00	8
K^{+}	20.37	12.13	18.79	17.78	19.97	16.97	16.72	15.70	12.30	20.90	13
Cl^{-}	30.56	30.41	27.66	27.16	23.43	25.68	23.90	23.19	22.40	29.00	26
Rb^{+}	28.20	27.21	26.97	26.04	27.44	24.95	24.49	23.91	20.40	25.80	20
Br^{-}	34.54	34.00	32.89	32.23	29.70	30.80	30.08	29.35	25.60	32.90	36
I^{-}	38.12	37.53	36.94	36.23	34.25	34.86	34.48	33.79	28.40	55.30	52

a) Csavinszky's S, Ref./20/
b) Sha and Srivastara's S, Ref. /6/.
c) experimental S, Ref. /22/

by the optimization of Z in the improvement of statistical TF, TFA, TFD, and TFAD energy values is self evident. As regards the t and p values, both tend asymptotically to the particular t and p for the inert gas of the isoelectronic series.

Calculated S values by TF(Z), TFD(Z), and TFAD(Z) are taken from previous papers /9-13/ using Jensen's electronic density. The results of Csavinszky /20/ were obtained from an universal analytical solution of the TF equation for ions. The error is similar to that of the TFA(Z_{op}) method. Sha and Srivastara's results /6/, using an eigh parameters trial density, show that values of S are higher compared to our best result TFAD(Z_{op}). Moreover, these results are in agreement with the trend of experimental results /22/, namely : S increases with increasing Z and the agreement with experimental value for I^- is fairly good. The comparison of results permits us to judge properly the real merits of the present procedure. We see the existence of a definite improvement as regards TFM susceptibilities, as well as in respect to TFA, TFD, and TFAD methods without Z optimization, and with other theoretical results.

We consider that these results of Z optimization in the TF-like methods confirm clearly our previous conclusions /16/, /17/ on the particular way of improving the statistical calculation.

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