IONIC ENTROPIES FOR THOMAS-FERMI-AMALDI DENSITY FUNCTIONAL

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Abstract:

The importance of the Thomas-Fermi (TF) theory in the calculation of informational entropies for neutral atoms is re-examined with respect to a recent work of Gadré. The present study, using a modified Thomas-Fermi-Amaldi density functional (TFA) with a trial density function, brings out interesting features about information entropies: the TF theory leads to entropies which incorporate $N \ln N$ linearly, for neutral atoms. Moreover, with the TFA functional it is possible to obtain information entropies, also for ionic species, since each atom/ion is characterized through the optimized parameters of the electronic density.

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I.   INTRODUCTION

The Density Functional Theory (DFT) has some advantages in the quantum theory of atoms, molecules and solid state /1-6/, resulting from the one-particle picture of many body systems, and it simplifies computational problems. Usually this approximate statistical theory is a tempting alternative to the exact quantum theory either when the accuracy of the latter is not necessary, or when the labor involved is not completely justified. The simplest and basic formulation of DFT is embodied in the Thomas-Fermi (TF) model /7-9/, since the kinetic energy is approximated by that corresponding to a free electron gas (homogeneous system) and only coulombic interactions are including among electron and nuclei /10/ . This model is quantitatively described by an ordinary non-linear differential equation of the second order, which has a universal solution for all neutral atoms. For positive ions the solution is less favorable because for these, the TF equation does not posses a universal solution, and has to be solved separately for each degree of ionization of each atom /1-3/, chiefly because this formalism involves the electrostatic-self interaction of the electrons /11/. From the universal TF atomic solution, which is obtained only in a numerical form /9,12,13/ important physical properties can be computed, such as diamagnetic susceptibilities, electronic potential and the electron density within the atom. A serious shortcoming of the TF theory lies in the fact that it leads to a radial electron density, which decreases as the inverse fourth power of the distance from the nucleus /6/ , whereas the Hartree approximation, its quantum mechanical equivalent /14/ gives an exponential decrease. This failure can be avoided by choosing a trial electron parametric function for the density with an adequate dependence on the distance /15-17/. The parameters are determined from different variational principles /15,18/ subjected to subsidiary constrains. Furthermore, these procedures are equivalent to solve the TF differential equation in an analytical form.

Several attempts have been made /19-21/ to verify the efficiency of introducing the self-interaction correction, proposed by Amaldi /22/ in the TF density functional. Within this context some integrated properties like atomic diamagnetic susceptibilities /18-21,24,25/, interaction energies between noble gas atoms /25,26/, etc., were calculated.

Gadré /27/ computed the information entropy for neutral atoms within the Thomas-Fermi Theory, but using the numerical solution of the TF equation.

The purpose of this work is to extend the calculation of the information entropy not only to neutral atoms, but also for their isoelectronic series, by applying our particular TF-Amaldi modified density functional together with an appropriate trial density function.

II.   THEORY

THOMAS-FERMI-AMALDI DENSITY FUNCTIONAL

The atomic total energy in the Thomas-Fermi (TF) functional and in the one modified by the correction of self-interaction as proposed by Amaldi /22/ are given in the following expressions (hereinafter we will use atomic units):

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

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

ρ being the electron charge density in the atom, r the distance from the nucleus, $dv = 4\pi r^2$, N is the number of electrons and V_N the electron -nucleus interaction, which in an atom with nuclear charge Z is ($- Z / r$). The first term of Eq.(1) and Eq.(2) represents the kinetic energy of the free electron gas, the second one the interaction energy of the electron gas with the nucleus and the third one is the electron-electron interaction. In the last term of Eq.(1), each electron interacts not only with the other ones, but also with itself. This spurius interaction is removed in the last term of Eq.(2), by using the Thomas-Fermi-Amaldi correction, ($N - 1 /N$) which appears as a simple factor. Obviously the main quantity is the electron density, ρ, that may be determined from the numerical solution of the TF equation /7-9/, which is written in terms of the screening function $\phi(x)$

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

where

$$x = r/a \; ; \quad a = 0.8853 \, a_B \, Z^{-1/3} \tag{4}$$

and a_B = Bohr radius. In the framework of TF theory ρ is related to ϕ by

$$\rho = \frac{Z}{4 \pi a^3} \left(\frac{\phi}{x}\right)^{3/2} \tag{5}$$

It is of considerable importance to point out here that ρ, (Eq.5), obtained by solving the TF equation , Eq.(3), is the same that is possible to obtain by minimizing the energy density functional, E_{TF} or E_{TFA}, regarding the variations in the density ρ, at the same time it is subjected to the normalization condition

$$\int \rho(r)dv = N \tag{6}$$

INFORMATION ENTROPY IN DENSITY FUNCTIONALS

The development of information theory and entropy has been traced from the time of Boltzman to the present /28/. Information-theoretic concepts have been employed in recent years for synthesis and analysis of electron densities of atoms and molecules /27-29/ . Many measures of information-theoretical entropy of a continuous probability distribution have been proposed, the most widely used is the Shannon entropy /30,31/ . Using the Shannon information entropy for an absolutely continuous distribution with a probability $\rho(r)$:

$$S_\rho = - \int \rho(r) \ln \rho(r) dr \tag{7}$$

The density $\rho(r)$ is normalized to the number of electrons N in the system (Eq.(6)). *Gadré* /27/ computed S_ρ for neutral atoms within the Thomas-Fermi theory, since the electron density ρ is the basic variable in the density functional formalism. By introducing ρ of Eq. (5) into the expression of the entropy (Eq.(7)) he obtained

$$S_\rho (N) = - N \int \phi^{3/2} x^{1/2} (\ln K. + \frac{3}{2} \ln \phi - \frac{3}{2} \ln x) dx \tag{8}$$

with $K = \dfrac{Z}{4 \pi a^3}$, and integrating:

$$S_{\rho G} (N) \cong N(5.59 - 2 \ln N) \tag{9}$$

He used the universal solution $\phi(x)$ of the TF equation for neutral atoms, Eq.(3). However as it has been already pointed out, this $\phi(x)$ falls off too slowly as the distance from the nucleus increases. It is possible to eliminate this " too big" feature of an atom by choosing and electron density with an adequate dependence on the distance and by using a minimum energy criterion for the energy density functional. In this work we suggest the Jensen function which has been widely used /18-21/.

$$\rho = \frac{N}{A} \frac{e^{-x}}{x^3} (1+cx)^3 \tag{10}$$

with

$$x = Z^{1/6} \left(\frac{\lambda}{a_B}\right)^{1/2} r^{1/2} \quad \text{and} \quad A = \frac{16\pi L_0}{Z\lambda^3} \tag{11}$$

c and λ are variational parameters obtainable from the minimization of the energy density functionals, Eqs.(1) and (2), while L_0 is a polynomial in c. Integrating S_ρ in the coordinate space:

$$S_{\rho J} = - \int \rho_J(r) \ln \rho_J(r) \, d\bar{r} \tag{12}$$

By replacing ρ_J, (Eq.(1c)), into the latter expression of S, with x from Eq.(11):

$$S_{\rho J}(N) = - \frac{N}{2L_0} \int_0^\infty x^2 \, e^{-x} \, (1+cx)^3 \ln \rho_J \, dx \tag{13}$$

we call

$$E_1 = x^2 \, e^{-x} \, (1 + cx)^3 \qquad \text{and}$$

$$S_{\rho J}(N) = - \frac{N}{2L_0} \left[\int_0^\infty E_1 \left(\ln N + \ln Z + 3\ln \lambda - \ln B \right) dx + \right.$$

$$\left. + \int_0^\infty E_1 \left(-x - 3\ln x + 3\ln (1 + cx) \right) dx \right] \tag{14}$$

With $\quad B = 16\pi L_0 \quad$ and $\quad L_0 = 1 + 9c + 36c^2 + 60c^3 \tag{15}$

For neutral atoms, $N = Z$, Eq.(14) takes the particular expression:

$$S_{\rho J}(N) = - \frac{N}{2L_0} \left[\int_0^\infty E_1 \left(2\ln N + 3\ln \lambda - \ln B \right) dx + \right.$$

$$+ \int_0^{\infty} E_1\left(-x - 3\ln x + 3\ln (1 + cx)\right)dx\Big] \qquad (16)$$

In the case of E_{TF} it is possible to obtain universal values for c and λ. In the case of E_{TFA} the minimization gives a particular set of (c,λ) for each element (neutral atom or ion).also for those ones belonging to the same isoelectronic series. So, it is possible to calculate the entropy not only for neutral atoms, but also for the corresponding ions, via the general expression given by Eq.(14), which can be fairly well represented by the form

$$S_\rho (N) = \alpha N + \beta N \ln N \qquad (17)$$

So, one special case of the S_{TFA} is the S_{TF}, in which $N = Z$, with $c = 0.265$ and $\lambda = 10.91$. By integrating with the Simpson's Rule, it is obtained convergence for $x = 30$, with 1000 intervals and the final result is:

$$S_{\rho J}(N) = N(5.087 - 2\ln N) \qquad (18)$$

III. RESULTS AND CONCLUSIONS

We have chosen a set of 40 atoms and 16 singly and doubly charged ions with a noble gas electronic structure. In previous papers /20,21,23/ we minimized the TF and TFA energy density functionals, associated with the Jensen function, Eq.(11). Thus, for TF formalism we have obtained the universal parameters $c = 0.265$ and $\lambda = 10.91$. For the TFA energy functional there is a set of (c,λ) values for each atomic species /23/. With that choice of the parameters we have used the optimum ρ to compute the TF, and TFA information entropies, in Eq.(14).and Eq.(16).

In Table I we present the TF and TFA entropies for neutral atoms, S_{TF} and S_{TFA} with the optimum (c,λ) values /20,21/, while identical quantities for ions are given /23/ in Table II. In Table I for the sake of comparison we also display the values of Gadré entropies, S_{TFG}, for neutral atoms. In Figure 1 we analyze the behaviour of the S_{TFA} as a function of N.

From the Figure and from the Tables we can observe a particular feature of S_{TFA} with N. Owing to the fact that the TFA screening function (or the electron density) is more "compact", since the Amaldi correction leads to a contraction of the electron cloud, the respective entropy is smaller than the TF one. Furthermore, we obtain a family of curves S_i, with i= $1^+,2^+,1^-,2^-$. S_0 is correlated with neutral atoms, S_1^+ and S_2^+ represent the single and double charged positive ions, while S_1^- and S_2^- show the behaviour of single and double charged negative ions. For the same value of N it is possible to obtain different entropies within each isoelectronic serie. This is one of the advantages of this TFA functional, since each atomic species is characterized for the optimum (c,λ) set, so it is applicable to neutral atoms, their anions and cations.

As regards S_{TF}, the expression en Eq.(18) is similar to that one obtained by *Gadré*, $S_{\rho G}$, Eq.(10), /27/. In our formalism S_{TF}, Eq.(16), is obtained as a particular case of S_{TFA}, Eq.(14), when $N = Z$, (neutral atoms) and (c,λ) are the abovementioned universal parameters. As it has been already pointed out by *Gadré*, the TF theory leads to entropy which incorporates N ln N linearly and it brings out an interesting feature of TF information entropy. Moreover, our S_{TF} is smaller than $S_{\rho G}$, since our ρ_J has an adequate exponential dependence on the distance.

These improvements over the TF theory are also the results of using the modified TFA density functional with an appropriate trial density function, which let to avoid the shortcomings owing to the non-realistic expansive TF electronic density.

As far isoelectronic series are concerned *Gadré et. al* . /31/ have presented values for the respective information entropies, but using in Eq.(7) near-Hartree-Fock atomic densities (NHF) /32/. In Ref. /31/ it is observed for Be(1s) and Ne(1s) isoelectronic series, that $S\rho$ diminishes with increasing Z, but it is not possible to infer any other general trend for all the negative and positive ions. We have obtained the same characteristic without taking recourse on the particular NHF density for each neutral atom or ion, since the more concentrate the density is, the lower the entropy.

Our density functional formalism allow us to calculate the respective information entropies, but starting from the same trial density function (Eq.(11)) and using the appropriate (c,λ) optimum parameters.

Moreover, we are able to obtain a numerical adjustment of the information entropies shown in Figure 1, using a polynomial in N. By this way, it is possible to interpolate for every N, in each curve, between 0 to 100.

It is important to highlight that our "good" entropies are built from trial density functions, which minimize the energy functional, or when the "information" of the energy is maximal.

To appreciate properly the abovementioned differences, we consider interesting to take into account that a considerable computational effort is involved in calculating the near-Hartree-Fock wave functions, while the present proposed Density Functional -Entropy formalism is direct, simple and fast.

IV. ACKNOWLEDGMENTS

V. REFERENCES

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TABLE I

At	N	S_{TFG}	S_{TF}	S_{TFA}	c	λ
Li	3	10.178	8.645	6.983	0.379	15.030
Be	4	11.270	9.226	7.513	0.351	14.014
B	5	11.856	9.301	7.543	0.335	13.424
C	6	12.039	8.973	7.181	0.324	13.023
N	7	11.887	8.310	6.492	0.316	12.732
O	8	11.449	7.361	5.545	0.309	12.484
F	9	10.760	6.161	4.305	0.305	12.335
Ne	10	9.848	4.738	2.874	0.301	12.190
Na	11	8.736	3.115	1.225	0.298	2.083
Mg	12	7.442	1.310	-0.980	0.295	11.977
Al	13	5.981	-0.662	-2.576	0.293	11.904
Si	14	4.336	-2.788	-3.853	0.291	11.883
P	15	2.608	-5.057	-4.937	0.289	11.763
S	16	0.717	-7.459	-9.415	0.288	11.725
Cl	17	-1.299	-9.986	-13.253	0.286	11.657
Ar	18	-3.433	-12.631	-14.603	0.285	11.626
Cu	29	-33.193	-48.012	-50.122	0.278	11.368
Zn	30	-36.372	-51.702	-54.017	0.277	11.336
Ga	31	-39.617	-55.458	-57.573	0.277	11.334
Ge	32	-42.927	-59.279	-61.332	0.276	11.302
As	33	-46.299	-63.162	-62.264	0.276	11.300
Se	34	-49.733	-67.106	-69.254	0.276	11.298
Br	35	-53.224	-71.109	-73.178	0.275	11.266
Kr	36	-56.773	-75.169	-77.289	0.275	11.270
Ag	47	-99.184	-123.201	-125.485	0.273	11.192
Cd	48	-103.315	-127.843	-130.178	0.273	11.191
In	49	-107.488	-132.527	-134.880	0.273	11.190
Sn	50	-111.702	-137.252	-139.481	0.272	11.160
Sb	51	-115.956	-142.017	-144.278	0.272	11.159
Te	52	-120.249	-146.821	-149.114	0.272	11.158
I	53	-124.581	-151.069	-153.987	0.272	11.157
Xe	54	-128.950	-156.544	-158.957	0.272	11.160
Au	79	-248.763	-289.132	-291.817	0.270	11.085
Hg	80	-253.924	-294.804	-297.529	0.270	11.085
Tl	81	-259.111	-300.502	-303.257	0.270	11.085
Pb	82	-264.322	-306.224	-308.993	0.270	11.084
Bi	83	-269.358	-311.970	-315.153	0.269	11.054
Po	84	-274.817	-317.741	-320.963	0.269	11.054
At	85	-280.101	-323.536	-326.799	0.269	11.054
Rn	86	-285.408	-329.354	-332.655	0.270	11.080

TABLE II

At	N	Z	S_{TFA}	c	λ
O^{--}	10	8	13.878	0.216	7.947
S^{--}	18	16	-3.151	0.241	9.314
Se^{--}	36	34	-67.299	0.254	10.132
Te^{--}	54	52	-149.244	0.258	10.348
F^-	10	9	7.832	0.265	10.171
Cl^-	18	17	-9.679	0.265	10.503
Br^-	36	35	-72.431	0.265	10.708
Ir^-	54	53	-154.014	0.265	10.776
Ne	10	10	4.738	0.301	12.190
Ar	18	18	-14.603	0.285	11.626
Kr	36	36	-77.289	0.275	11.270
Xe	54	54	-158.957	0.272	11.160
$Na+$	10	11	-1.352	0.329	14.071
K^+	18	19	-19.097	0.303	12.713
Rb^+	36	37	-82.030	0.285	11.832
Cs^+	54	55	-163.560	0.278	11.512
Mg^{++}	10	12	-5.014	0.351	15.825
Ca^{++}	18	20	-23.194	0.318	13.739
Sr^{++}	36	38	-86.367	0.293	12.345
Ba^{++}	54	56	-168.104	0.284	11.871
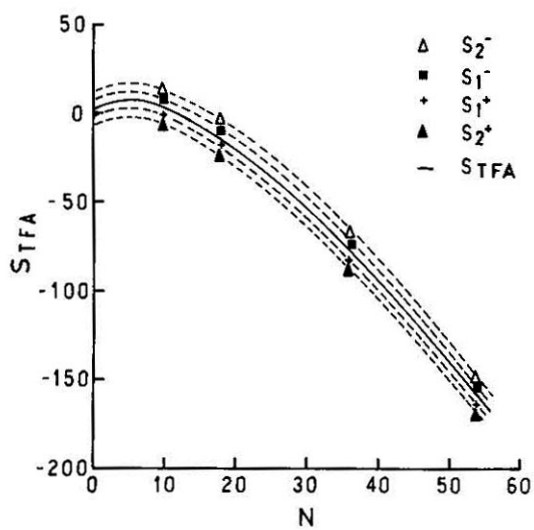
CAPTIONS FOR TABLES

TABLE I: TF and TFA-.information entropies for neutral atoms.

TABLE II: TFA-Information entropies for ions with noble gas structures and for noble gas atoms.

CAPTIONS FOR FIGURES

FIGURE 1:   TFA-information entropies for neutral atoms and their isoelectronic series.