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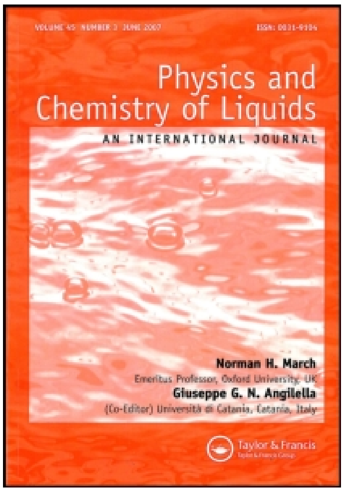

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LETTER

DIFFERENTIAL EQUATION FOR GROUND-STATE ELECTRON DENSITY IN AN INHOMOGENEOUS RELATIVISTIC ELECTRON LIQUID

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The theory of the inhomogeneous electron liquid is recast into the form of a differential equation for the ground-state electron density in the case of the relativistic treatment of heavy atoms. The way density gradients enter this self-consistent theory is the focal point.

Keywords: Relativistic electron liquid; Vallarta-Rosen theory

1. INTRODUCTION

A lot of attention has recently been focussing on the role of electron density derivatives, such as ∇n and $\nabla^2 n$, with n the ground-state electron density – the central tool of density functional theory. The merit of introducing ∇n is discussed, for example, in the work of Pearson *et al.* [1]. In the present study, the simplest relativistic generalization of density functional theory, namely the self-consistent relativistic Thomas-Fermi method [2], will be used to treat an inhomogeneous electron liquid. This will be exemplified with specific reference to the ground-state density in heavy atoms, previously explored numerically by Hill *et al.* [3, 4].

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Here attention will be devoted exclusively to the analytical properties of this self-consistent relativistic Thomas-Fermi theory. The basic equation of this approach represents the chemical potential, constant throughout the entire inhomogeneous electronic cloud of the atom, as a sum of separate (spatially dependent) contributions from kinetic and potential energies. Thus, using the Special Relativity relation between momentum and kinetic energy for an electron at the Fermi (F) level, one can write immediately (see, eg., ref [5])

$$\mu = [c^2 p_F^2(r) + m_0^2 c^4]^{1/2} - m_0 c^2 + V(r) \tag{1}$$

where $V(r)$ is the self-consistent potential energy to be determined. The Fermi momentum $p_F(r)$ is related to the ground-state electron density $n(r)$ by simple phase space considerations:

$$n(r) = \frac{8\pi}{3h^3} p_F^3(r). \tag{2}$$

Using Eqn. (2) to eliminate $p_F(r)$ from Eqn. (1), the chemical potential equation becomes

$$\mu = [Bc^2 n^{2/3}(r) + m_0^2 c^4]^{1/2} - m_0 c^2 + V(r) \tag{3}$$

where $B = (3/8\pi)^{2/3} h^2$. To Eqn. (3), one must now add the explicit requirement of self-consistency: namely that $V(r)$ is related to the ground-state electron density by Poisson's equation of electrostatics:

$$\nabla^2 V = 4\pi n e^2 \tag{4}$$

Substituting for $n(r)$ the solution from Eqn. (3), one is accustomed to use the resulting equation for V in scaled form for the 'screening function' ϕ defined as the ratio of V to the bare Coulomb potential energy $-Ze^2/r$, for an atom of atomic number Z. In the work of Hill *et al.* [3, 4], the resulting differential equation for ϕ was solved numerically.

Since, in the present approach, we are focussing on what can be learnt about relativistic density fuctional theory by exploring the Thomas-Fermi limit more fully, it is natural to substitute $V(r)$ from Eqn. (1) into the Poisson Eqn. (4). We turn to develop in this way the differential equation satisfied by the ground-state electron density $n(r)$ of the relativistic TF atom.

2. DIFFERENTIAL EQUATION FOR GROUND-STATE ATOMIC DENSITY *n*(*r*)

From Eqn. (3) we find straightforwardly for the derivative $\partial V/\partial r$ the result

$$\frac{\partial V}{\partial r} = -\frac{Bc^2}{3} n^{-\frac{1}{3}} \frac{\partial n}{\partial r} \left[Bc^2 n^{\frac{2}{3}} + m_0^2 c^4 \right]^{-\frac{1}{2}} \tag{5}$$

Forming $\partial^2 V/\partial r^2$, and hence the Laplacian $\nabla^2 V$, in the spherically symmetrical TF atom, one is led to the desired differential equation for the electron density $n(r)$:

$$\left[\frac{\nabla^2 n}{n} - \frac{1}{3} \left(\frac{\nabla n}{n} \right)^2 \right]^2 = \frac{n^{\frac{2}{3}}}{l^2} \left[\frac{Bn^{\frac{2}{3}}}{m_0^2 c^2} + 1 \right] \tag{6}$$

Taking the non-relativistic limit $c \to \infty$ in Eqn. (6) one recovers the earlier result of the present writer [6], namely

$$\frac{\nabla^2 n}{n} - \frac{1}{3} \left(\frac{\nabla n}{n} \right)^2 = \frac{n^{\frac{1}{3}}}{l} \tag{7}$$

where the length l is given in terms of the Bohr radius $a_0 = \hbar^2/me^2$ by

$$l = \left(\frac{\pi}{3} \right)^{\frac{1}{3}} \frac{a_0}{4} \tag{8}$$

Let us turn immediately to use Eqn. (6), which essentially relates a 'local' quantity $n^{\frac{2}{3}}(r)$ to the 'reduced' density gradient terms $\nabla^2 n/n$ and $(\nabla n/n)$, to construct a form for the functional derivative $\delta T/\delta n(r)$, with T the total kinetic energy of the relativistic TF atom.

3. FUNCTIONAL DERIVATIVE OF KINETIC ENERGY T WITH RESPECT TO ELECTRON DENSITY *n*(*r*)

One can rewrite the chemical potential equation formally within density functional theory (DFT) as discussed, eg., by Parr and Yang [7]:

$$\mu = \frac{\delta T}{\delta n(r)} + V(r). \tag{9}$$

Comparing this Eqn. (9) with Eqn. (3) for the relativistic TF atom then allows one to write for this case

$$\frac{\delta T}{\delta n(r)} = \left[Bc^2 n^{\frac{2}{3}} + m_0^2 c^4\right]^{\frac{1}{2}} - m_0 c^2. \tag{10}$$

Since the differential Eqn. (6) for $n(r)$ can be viewed alternatively as a quadratic equation to be solved for $n^{2/3}$ in terms of the linear (L) combination of reduced density gradients defined by

$$L = \frac{\nabla^2 n}{n} - \frac{1}{3}\left(\frac{\nabla n}{n}\right)^2 \tag{11}$$

it is already clear that $\delta T/\delta n(r)$ takes the form for the relativistic TF atom:

$$\frac{\delta T}{\delta n(r)} = R(L). \tag{12}$$

Below we construct the form of the function $R(L)$. Of course it must be clear that Eqns. (10) and (12) are equivalent expressions when combined with the differential Eqn. (6) for the self-consistent density $n(r)$. In reaching the precise form of $R(L)$, it is worthwhile as a preliminary step to consider briefly this function in the non-relativistic limit c → ∞. Evidently, from Eqn. (10):

$$\lim_{c\to\infty} \frac{\delta T}{\delta n(r)} = \lim_{c\to\infty} R(L) = \frac{B}{2m_0} n^{\frac{2}{3}}. \tag{13}$$

When use is made of the non-relativistic Eqn. (7) in Eqn (13), one recovers the earlier result of the writer [6] for the non-relativistic TF atom:

$$\lim_{c\to\infty} R(L) = \frac{B}{2m_0} l^2 L^2 \tag{14}$$

showing that in this limit $R(L)$ has a simple quadratic dependence on L defined in Eqn. (11).

3.1. Relativistic Form of Function R(L) in Eqn. (12)

To proceed with the TF relativistic atom, one can utilize Eqns (11) and (6) to write

$$L = \frac{n^{\frac{1}{3}}}{lm_0c^2}\left[Bc^2 n^{\frac{2}{3}} + m_0^2 c^4\right]^{\frac{1}{2}} \tag{15}$$

Substituting from Eqn. (15) for the square root term in Eqn (10) yields then

$$\frac{\delta T}{\delta n(r)} = m_0 c^2 \left[\frac{lL}{n^{\frac{1}{3}}} - 1\right] \tag{16}$$

To find $n^{1/3}$ to substitute in Eqn (16) let us next solve the quadratic Eqn (6) for $n^{2/3}$ in terms of L. The desired solution is readily obtained as

$$n^{\frac{2}{3}} = \frac{m_0^2 c^2}{2B}\left[\left(1 + \frac{4Bl^2 L^2}{m_0^2 c^2}\right)^{\frac{1}{2}} - 1\right] \tag{17}$$

Using the positive square root of Eqn. (17) in Eqn. (16) one has the final result for the relativistic TF atom that

$$\frac{\delta T}{\delta n(r)} = R(L) = m_0 c^2 \left[\frac{(2B)^{\frac{1}{2}} lL}{m_0 c\left\{\left(1 + \frac{4Bl^2L^2}{m_0^2c^2}\right)^{\frac{1}{2}} - 1\right\}^{\frac{1}{2}}} - 1\right] \tag{18}$$

More care is needed now than hitherto, at this point, in taking the limit of Eqn. (18) as $c \to \infty$. However, when expanding the first root, provided one retains second-order terms, Eqn. (18) yields correctly Eqn. (14).

4. SUMMARY AND CONCLUSION

The main results of the present paper are (i) the differential Eqn. (6) satisfied by the ground-state electron density $n(r)$ of the self-consistent relativistic TF atom and (ii) the result Eqn. (18) for the functional derivative of the kinetic energy T with respect to $n(r)$ in terms of the linear combination L of the density gradient quantities $\nabla^2 n/n$ and $(\nabla n/n)^2$ as defined in Eqn. (11).

Of course, the relativistic TF theory, being statistical in character, will come into its own for sufficiently large numbers of electrons N. Thus, it is tempting to conjecture that for the range of N encountered in the Periodic Table:

$$\frac{\delta T}{\delta n(r)} = G\left(\frac{\nabla^2 n}{n}, \left(\frac{\nabla n}{n}\right)^2, N\right) \tag{19}$$

instead of the formally exact statement that $\delta T/\delta n(r)$ is a unique (but presently unknown!) functional of the electron density n. The function G introduced in Eqn. (19) must then evidently tend to $R(L)$ in Eqn. (18) as given by the present study, in the limit of sufficiently large numbers of electrons N. Should the generalization of the relativistic TF atom form conjectured in Eqn. (19) prove a useful approximation for small and medium N encountered in the Periodic Table, that would considerably simplify, as discussed by Pearson *et al.* [1], current computational practices in DFT. But that is, of course, a matter that can only be settled by extensive future studies.

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References

[1] Pearson, M., Smargiassi, E. and Madden, P. A. (1993). *J. Phys. C Condens. Matter*, **5**, 3321.
[2] Vallarta, M. S. and Rosen, N. (1932). *Phys. Rev.*, **41**, 708.
[3] Hill, S. H., Grout, P. J. and March, N. H. (1984). *J. Phys. B. At. Mol. Phys.*, **17**, 4819.
[4] Hill, S. H., Grout, P. J. and March, N. H. (1987). *J. Phys. B. At. Mol. Phys.*, **20**, 11.

[5] March, N. H. (1992). Electron density theory of atoms and molecules (New York: Academic).
[6] March, N. H. (1997) to appear.
[7] Parr, R. G. and Yang, W. (1989). Density functional theory of atoms and molecules (New York: Oxford University Press).