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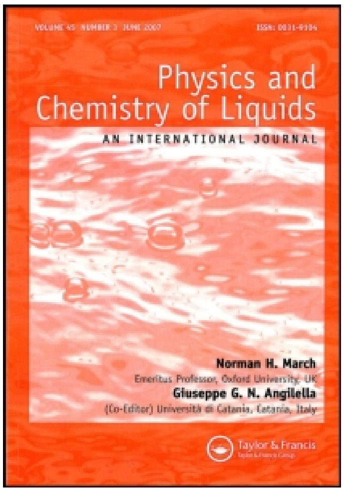

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Letter

THE SHAPE OF THE SELF-CONSISTENT FIELD FORM OF THE DIFFERENTIAL EQUATION FOR THE GROUND-STATE ELECTRON DENSITY OF A WEAKLY INHOMOGENEOUS BUT FULLY INTERACTING ELECTRON LIQUID

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Recent work by the writer, and by March, Holas and Nagy, has exposed the form of the differential equation for the ground-state electron density of a heavy atom or molecule in the Thomas-Fermi statistical limit, corrected by exchange and correlation. Here, a formally exact summation is proposed of the so-called local density approximation, appropriate to a weakly inhomogeneous, but fully interacting, electron liquid.

Keywords: Self-consistent field; inhomogeneous electron liquid

In recent work by the writer [1], the self-consistent form of the Thomas-Fermi statistical theory has been used to construct a differential equation for the ground-state electron density $\rho(\mathbf{r})$, namely

$$\frac{\nabla^2\rho}{\rho} - \frac{1}{3}\left(\frac{\nabla\rho}{\rho}\right)^2 = \frac{\rho^{1/3}}{l_1} \; : \; l_1 = \frac{1}{4}\left(\frac{\pi}{3}\right)^{1/3} a_0 \tag{1}$$

where a_0 is the Bohr radius $\hbar^2/me^2$. Subsequently exchange (x) and correlation (c) have been added as in the Thomas-Fermi-Dirac (TFD) theory for exchange [2] and the Gell-Mann and Brueckner [3] (GB) treatment of correlation in a high density electron liquid. The resulting differential equation has the form [4]

$$F\left(\rho(\mathbf{r}),\ \frac{\nabla^2\rho}{\rho},\left(\frac{\nabla\rho}{\rho}\right)^2\right) = 1. \tag{2}$$

The form of F, denoted by F_{TFxc} in the TFD exchange theory plus GB correlation, was shown in ref 4 to be

$$F_{TFxc} = l_1\rho^{-1/3}L_{(1)} + l_2\rho^{-2/3}L_{(2)} + L_3\rho^{-3/3}L_{(3)}. \tag{3}$$

Here $l_2 = -(1/4)/(3\pi^2)^{2/3}$, $l_3 = -(1-\ln 2)/12\pi^3 a_0$ while $L_{(i)}$ is defined as [4]

$$L_{(i)} = \frac{\nabla^2\rho}{\rho} - \frac{i}{3}\left(\frac{\nabla\rho}{\rho}\right)^2. \tag{4}$$

The object of this Letter is twofold: (i) to propose that eqn. (4) has an infinite order generalization to read

$$F_\infty = \sum_{i=1}^{\infty} l_i\,\rho^{-i/3}\,L_{(i)} \tag{5}$$

and (ii) to effect a formal summation of the assumed infinite series (5).

Given eqn. (5) as starting point, let us immediately use eqn. (4) to separate F_∞ into the sum of two parts, namely

$$F = \frac{\nabla^2\rho}{\rho}S(\rho(\mathbf{r})) - \frac{1}{3}\left(\frac{\nabla\rho}{\rho}\right)^2 T(\rho(\mathbf{r})) \tag{6}$$

where the functions S and T of the ground-state electron density $\rho(\mathbf{r})$ are defined explicitly by the two series below:

$$S(\rho(\mathbf{r})) = \sum_{i=1}^{\infty} l_i\,\rho^{-i/3} \tag{7}$$

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and

$$T(\rho(\mathbf{r})) = \sum_{i=1}^{\infty} i l_i \, \rho^{-i/3}. \tag{8}$$

But T can be expressed in terms of S by taking the gradient of eqn. (7) to find

$$\begin{aligned} \nabla_{\mathbf{r}} S &= -\frac{1}{3}\sum_{i=1}^{\infty} i l_i \, \rho^{-(i/3)-1} \nabla_{\mathbf{r}}\rho \\ &= -\frac{1}{3}\frac{\nabla_{\mathbf{r}}\rho}{\rho} \, T. \end{aligned} \tag{9}$$

Hence, replacing in eqn. (6) in the final term the quantity $-\frac{1}{3}\frac{\nabla\rho}{\rho} T$ by $\nabla_{\mathbf{r}} S$ according to eqn. (9) we find

$$F_{\infty} = \frac{\nabla^2\rho}{\rho} S(\rho(\mathbf{r})) + \frac{\nabla\rho}{\rho} \cdot \nabla_{\mathbf{r}} S. \tag{10}$$

Returning to eqn. (2), and replacing F by F_{∞}, one has the desired result for the shape of the self-consistent field form of the differential equation for the ground-state density $\rho(\mathbf{r})$ for a weakly inhomogeneous, but fully interacting, electron liquid:

$$\frac{\nabla^2\rho}{\rho} S(\rho(\mathbf{r})) + \frac{\nabla\rho}{\rho} \cdot \nabla_{\mathbf{r}} S = 1. \tag{11}$$

This result (11) is the central result of this letter.

We note that in the Thomas-Fermi (TF) limit (compare eqn. (1))

$$S_{TF} = l_1 \rho^{-1/3}; \; \nabla_{\mathbf{r}} S_{TF} = -\frac{1}{3} l_1 \, \rho^{-1/3} \frac{\nabla\rho}{\rho} \tag{12}$$

and similar results can be written for S_{TFx} and S_{TFxc} using the results of Ref. [4].

Presently, because of the difficulties of establishing analytical results for l_i in the series (7) for $S(\rho(\mathbf{r}))$ beyond $i = 2$, closed form calculation of $S(\rho)$ is not feasible. However, for a heavy closed shell atom, one might expect eventually measurements of $\rho(\mathbf{r})$ by X-ray or electron

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scattering, or accurate approximations to $\rho(\mathrm{r})$ from theory, to become available. Hence knowing $\nabla^2\rho/\rho$ and $\nabla\rho/\rho$, one can integrate numerically the first-order differential equation for $S(\mathrm{r})$, namely

$$q(\mathbf{r})\frac{\partial S}{\partial r}-\frac{1}{\mathrm{r}\rho}\frac{\partial^2}{\partial \mathrm{r}^2}(\mathrm{r}\rho)S+1=0, \tag{13}$$

to obtain $S(\mathrm{r})$. The quantity $q(\mathbf{r})=-\rho^{-1}\partial\rho/\partial\mathrm{r}$ has been previously investigated by Nagy and March [5]. Such calculations are now being planned. Since $\rho(\mathrm{r})$ for a closed shell atom is a monotonically decreasing function of r out from the nucleus of an atom, $S(\rho)$ can then be obtained for the selected atom.

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