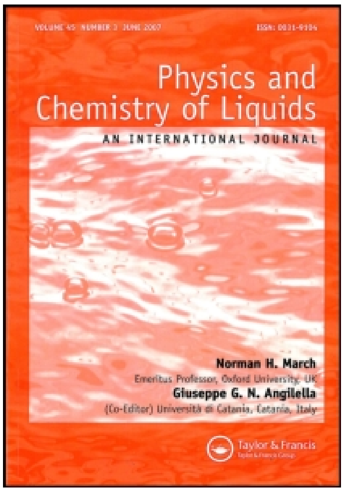

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GENERALIZED LOCAL DENSITY APPROXIMATION IN AN INHOMOGENEOUS ELECTRON LIQUID

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A differential equation relating an unknown, but local, function of ground-state electron density ρ, say $S(\rho)$, is shown first to have an analytical solution for $S(r)$ in terms of $\rho(r)$ for spherically symmetric systems. For closed shell atoms Kr and Xe, $S(r)$ and $S(\rho)$ over the density range $0 < \rho < \rho(r = 0)$ are plotted and examined. $S(r)$ has a roughly monotonically decreasing behaviour with small additional features reflecting electronic shell structure. The general shape of $S(\rho)$ is also found to be the same for these atoms, use of which is made to present an approach to the non-relativisitic limit of large numbers of electrons *via* these closed shell atoms. Relaxing spherical symmetry, it is proposed that the resulting partial differential equation should be powerful enough to describe the ground-state electron density in neutral homonuclear molecules and clusters for large number of electrons.

Keywords: Inhomogeneous electron liquid; Thomas – Fermi theory

1. INTRODUCTION

In recent work, one of the authors have proposed a route whereby a generalized local density approximation can be set up [1]. The philosophy underlying the approach is that of the Thomas – Fermi statistical theory [2, 3], as corrected to include exchange by Dirac [4]. Recently, Gell-Mann – Brueckner correlation energy [5] has been incorporated explicitly into the Thomas – Fermi – Dirac framework [6].

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In Ref. [1], the proposal was made for this so-called generalized local density approximation (GLDA) that the differential equation satisfied by the ground-state electron density $\rho(r)$ should have the following shape:

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

The form of $S(\rho)$ in the Thomas–Fermi method is explicitly

$$S_{TF}(\rho)=l_1\rho^{(-1/3)}, \tag{2}$$

where $l_1=(1/4)(\pi/3)^{1/3}a_B$ with a_B being the Bohr radius, while with the introduction of exchange and Gell-Mann–Brueckner correlation [6] one has

$$S_{TF_{XC}}(\rho)=l_1\rho^{(-1/3)}+l_2\rho^{(-2/3)}+l_3\rho^{(-3/3)}, \tag{3}$$

where $l_2=(1/4)(3\pi^2)^{-2/3}$ and $l_3=(1-\ln 2)/(12\pi^3a_B)$. The proposal is now to assert, but strictly for finite systems, that $S(\rho)$ can be generalized from Eq. (3) to read [1]

$$S(\rho)=\sum_{i=1}^{\infty}l_i\rho^{(-i/3)}. \tag{4}$$

Because of the lack of knowledge of the coefficients $l_i : i>3$ in the GLDA form Eq. (4), in the present study known densities of closed shell atoms Kr and Xe will be used as input in order to extract forms of $S(\rho)$. Naturally, the function thus obtained will be somewhat different for different atoms. Nevertheless, the calculations presented in Section 3 show that $S(\rho)$ has the same basic shape, on the basis of which an attempt will be made to represent the limit of large numbers of electrons by an approximate form.

In the concluding Section 4 the possibility will be discussed that a form of $S(\rho)$ obtained this way, inserted into Eq. (1), could lead to a differential equation which is of useful accuracy in describing the ground-state density $\rho(r)$ in neutral homonuclear assemblies, and in particular in clusters having many electrons.

2. ANALYTICAL SOLUTION FOR *S* IN TERMS OF THE DENSITY FOR A SPHERICALLY SYMMETRIC SYSTEM

For spherically symmetric systems Eq. (1) has the form

$$-q(r)\frac{\partial S(\rho(r))}{\partial r}+\left(\frac{\rho''(r)}{\rho(r)}-\frac{2}{r}q(r)\right)S(\rho(r))=1, \tag{5}$$

where $q(r)=-(\rho'(r)/\rho(r))$ is the local wavenumber introduced earlier by Nagy and March [7], and the prime $'$ denotes differentiation with respect to r. This is a first-order differential equation for $S(r)$ which can be solved analytically:

$$S(r)=\frac{N(r)}{r^2\rho'(r)}=-\frac{1}{q(r)}\frac{N(r)}{r^2\rho(r)}, \tag{6}$$

where

$$N(r)=\int_0^r r^2\rho(r)dr. \tag{7}$$

If $r\rightarrow\infty$ $N(r)$ is proportional to the number of electrons $N:4\pi N(r)\rightarrow N$.

Taking into account that asymptotically [8]

$$\rho(r)\sim \mathrm{Ar}^p\exp(-\mathrm{Qr}), \tag{8}$$

where $Q=2\sqrt{2I}$ with I being the first ionization potential, and $q(r\rightarrow\infty)=Q$ [7],

$$S(r)\sim N(4\pi A)^{-1}\frac{\exp(\mathrm{Qr})}{r^{p+2}((p/r)-Q)} \tag{9}$$

can be obtained for the asymptotic behaviour of $S(r)$ *via* integrations by parts since $\int_0^r r^2\rho dr=N/(4\pi)-\int_r^\infty r^2\rho dr$. (The *const.*$\cdot r^{-n}$–like parts beside the $\exp(r)\cdot r^{-m}$–like one can be neglected.) Eq. (9) also means that

$$\lim_{r\rightarrow\infty}S(r)=-\infty. \tag{10}$$

On the other hand, using l'Hospital's rule,

$$\lim_{r\to 0} S(r) = 0 \tag{11}$$

and, the $r \to 0$ limit of the second part of the left hand side of Eq. (5),

$$\lim_{r\to 0}\left(\frac{\nabla^2\rho(r)}{\rho(r)}S(r)\right) = \frac{2}{3} \tag{12}$$

are obtained.

3. NUMERICAL RESULTS FOR FUNCTION *S* FOR CLOSED SHELL ATOMS

Using analytical Hartree–Fock densities computed from wave functions from Koga *et al.* [9] S is calculated and plotted in Figures 1 and 2 as a function of radial distance r for the closed shell atoms Kr and Xe. As can be seen from Figures 1 and 2 (which is an enlargement of Figure 1

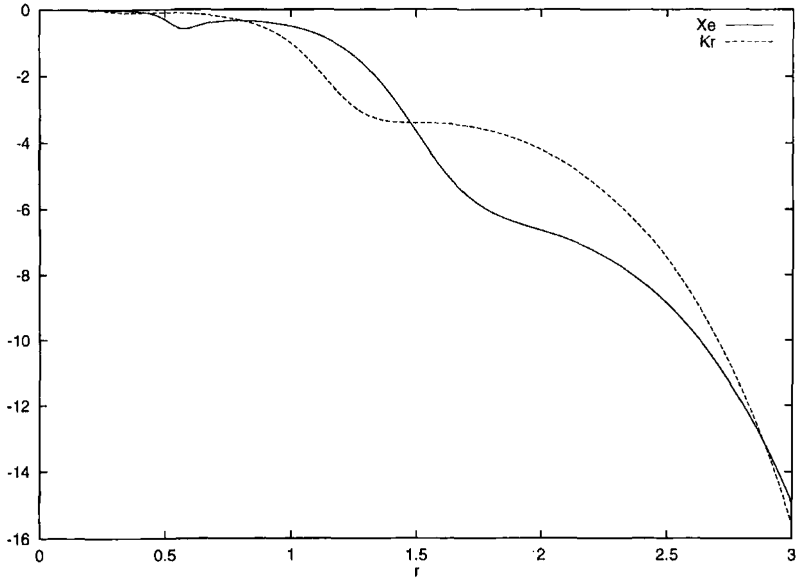

FIGURE 1 $S(r)$ for Kr for Xe in the $0 < r < 3$ region, the origin being on the nucleus itself (in a.u.).

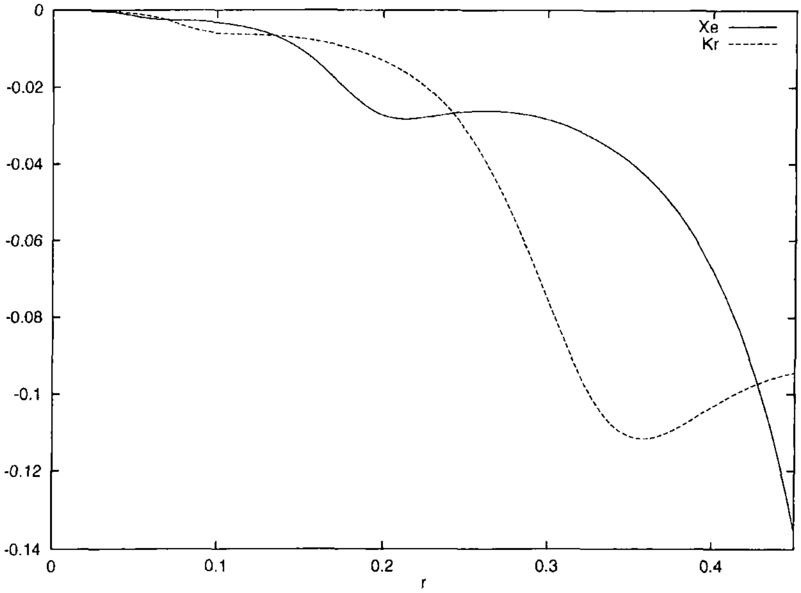

FIGURE 2 $S(r)$ for Kr and Xe in the $0 < r < 0.45$ region, the origin being on the nucleus itself (in a.u.).

for smaller radial distances from the nucleus), $S(r)$ has a roughly monotonically decreasing behaviour, and reflects the electronic shell structure of atoms with its positions of local minima or pairs of inflection points: the $S(r)$ curve of Kr has four 'shells' while the curve for Xe has five. (Similar properties also hold for Ne and Ar.)

Since the density $\rho(r)$ in each atom decreases monotonically from its value $\rho(0)$ at the nucleus, $S(r)$ can be translated into $S(\rho)$, the curves obtained in this way being shown in Figure 3 for Kr and Xe. Also in Figure 3, curves are plotted for Ne and Ar in order to display the dependence on the number of electrons in the closed shell series. As is also expected on the basis of Eqs. (10) and (11) and the results for the shape of $S(r)$, from

$$\lim_{\rho \to 0} S(\rho) = -\infty \tag{13}$$

$S(\rho)$ roughly monotonically increases tending to zero as $\rho \to \rho(0)$,

$$\lim_{\rho \to \rho(0)} S(\rho) = 0. \tag{14}$$

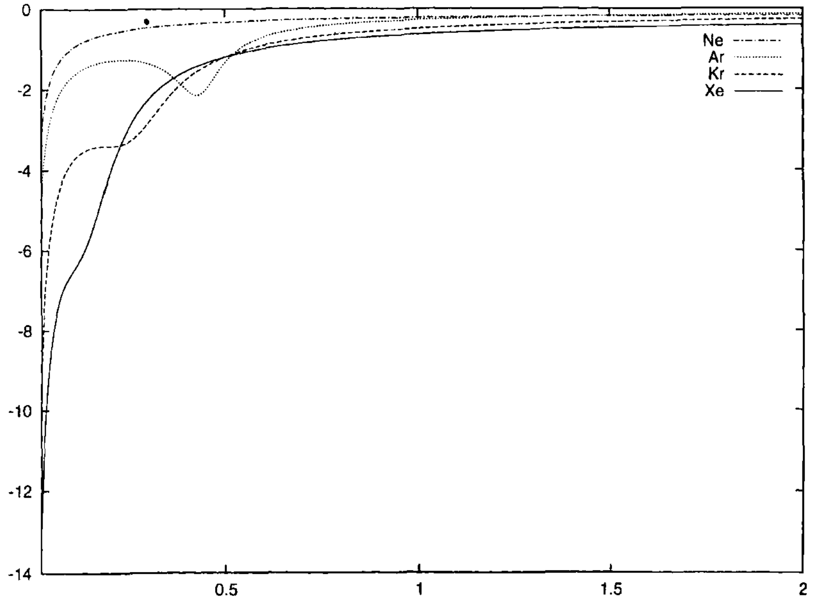

FIGURE 3 $S(\rho)$ for Ne, Ar, Kr and Xe, the origin being on the nucleus itself (in a.u.).

In accord with what is expected, namely that these curves of $S(\rho)$ should tend to a limit for large numbers of electrons, the curves for Kr and Xe are closer to each other than for the other pairs of atoms. These two curves have six intersections (that is common points) while the other pairs have only two or none. The six intersection points of the $S(\rho)$ curves of Kr and Xe, displayed in Figure 4, make it possible to estimate the shape of a function of ρ, which can be considered as an approximation to $S(\rho)$ in the limit of large electron numbers.

It may be worth noting that if p in Eq. (8) equals zero (or r^p is neglected beside exp(−Qr)) an asymptotic formula can be obtained for $S(\rho)$. Inverting Eq. (8) to get $r(\rho)$ then inserting it into Eq. (9),

$$S(\rho) \sim -N(4\pi)^{-1}Q\frac{1}{\rho(\ln\rho - \ln A)^2} \tag{15}$$

arises for low densities, which can be useful in finding analytic forms for $S(\rho)$.

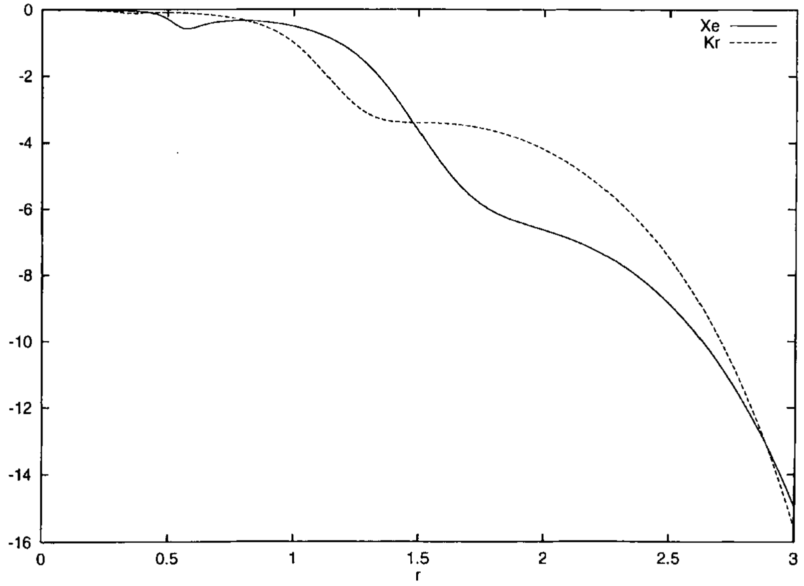

FIGURE 4 $S(\rho)$ *vs.* $\ln(\rho)$ for Kr and Xe, with their intersection points, the nuclei being at $r = 0$.

4. SUMMARY AND FUTURE DIRECTIONS

Equation (1) is the proposed generalized local density approximation, where $S(\rho)$ is represented by the infinite series of Eq. (4) for the finite systems this present investigation solely has been concerned with. Because of the lack of knowledge of all but the first three coefficients (see Eq. (3)) in the form Eq. (4), forms of $S(\rho)$ have been extracted numerically for closed shell atoms, and these are presented in Figure 3.

As for future directions, the form of $S(\rho)$ for neutral systems with large numbers of electrons proposed here may afford a route to calculating the density from the (now partial) differential equation Eq. (1), given $S(\rho)$, say in large homonuclear clusters such as Si. Of course, here directional bonding is important, and it remains to be seen whether the universality of functionals underlying density functional theory is an adequate basis for expecting that $S(\rho)$ derived from neutral closed shell atoms can be taken over to apply to homonuclear complexes with large numbers of electrons. Naturally, even for given $S(\rho)$, the task of solving Eq. (1) for a multicentre molecule or cluster remains formidable, and probably basis sets plus a suitable 'least squares' reformulation of Eq. (1) may be essential for progress.

Nevertheless the approach advocated here seems to be a step towards attaining a long-term goal of density functional theory: namely a differential equation to be solved directly for the ground-state electron density $\rho(r)$, without recourse to wave functions. The present proposal, as stressed above, should come into its own for homonuclear multicentre complexes with many electrons, though, of course, the entire proposal is within the general framework afforded by the nonrelativistic many-electron Schrödinger equation.

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