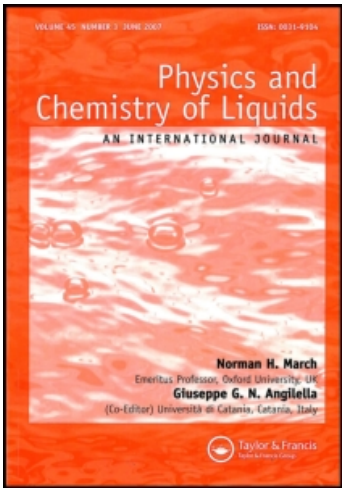

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Kinetic Energy of an Inhomogeneous Electron Liquid: Form for Atom With on *p* Plus *s* Shells

A. Nagy[a]; N. H. March[b]
[a] Institute of Theoretical Physics, Kossuth Lajos Univeristy, Debrecen, Hungary [b] Oxford University, Oxford, England

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KINETIC ENERGY OF AN INHOMOGENEOUS ELECTRON LIQUID: FORM FOR ATOM WITH ON *p* PLUS *s* SHELLS

A. NAGY[1] and N. H. MARCH[2]

[1] *Institute of Theoretical Physics, Kossuth Lajos Univeristy, H-4010 Debrecen, Hungary*
[2] *Oxford University, Oxford, England*

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The form for the kinetic energy of an inhomogeneous electron liquid in terms of the ground-state electron density is of continuing interest. The case treated here is that of spherically symmetric systems having one *p* shell and one or more *s* shells. It is shown that the total kinetic energy in this example can be written explicitly in terms of the total and the *s* electron densities.

Keywords: Kinetic energy; total *p* and *s* electron densities.

INTRODUCTION

In the theory of the inhomogeneous electron liquid, the form of the kinetic energy in terms of the ground-state electron density $\rho(\mathbf{r})$ plays a major role. It is known in a heavy atom, treated non-relativistically, that the kinetic energy density is proportional to the 5/3rds power of $\rho(\mathbf{r})$. But this formula is not adequate in the range of the Periodic Table because of its neglect of electron density gradients. In an atom, these gradients are large in at least two regions, one very near the nucleus, and secondly far from the nucleus where the density decreases exponentially.

Therefore, the search for more accurate kinetic energy forms remains very worthwhile, and this has motivated us to treat a very specific atomic-like case in this present study. Consider, for example, the Ne atom, or, in a more simplistic way, the methane molecule. Both are ten-electron systems, and in

the case of CH_4 the use of the first term in the so-called one-centre expansion reduces this case, like Ne, to a central field problem. It is immediately relevant to the closed shell atom Ne that recently, one of us [1] has derived an exact spatial generalization of Kato's theorem. It states that in a bare Coulomb potential field for independent electrons in arbitrary number of closed shells

$$\frac{\partial n(r)}{\partial r} = -\frac{2Zn_s(r)}{a_0}, \tag{1}$$

where n, n_s and Z are the total electron density, the electron density of s states and the atomic number, respectively. Kinetic energy functionals for s and p states in a bare Coulomb field have also been studied [2, 3]. One of the authors [2] has shown that the kinetic energy functional for s states can be given as an integral on the total density $n(r)$:

$$T_s = \pi \int_0^\infty n(r)\, dr \tag{2}$$

Furthermore, we have derived the total kinetic energy of atomic s and p shells [4].

$$T = 2\pi \int_0^\infty \left\{ \frac{n'}{Z} + 2n + \int_\infty^r \left[\frac{3n}{Zr_1} + n\left(\frac{2}{r_1} - Z \right) \right] dr_1 \right\} dr, \tag{3}$$

where n' denotes the derivative with respect to the radial distance r. However, all these expressions are valid only for a simple model system: noninteracting electrons moving in a bare Coulomb potential $V(r) = -Z/r$.

An asymptotic spatial generalization of Kato's theorem for really heavy atoms has been derived by [4]. Using the Thomas-Fermi statistical theory the generalized Kato's theorem has the form:

$$\frac{\partial n(r)}{\partial r} = -\frac{2Zn_s(r)}{a_0} \left[\frac{\partial V(r)}{\partial r} \frac{r^2}{Ze^2} \right]. \tag{4}$$

This is an asymptotically valid relation for a given screened potential $V(r)$. An asymptotically valid expression for the total kinetic energy can be

written in terms of the densities $n(r)$ and $n_s(r)$:

$$T = -\frac{1}{4}\int \frac{n(r)}{n_s(r)} \frac{1}{r} \frac{\partial n(r)}{\partial r}\, dr. \tag{5}$$

In this paper spherically symmetric systems like Ne or CH_4 mentioned above having one p shell and one or more s shells are studied. The total kinetic energy is written in terms of the total and s electron densities. The expression derived is valid for any Slater-Kohn-Sham potential [5].

EXACT RELATION FOR THE TOTAL KINETIC ENERGY IN TERMS OF THE TOTAL AND THE s ELECTRON DENSITIES

The kinetic energy density for a single p shell can be written as

$$\begin{aligned}\tau_p &= -\frac{1}{2}\sum_k \psi_k^*(r)\nabla^2\psi_k(r) \\ &= -\frac{1}{2} n_p^{1/2} \frac{1}{r}\frac{d^2}{dr^2}(r n_p^{1/2}(r)) + \frac{n_p}{r^2}.\end{aligned} \tag{6}$$

It is more convenient to work with the radial kinetic energy density:

$$t_p = 4r^2\pi\tau_p \tag{7}$$

and the radial electron density

$$\varrho_p = 4r^2\pi n_p \tag{8}$$

From Eqns. (6–8) the radial p-electron kinetic energy density is given by

$$t_p = -\frac{1}{2}\varrho_p^{1/2}\frac{d^2}{dr^2}\varrho_p^{1/2} + \frac{\varrho_p}{r^2}. \tag{9}$$

Now the differential from the virial theorem derived by [6]

$$t_s' = -\frac{1}{8}\varrho''' - \frac{1}{2}\varrho_s V' \tag{10}$$

and the generalized differential virial theorem by [7]

$$t' = -\frac{1}{8}\varrho''' - \frac{1}{2}\varrho V' + \frac{\varrho_p'}{r^2} - \frac{\varrho_p}{r^3} \tag{11}$$

are applied. t and t_s are the total kinetic energy density and the kinetic energy density for s electrons, respectively. ϱ and ϱ_s are the total radial electron density and the radial electron density for s electrons, respectively. V denotes the common spherically symmetric potential.

From Eqns. (9–11) after some algebra the following expression for the kinetic energy is obtained:

$$T = \int_0^\infty t(r)dr = \int_0^\infty \left\{ \left(\frac{\varrho_s}{\varrho_p} + 1 \right) \frac{d}{dr} \left[\frac{\varrho_p}{r^2} - \frac{1}{2} \varrho_p^{1/2} \frac{d^2}{dr^2} \varrho_p^{1/2} \right] \right.$$

$$\left. - \frac{1}{8}\varrho_s''' + \frac{1}{8}\varrho_s \frac{\varrho_p'''}{\varrho_p} - \varrho_s \left(\frac{\varrho_p'}{\varrho_p r^2} - \frac{1}{r^3} \right) \right\} dr \tag{12}$$

It can be easily expressed in terms of the total and the s electron densities and written in the final form:

$$T = -\int_0^\infty \left\{ \frac{1}{\varrho - \varrho_s} \left\{ \varrho \frac{d}{dr} \left[\frac{\varrho - \varrho_s}{r^2} - \frac{1}{2}(\varrho - \varrho_s)^{1/2} \frac{d^2}{dr^2}(\varrho - \varrho_s)^{1/2} \right] \right.\right.$$

$$\left.\left. + \frac{1}{8}(\varrho_s \varrho''' - \varrho \varrho_s''') - \varrho_s \left(\frac{\varrho' - \varrho_s'}{r^2} - \frac{\varrho - \varrho_s}{r^3} \right) \right\} dr \tag{13}$$

We conclude that the total kinetic energy can be written explicitly in terms of the total and the s electron densities. Eqn. (13) is the main result of this paper, which is an exact expression, valid for any spherically symmetric system with one p shell and one or more s shells.

Finally, it is to be noted that generalization of Kato's theorem valid for any spherically system is still missing. (The spatial generalization of Kato's cusp condition has been studied by Porras and Gálvez [8,9] Angulo and Dehesa [10] and Dehesa *et al.* [11]. In a recent study by the present authors the ratio of density gradient to electron density is analyzed [12]). A relationship between the total and the s electron densities is required to obtain the kinetic energy as a functional of the density.

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