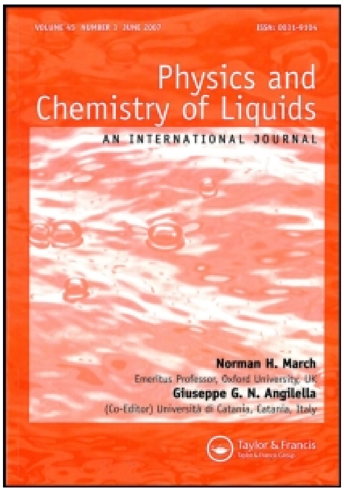

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RELATION BETWEEN THE PAULI POTENTIAL AND THE PAULI ENERGY DENSITY IN AN INHOMOGENEOUS ELECTRON LIQUID

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An approximate relation between the Pauli potential and the Pauli energy density is derived. A further simpler approximation is used to obtain the kinetic energy.

KEY WORDS: Kinetic energy density, Weizsäcker inhomogeneity energy, Pauli potential

1 INTRODUCTION

The kinetic energy functional of the density functional[1] theory has been at the centre of interest for a long time in the theory of an inhomogeneous electron liquid. Separating the Weizsäcker term from the kinetic energy the remaining term is called the Pauli (kinetic) energy. The Pauli potential[2] is the functional derivative of the Pauli energy.

The exact form of the Pauli energy is not known. In this paper the relation between the Pauli potential and the Pauli kinetic energy density is studied. With a further simple approximation the kinetic energy is determined for a few atoms.

2 EXACT RELATION BETWEEN THE PAULI POTENTIAL AND PAULI ENERGY DENSITY

The Slater–Kohn–Sham equations[3] of the density functional theory[2] are:

$$[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{SKS}}]u_i = \varepsilon_i u_i; \qquad (1)$$

$v_{\rm SKS}$ is the Slater–Kohn–Sham potential, while u_i and ε_i are the spin orbitals and orbital energies, respectively. The content of these equations can be rewritten to provide the Pauli potential[2] $v_{\rm P}$

$$[-\tfrac{1}{2}\nabla^2 + v_{\rm P} + v_{\rm SKS}]n^{1/2} = \varepsilon_{\rm M} n^{1/2} \tag{2}$$

Eq. (2) is a Schrödinger equation for the square root of the density of the inhomogeneous electron liquid. It contains another potential, called Pauli potential $v_{\rm P}$, in addition to the Slater–Kohn–Sham potential $v_{\rm SKS}$. $\varepsilon_{\rm M}$ is the one-electron energy associated with the solution n.

The total kinetic energy functional can be separated into two terms as

$$T = T_{\rm W} + T_{\rm P}, \tag{3}$$

where $T_{\rm W}$ and $T_{\rm P}$ are the Weizsäcker and the Pauli kinetic energy functionals respectively. The Weizsäcker functional is given by

$$T_{\rm W} = \int n^{1/2}(-\tfrac{1}{2}\nabla^2 n^{1/2})\,d\mathbf{r}. \tag{4}$$

The functional derivatives are

$$\frac{\delta T_{\rm W}}{\delta n} = n^{-1/2}(-\tfrac{1}{2}\nabla^2)n^{1/2} \tag{5}$$

and[1]

$$\frac{\delta T_{\rm P}}{\delta n} = v_{\rm P}. \tag{6}$$

Let us write the Pauli energy density and the Pauli potential as[1]

$$t_{\rm P}^{(d)} = c_{\rm K}^{(d)} n^{1+2/d} f^{(d)}(\mathbf{r}) \tag{7}$$

and

$$v_{\rm P}^{(d)} = \left(1 + \frac{2}{d}\right) c_{\rm K}^{(d)} n^{2/d} g^{(d)}(\mathbf{r}) \tag{8}$$

in d-dimensions. Then the Pauli potential has the form

$$v_{\rm P}^{(d)} = \left(1 + \frac{2}{d}\right) \frac{g^{(d)}(\mathbf{r})}{f^{(d)}(\mathbf{r})} \frac{t_{\rm P}^{(d)}}{n}, \tag{9}$$

while for the Pauli energy we find

$$T_{\mathrm{P}}^{(d)} = \int t_{\mathrm{P}}\, d\mathbf{r} = \frac{1}{1+\frac{2}{d}} \int \frac{f^{(d)}(\mathbf{r})}{g^{(d)}(\mathbf{r})} n v_{\mathrm{P}}^{(d)}\, d\mathbf{r}. \tag{10}$$

Using the Euler equation

$$\frac{\delta T_{\mathrm{W}}}{\delta n} + v_{\mathrm{P}} + v_{\mathrm{SKS}} = \mu \tag{11}$$

one readily obtains for the Pauli energy

$$T_{\mathrm{P}}^{(d)} = \frac{1}{1+\frac{2}{d}} \int \frac{f^{(d)}(\mathbf{r})}{g^{(d)}(\mathbf{r})} n \left[-\frac{\delta T_{\mathrm{W}}}{\delta n} - v_{\mathrm{SKS}} + \mu \right] d\mathbf{r} \tag{12}$$

or using Eq. (5)

$$T_{\mathrm{P}}^{(d)} = \frac{1}{1+\frac{2}{d}} \int \frac{f^{(d)}(\mathbf{r})}{g^{(d)}(\mathbf{r})} n[\varepsilon_{\mathrm{M}} - v_{\mathrm{SKS}} + n^{-1/2}\nabla^2 n^{1/2}]\, d\mathbf{r} \tag{13}$$

is obtained.

On the other hand, the functional derivative of T_{P} using the Pauli energy density in Eq. (10) becomes

$$v_{\mathrm{P}}(\mathbf{r}) = \frac{\delta T_{\mathrm{P}}}{\delta n} = \left(1 + \frac{2}{d}\right) c_{\mathrm{K}}^{(d)} n^{2/d}(\mathbf{r}) f^{(d)}(\mathbf{r}) + c_{\mathrm{K}}^{(d)} \int n^{1+2/d}(\mathbf{r}') \frac{\delta f^{(d)}(\mathbf{r}')}{\delta n(\mathbf{r})}\, d\mathbf{r}'. \tag{14}$$

Comparing the expressions (9) and (14) for the Pauli potential, the relation between $f^{(d)}$ and $g^{(d)}$

$$g^{(d)}(\mathbf{r}) = f^{(d)}(\mathbf{r}) + \frac{n^{2/d}(\mathbf{r})}{1+\frac{2}{d}} \int n^{1+2/d}(\mathbf{r}') \frac{\delta f^{(d)}(\mathbf{r}')}{\delta n(\mathbf{r})}\, d\mathbf{r}' \tag{15}$$

is obtained.

3 APPROXIMATE RELATION BETWEEN THE PAULI POTENTIAL AND ENERGY DENSITY

One of the authors has recently determined the Pauli potential[4] and energy density for several atoms in the exact exchange-only scheme. It has been discovered that the functions f and g are quite close together. So a natural first approximation is

$$g \approx f. \tag{16}$$

Substituting Eq. (16) in Eq. (9)

$$v_{\mathrm{P}}^{(d)} = \left(1 + \frac{2}{d}\right)\frac{t_{\mathrm{P}}^{(d)}}{n} \tag{17}$$

is obtained for the Pauli potential and

$$T_{\mathrm{P}}^{(d)} = \frac{1}{1+\frac{2}{d}} \int n\left[\mu - \frac{\delta T_{\mathrm{W}}}{\delta n} - v_{\mathrm{KS}}\right] d\mathbf{r} \tag{18}$$

for the Pauli energy.

From Eq. (18) the Pauli energy and from Eq. (3) the total kinetic energy can be determined from knowledge of n and μ. As was set out in detail in Ref. 4 the Slater–Kohn–Sham potential v_{SKS} can be determined by inversion of Eq. (1) if the density is known. The Hartree–Fock density has been applied to determine v_{SKS}. μ has been taken to be the highest occupied Hartree–Fock one-electron energy $\varepsilon_{\mathrm{M}}^{\mathrm{HF}}$. The first column of Table 1 contains the exact exchange-only kinetic energy for several atoms. The second column shows the kinetic energies determined with the approximation (16) using Eq. (18). They highly overestimate the exact kinetic energy. The reason can be easily explained. Figure 1 shows the ratio f/g for the Ne atom. Apparently, the approximation $f \simeq g$ is not good for small values of r

Table 1 Kinetic energy (in Ry) determined by the exact exchange-only density functional theory, with approximation (16) and the radius r_0 (in a.u.) in Eq. (19) for some light atoms.

	T	$\tilde{T}$	r_0
B	49.0556	63.3001	1.551
C	75.3726	95.3327	0.9496
N	108.7967	134.7077	0.6338
O	149.6165	181.7390	0.4874
F	198.8152	236.9472	0.3775
Ne	257.0896	300.7566	0.3003
Na	323.6871	385.6884	0.2977
Mg	399.2041	474.6364	0.2662
Al	483.7165	576.5630	0.2464

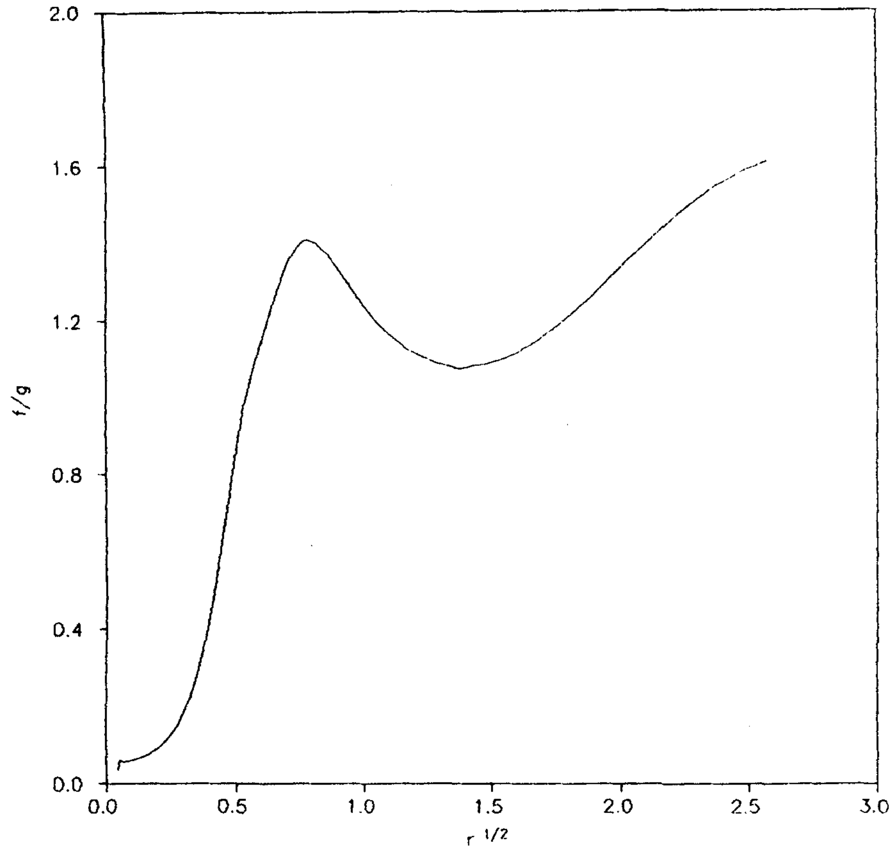

Figure 1 The ratio f/g for the Ne atom with a radial scale which is linear with respect to $r^{1/2}$.

To obtain a better approximation for the Pauli energy the ratio f/g is taken to be

$$\frac{f}{g} = \begin{cases} \dfrac{r}{r_0} & \text{if} \quad r < r_0 \\ 1 & \text{if} \quad r \geq r_0 \end{cases}. \tag{19}$$

The value of r_0 can be determined so that the Pauli potential obtained with Eqs (3), (10) and (19) be equal to the exact one. The third column of Table 1 collects these r_0 for several atoms.

5 DISCUSSION AND SUMMARY

As can be seen in Ref. 4 the functions $f(r)$ and $g(r)$ reflect the shell structure of atoms. So it is not surprising that the characteristic length r_0 has also to do with the form

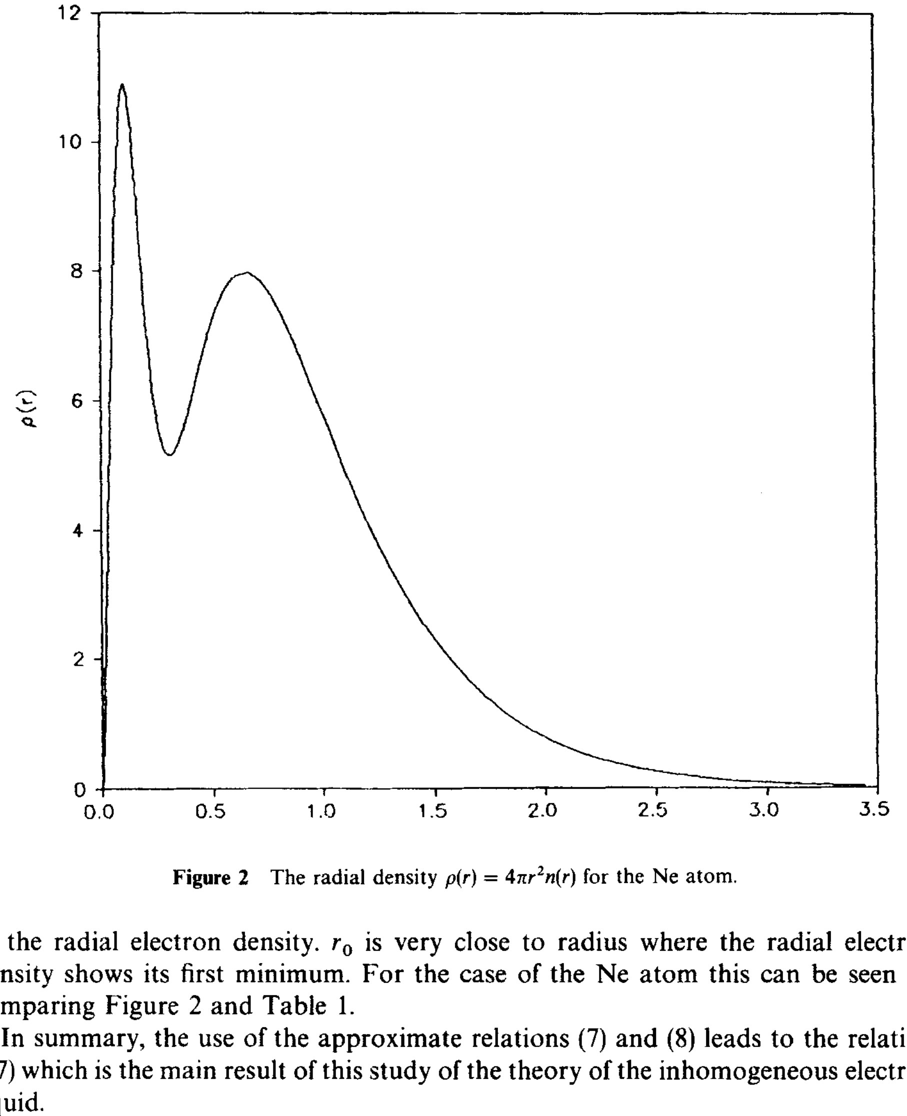

Figure 2 The radial density $\rho(r) = 4\pi r^2 n(r)$ for the Ne atom.

of the radial electron density. r_0 is very close to radius where the radial electron density shows its first minimum. For the case of the Ne atom this can be seen by comparing Figure 2 and Table 1.

In summary, the use of the approximate relations (7) and (8) leads to the relation (17) which is the main result of this study of the theory of the inhomogeneous electron liquid.

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