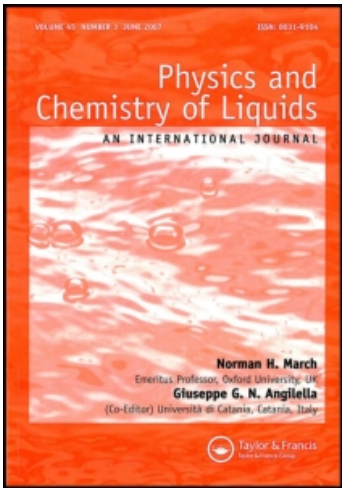

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VARIATIONAL PRINCIPLE OF RELATIVISTIC DENSITY FUNCTIONAL THEORY FOR WEAKLY INHOMOGENEOUS ELECTRON LIQUID

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A variational principle is set up in the framework of relativistic density functional theory, which yields the relativistic linear-response relation between displaced charge $v(\mathbf{x})$ and weak perturbing potential $V(\mathbf{x})$ in an electron liquid. In particular, the kinetic energy is calculated to second-order in the displaced charge $v(\mathbf{x})$.

KEY WORDS: Dirac equation, linear response, kinetic energy.

1 INTRODUCTION

In relativistic density functional theory of inhomogeneous electron assemblies functionals have been approximated under the assumption of sufficiently slowly varying densities, see e.g. Ref. 1 and references therein. However, the opposite situation of weak, but arbitrarily rapid variation seems not to be treated in the relativistic domain up to now. It is just this area in which the present contribution lies.

Specifically, in this paper, and in order to set up quite explicit results for the kinetic energy functional of the relativistic theory, we consider the case of weakly inhomogeneous electron assemblies, produced by inserting a weak single-particle potential energy $V(\mathbf{x})$ into an initially uniform electron liquid. Such an approach has been fruitful when applied, for example, to defects[2] and to their interaction[3] in metals, but these early studies were made with the single-particle Schrödinger equation as starting point.

In the present work then, based on the Dirac relativistic wave equation, we let $n(\mathbf{x})$ be the perturbed density due to a localized potential $V(\mathbf{x})$ introduced into a relativistic electron liquid of homogeneous density n_0.

Since $V(\mathbf{x})$ is taken to be weak, $n(\mathbf{x})$ becomes

$$n(\mathbf{x}) = n_0 + v(\mathbf{x}) \tag{1.1}$$

where we have weak deviations v from homogeneity such that

$$\left|\frac{v(\mathbf{x})}{n_0}\right| \ll 1. \tag{1.2}$$

Within this framework, our initial aim below is to set up the relativistic kinetic energy functional to second order in the displaced electron density $v(\mathbf{x})$.

2 KINETIC ENERGY FOR HOMOGENEOUS FREE ELECTRON LIQUID

The kinetic energy density $t[n_0]$ of a uniform relativistic liquid of free electrons was first given by Jensen[4]. In early work on the model of independent electrons in the presence of a square barrier[5], we regained $t[n_0]$ as a byproduct, which was shown to be compatible with the Vallarta–Rosen[6] (VR) relativistic generalization of Thomas–Fermi theory. $t[n_0]$ is given by

$$\begin{aligned} t[n_0] &= t^{\mathrm{VR}}[n_0] \\ &= a[g_0(\tfrac{1}{2} + g_0^2)\sqrt{1 + g_0^2} - \tfrac{4}{3}g_0^3 - \tfrac{1}{2}\ln(g_0 + \sqrt{1 + g_0^2})] \end{aligned} \tag{2.1}$$

with

$$a \equiv \frac{1}{4\pi^2}\left(\frac{mc}{\hbar}\right)^3 mc^2; \quad g_0 \equiv (3\pi^2)^{1/3}\frac{\hbar}{mc}n_0^{1/3} \tag{2.2a,b}$$

Thus the kinetic energy contained in a finite volume Ω is given by

$$\begin{aligned} T_\Omega^{\mathrm{VR}}[n_0] &= \int_\Omega t^{\mathrm{VR}}[n_0]\, d^3x \\ &= \Omega t^{\mathrm{VR}}[n_0]. \end{aligned} \tag{2.3}$$

Of course, $\lim_{\Omega\to\Omega_\infty} T_\Omega^{\mathrm{VR}}[n_0] = \infty$. ($\Omega_\infty$ is the infinite space). Our main objective in the present work is to generalize the above result (2.3) to include all terms up to and including second-order contributions in the displaced charge $v(\mathbf{x})$.

3 KINETIC ENERGY TO FIRST ORDER IN THE DENSITY DEVIATION $v(\mathbf{x})$

When the potential $V(\mathbf{x})$ is switched on, the change of kinetic energy density must be of the form

$$t_1[v](\mathbf{x}) = \int_{\Omega_\infty} w_1(n_0, |\mathbf{x} - \mathbf{y}|)v(\mathbf{y})\, d^3y \tag{3.1}$$

where the (yet unknown) function w_1 depends not only on n_0 but also on the distance $|\mathbf{x} - \mathbf{y}|$, because the disturbed system was homogeneous originally. The correspond-

ing contribution to the kinetic energy, contained in the whole space Ω_∞, is then given by

$$T_1[v] = \int_{\Omega_\infty} d^3x \left[\int_{\Omega_\infty} w_1(n_0, |\mathbf{x} - \mathbf{y}|) v(\mathbf{y})\, d^3y \right]. \tag{3.2}$$

Both t_1 and T_1, are supposed to exist even in the case $\Omega = \Omega_\infty$ corresponding to our assumption of localization of V.

When the order of integrations is changed, T_1 takes the form

$$T_1[v] = W_1(n_0) \int_{\Omega_\infty} v(\mathbf{x})\, d^3x \tag{3.3}$$

where

$$W_1(n_0) \equiv \int_{\Omega_\infty} w_1(n_0, |\mathbf{x}'|)\, d^3x', \tag{3.4}$$

which is the structure we were seeking for the first-order kinetic energy.

4 KINETIC ENERGY TO SECOND ORDER IN THE DENSITY DEVIATION $v(\mathbf{x})$

The most general form of the second order term of t can be written as

$$t_2[v](\mathbf{x}) = \int_{\Omega_\infty} \int_{\Omega_\infty} w_2(n_0, |\mathbf{x} - \mathbf{y}|, |\mathbf{x} - \mathbf{z}|, |\mathbf{y} - \mathbf{z}|) \times v(\mathbf{y}) v(\mathbf{z})\, d^3y\, d^3z, \tag{4.1}$$

again because of the homogeneity of the unperturbed system. Thus the contribution to the kinetic energy from (4.1) is given by

$$T_2[v] = \int_{\Omega_\infty} d^3x \left[\int_{\Omega_\infty} d^3y \int_{\Omega_\infty} d^3z v(\mathbf{y}) v(\mathbf{z}) \times w_2(n_0, |\mathbf{x} - \mathbf{y}|, |\mathbf{x} - \mathbf{z}|, |\mathbf{y} - \mathbf{z}|) \right] \tag{4.2}$$

which can be transformed to yield

$$T_2[v] = \int_{\Omega_\infty} d^3y \int_{\Omega_\infty} d^3v W_2(n_0, v) v(\mathbf{y}) v(\mathbf{v} + \mathbf{y}) \tag{4.3}$$

where

$$W_2(n_0, v) \equiv \int_{\Omega_\infty} d^3u w_2(n_0, u, |\mathbf{u} - \mathbf{v}|, v). \tag{4.4}$$

Noting that

$$|\mathbf{u} - \mathbf{v}| = \sqrt{u^2 + v^2 - 2uv \cos \vartheta} \tag{4.5}$$

where ϑ is the angle between vectors $\mathbf{u}$ and $\mathbf{v}$, integration over polar coordinates u, ϑ, φ in $\mathbf{u}$-space shows that W_2 in fact is dependent on n_0 and v only.

Summarizing the results of Sections 2–4, we obtain, within the framework of our specified approximation

$$\lim_{\Omega\to\Omega_\infty} [T_\Omega[n_0 + v] - T_\Omega^{\mathrm{VR}}[n_0]] = T_1[v] + T_2[v] \tag{4.6}$$

with T^{VR}, T_1, and T_2 given by Eqs (2.3), (3.3) and (4.3). Of course, the limit $\Omega \to \Omega_\infty$ exists only for the difference on the l/hs., the separate terms $T_\Omega[n_0 + v]$ and $T_\Omega^{\mathrm{VR}}[n_0]$ being divergent in this limit.

5 VARIATION OF THE DENSITY WITH n_0 KEPT FIXED; EULER EQUATION

An electronic assembly having strictly constant density n_0 in space must be infinite; in particular the number of electrons is infinite so that we cannot speak of conservation of the *particle number* when performing a variation of the density. Rather, we have to keep fixed the *chemical potential* or, equivalently, to keep fixed n_0.

Using Eqs. (2.3), (3.3), (4.3) and (4.6), the variation of $T_\Omega[n_0 + v]$ yields

$$\begin{aligned}
&\delta\left\{\lim_{\Omega\to\Omega_\infty} (T_\Omega[n_0 + v] - T_\Omega^{\mathrm{RV}}[n_0])\right\} \\
&\quad = W_1(n_0)\int_{\Omega_\infty} \delta v(\mathbf{x})\, d^3x + \int_{\Omega_\infty}\int_{\Omega_\infty} d^3x\, d^3y W_2(n_0, y) \\
&\qquad \times [v(\mathbf{x} + \mathbf{y})\delta v(\mathbf{x}) + v(\mathbf{x})\delta v(\mathbf{x} + \mathbf{y})] \\
&\quad = \int_{\Omega_\infty} d^3x \left\{W_1(n_0) + \int_{\Omega_\infty} W_2(n_0, y)[v(\mathbf{x} + \mathbf{y}) + v(\mathbf{x} - \mathbf{y})]\, d^3y\right\}\delta v(\mathbf{x})
\end{aligned} \tag{5.1}$$

i.e. we can read off

$$\begin{aligned}
\frac{\delta \bar{T}[n_0, v]}{\delta v(\mathbf{x})} &= W_1(n_0) + \int_{\Omega_\infty} W_2(n_0, y)[v(\mathbf{x} + \mathbf{y}) + v(\mathbf{x} - \mathbf{y})]\, d^3y \\
&= W_1(n_0) + 2\int_{\Omega_\infty} W_2(n_0, |\mathbf{x} - \mathbf{x}'|)v(\mathbf{x}')\, d^3x'
\end{aligned} \tag{5.2}$$

where

$$\bar{T} \equiv \lim_{\Omega\to\Omega_\infty} (T_\Omega - T_\Omega^{\mathrm{VR}}). \tag{5.3}$$

Hence the Euler equation

$$\frac{\delta \bar{T}}{\delta v} + V = \mu \tag{5.4}$$

reads

$$W_1(n_0) + 2\int_{\Omega_\infty} W_2(n_0, |\mathbf{x} - \mathbf{x}'|)v(\mathbf{x}')\, d^3x' + V(\mathbf{x}) = \mu \tag{5.5}$$

In this equation, however, μ is fixed and equals μ_0, the chemical potential with $V \equiv 0$. For this case, Eq. (5.5) becomes

$$W_1(n_0) = \mu_0 = \sqrt{m^2c^4 + \hbar^2c^2(3\pi^2 n_0)^{2/3}} - mc^2 \tag{5.6}$$

since $v(\mathbf{x}) \equiv 0$ for $V \equiv 0$. Using $\mu = \mu_0$ and Eq. (5.6), Eq. (5.5) yields

$$2\int_{\Omega_\infty} W_2(n_0, |\mathbf{x} - \mathbf{x}'|)v(\mathbf{x}')\, d^3x' + V(\mathbf{x}) = 0. \tag{5.7}$$

6 RELATION OF W_2 TO LINEAR-RESPONSE v-V-RELATION

Equation (5.7) has to be compared with the linear-response relation

$$v(\mathbf{x}) = \int_{\Omega_\infty} F(n_0, |\mathbf{x} - \mathbf{x}'|)V(\mathbf{x}')\, d^3x' \tag{6.1}$$

where $F(n_0, |\mathbf{x} - \mathbf{x}'|)$ was derived in earlier work[7]

$$\begin{aligned} F(n_0, |\mathbf{x} - \mathbf{x}'|) = &-\frac{m}{\pi^3\hbar^2|\mathbf{x} - \mathbf{x}'|} \\ &\times \int_0^{k_F} \left[j_0(2k|\mathbf{x} - \mathbf{x}'|) + \left(\frac{\hbar}{mc}\right)^2 \frac{kj_1(2k|\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|} \right] \\ &\times \frac{k^2 dk}{\left[1 + \left(\frac{\hbar k}{mc}\right)^2\right]^{1/2}} \end{aligned} \tag{6.2}$$

with Fermi wave number

$$k_F = (3\pi^2 n_0)^{1/3}. \tag{6.3}$$

Equation (6.1) is a generalization of the non-relativistic result of March and Murray[2].

To effect this comparison, we have to solve Eq. (5.7) for $v(\mathbf{x})$, which can be done by use of Fourier transforms. Multiplying Eq. (5.7) by $e^{i\mathbf{k}\cdot\mathbf{x}}$ and integrating over $\mathbf{x}$ we obtain

$$2\tilde{W}_2(n_0, k)\tilde{v}(\mathbf{k}) + \tilde{V}(\mathbf{k}) = 0 \tag{6.4}$$

or

$$\tilde{v}(\mathbf{k}) = -\frac{\tilde{V}(\mathbf{k})}{2\tilde{W}_2(n_0, k)} \tag{6.5}$$

where the tilde denotes the Fourier transform. It should be noted that the Fourier transform of $W_2(n_0, |\mathbf{x}|)$ depends on $k = |\mathbf{k}|$ only.

On the other hand, the Fourier transform of (6.1) reads

$$\tilde{v}(\mathbf{k}) = \tilde{F}(n_0, k)\tilde{V}(\mathbf{k}) \tag{6.6}$$

where the Fourier transform of $F(n_0, |\mathbf{x}|)$ is given by[8]

$$\begin{aligned}\tilde{F}(n_0, k) = -\frac{mk_F}{\hbar^2\pi^2}\Bigg\{&\frac{2}{3}\gamma_F - \frac{\kappa^2}{6\kappa_F}\ln(\kappa_F + \gamma_F) \\ &+ \frac{\gamma_F - \gamma}{\kappa_F}\left[\frac{1}{3\kappa}(2 + \kappa_F^2 + \gamma\gamma_F) - \frac{\kappa}{6}\right]\ln\left|\frac{2\kappa_F + \kappa}{2\kappa_F - \kappa}\right| \\ &+ \frac{\gamma}{\kappa_F}\left(\frac{1}{3\kappa} - \frac{\kappa}{6}\right)\ln\left(\frac{2 + 2\gamma\gamma_F - \kappa\kappa_F}{2 + 2\gamma\gamma_F + \kappa\kappa_F}\right)\Bigg\}\end{aligned} \tag{6.7}$$

In Eq. (6.7), the following abbreviations have been adopted

$$\lambda\!\!\!^{-} \equiv \frac{\hbar}{mc};\ \kappa_F \equiv \lambda\!\!\!^{-}k_F;\ \gamma_F \equiv (1 + \kappa_F^2)^{1/2} \tag{6.8a,b,c}$$

$$\kappa \equiv \lambda\!\!\!^{-}k;\ \gamma \equiv (1 + \tfrac{1}{4}\kappa^2)^{1/2}. \tag{6.8d,e}$$

Comparing Eq. (6.5) with Eq. (6.6), we immediately see that

$$\tilde{W}_2(n_0, k) = -\frac{1}{2\tilde{F}(n_0, k)} \tag{6.9}$$

which is the relation sought. Formally we obtain from (6.9)

$$\begin{aligned}W_2(n_0, x) &= \frac{1}{(2\pi)^3}\int \tilde{W}_2(n_0, k)e^{-i\mathbf{k}\cdot\mathbf{x}}\,d^3k \\ &= -\frac{1}{2(2\pi)^3}\int \frac{e^{-i\mathbf{k}\cdot\mathbf{x}}}{\tilde{F}(n_0, k)}\,d^3k.\end{aligned} \tag{6.10}$$

To obtain well-defined expressions we have to investigate the asymptotic behaviour of $1/\tilde{F}$ as $k \to \infty$:

$$\tilde{F}(n_0, k) = \frac{c_2(n_0)}{k^2} + \frac{c_4(n_0)}{k^4} + O(k^{-6}) \tag{6.11}$$

as $k \to \infty$, where

$$c_2(n_0) \equiv -\frac{m}{\pi^2\hbar^2\lambda\!\!\!^{-3}}\left[\kappa_F\gamma_F(1 + \tfrac{2}{3}\kappa_F^2) + \tfrac{1}{2}\ln\left(\frac{\gamma_F - \kappa_F}{\gamma_F + \kappa_F}\right)\right] \tag{6.12}$$

$$c_4(n_0) \equiv -\frac{2m}{3\pi^2\hbar^2\lambda\!\!\!^{-5}}\left[\tfrac{2}{3}\kappa_F\gamma_F(\tfrac{4}{5}\kappa_F^4 + 2\kappa_F^2 - 3) - \ln\left(\frac{\gamma_F - \kappa_F}{\gamma_F + \kappa_F}\right)\right]. \tag{6.13}$$

Therefore

$$\begin{aligned}\frac{1}{\tilde{F}(n_0, k)} &= \frac{k^2}{c_2 + \dfrac{c_4}{k^2} + O(k^{-4})} \\ &= \frac{k^2}{c_2} - \frac{c_4}{c_2^2} + O(k^{-2}).\end{aligned} \tag{6.14}$$

Using the relation

$$\int k^2 e^{-i\mathbf{k}\cdot\mathbf{x}}\, d^3k = -\nabla_x^2 \int e^{-i\mathbf{k}\cdot\mathbf{x}}\, d^3k$$

$$= -(2\pi)^3 \nabla_x^2 \delta(\mathbf{x}), \tag{6.15}$$

$W_2(n_0, x)$ can be written

$$W_2(n_0, x) = -\frac{1}{2(2\pi)^3}\left\{\int\left[\frac{1}{\tilde{F}(n_0, k)} - \frac{k^2}{c_2} + \frac{c_4}{c_2^2}\right]e^{-i\mathbf{k}\cdot\mathbf{x}}\, d^3k + \int\left(\frac{k^2}{c_2} - \frac{c_4}{c_2^2}\right)e^{-i\mathbf{k}\cdot\mathbf{x}}\, d^3k\right\}$$

$$W_2(n_0, x) = S(n_0, x) + \frac{1}{2c_2}\nabla_x^2\delta(\mathbf{x}) + \frac{c_4}{2c_2^2}\,\delta(\mathbf{x}) \tag{6.16}$$

where the integrand of

$$S(n_0, x) \equiv -\frac{1}{2(2\pi)^3}\int\left[\frac{1}{\tilde{F}(n_0, k)} - \frac{k^2}{c_2} + \frac{c_4}{c_2^2}\right]e^{-i\mathbf{k}\cdot\mathbf{x}}\, d^3k \tag{6.17}$$

falls off rapidly enough as $k \to \infty$ to guarantee convergence.

7 THE RELATIVISTIC ENERGY FUNCTIONAL TO SECOND ORDER IN DISPLACED CHARGE v

We are now able to establish the relativistic kinetic energy expression to second order with respect to the displaced charge $v(\mathbf{x}) = n(\mathbf{x}) - n_0$. Using equations (3.3), (4.3), (4.6), (5.6) and (6.16) we obtain

$$\lim_{\Omega\to\Omega_\infty}\{T_\Omega[n_0 + v] - T_\Omega^{\mathrm{VR}}[n_0]\} = \mu_0\int_{\Omega_\infty} v(\mathbf{x})\, d^3x + \int_{\Omega_\infty}\int_{\Omega_\infty} S(n_0, x')v(\mathbf{x})v(\mathbf{x}+\mathbf{x}')\, d^3x\, d^3x' + \int_{\Omega_\infty}\int_{\Omega_\infty}\frac{1}{2c_2(n_0)}[\nabla_{x'}^2\delta(\mathbf{x}')]v(\mathbf{x})v(\mathbf{x}+\mathbf{x}')\, d^3x\, d^3x' + \int_{\Omega_\infty}\int_{\Omega_\infty}\frac{c_4(n_0)}{2c_2^2(n_0)}\delta(\mathbf{x}')v(\mathbf{x})v(\mathbf{x}+\mathbf{x}')\, d^3x\, d^3x'$$

$$= \mu_0\int_{\Omega_\infty} v(\mathbf{x})\, d^3x + \int_{\Omega_\infty}\int_{\Omega_\infty} S(n_0, x')v(\mathbf{x})v(\mathbf{x}+\mathbf{x}')\, d^3x\, d^3x' + \frac{1}{2c_2(n_0)}\int_{\Omega_\infty} v(\mathbf{x})\nabla_x^2 v(\mathbf{x})\, d^3x + \frac{c_4(n_0)}{2c_2^2(n_0)}\int_{\Omega_\infty} v^2(\mathbf{x})\, d^3x \tag{7.1}$$

The first expression on the right hand side corresponds to the non-relativistic term, Eq. (2.12), of the work of Corless and March[3]. However, whereas in Ref. 3 the higher-order terms were written in terms of V, Eq. (7.1) is expressed only in terms of the displaced charge, as required for density functional theory.

8 SUMMARY

Equation (7.1) is the main result of the present work, expressing the independent-particle kinetic energy, measured relative to the Vallarta-Rosen[6] homogeneous result, solely in terms of the displaced charge $v(\mathbf{x})$ to second-order in this quantity. Variation of Eq. (7.1) with respect to v leads back to an Euler equation which is the linear response relation between displaced electron density and perturbing potential V in an electron liquid. Within an independent-particle framework, it is therefore clear that an acceptable relativistic kinetic energy functional must expand, to second-order in v, to this expression (7.1). Applications of such a result to interaction between defects in metals has been worked out fully in Ref. 3 in the limit when the fine structure constant tends to zero; the reader interested in specific applications is referred to that study.

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