Square Barrier Model of a One-dimensional Inhomogeneous Electron Liquid in Relation to Relativistic Density Functional Theory

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SQUARE BARRIER MODEL OF A ONE-DIMENSIONAL INHOMOGENEOUS ELECTRON LIQUID IN RELATION TO RELATIVISTIC DENSITY FUNCTIONAL THEORY

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A long-term objective of density functional theory (DFT) has been to obtain the electronic kinetic energy density directly from the ground-state density, without recourse to wave functions. This is the more important in relativistic DFT since Dirac wave functions have four components. The above aim is here achieved for the admittedly specialized square barrier model of a one-dimensional inhomogeneous electron liquid.

1. INTRODUCTION

Density functional theory (DFT), having its orgins in the pioneering studies of Thomas [1], Fermi [2] and Dirac [3, 4] and being formally completed by the theorem of Hohenberg and Kohn [5], seeks to express the ground-state energy of an N-electron assembly as a functional of the electron density ρ. One part of such a functional is the single-particle kinetic energy $T[\rho]$, which is widely used in current applications of DFT, following the work of Slater [6], which was formalized in the later study of Kohn and Sham [7].

Though most applications at the present time return to one-electron wave functions (the so-called Slater–Kohn–Sham (SKS) orbitals) to calculate the single-particle kinetic energy T, it is widely recognized that 'orbital-free' theory affords a very desirable longer-term objective [8].

This situation is the more important in relativistic DFT, our dominant concern here, since in contrast to Schrödinger (or SKS) wave functions, Dirac spinors have four components. Hence to work with the ground-state density ρ alone, without recourse to individual Dirac one-electron wave functions, is an extremely attractive prospect for the future.

This is the motivation for the present study, but because of the complexity of the problem we shall approach the task of calculating the (single-particle) kinetic energy from the ground-state density *via* an admittedly very specialized model. This is chosen here as the square barrier model of a one-dimensional inhomogeneous electron liquid. Appeal can then be made to an earlier investigation of Baltin and March [9], in which separate expressions were obtained for the kinetic energy per unit length ('density' in one-dimension) $t(z)$, and for the ground-state electron density $\rho(z)$.

2. SUMMARY OF NON-RELATIVISTIC RESULTS
   FOR KINETIC ENERGY AND ELECTRON DENSITY
   OF A SEMI-INFINITE ELECTRON LIQUID
   IN d DIMENSIONS

Before appealing to this relativistic study of Baltin and March [9] for a finite square barrier of height V_0 say, it will be useful for what follows to summarize earlier work by the present writer [10] pertaining to semi-infinite electron liquids in Schrödinger wave mechanics: *i.e.*, in the limit when the barrier height V_0 tends to infinity, but now in d dimensions. The passage to the limit $V_0 \to \infty$ is straightforward in non-relativistic theory, as this theory already corresponds to the limiting case $c \to \infty$, c being the velocity of light. As further emphasized below, one has to compare V_0 with mc^2 in relativistic theory, m being the rest mass of the electron. Then, one must take first the limit $c \to \infty$, before proceeding to the infinite barrier case.

For this non-relativistic model when $V_0 \to \infty$, the resulting semi-infinite electron liquid problem was solved by the writer [10] in d dimensions. For singly occupied levels, the density $\rho_d(z)$ was then obtained as

$$\rho_d(z) = \frac{k_f^d}{2^d \pi^{(d+1)/2}(1/2) \cdot (3/2) \cdots (d/2)}$$
$$- \left(\frac{2}{\pi}\right)^{1/2} \frac{1}{(2\pi)^{d/2}} k_f^d \frac{j_{(d-1)/2}(2k_f z)}{(2k_f z)^{(d-1)/2}} \qquad (2.1)$$

where k_f is the Fermi wave number. This result (2.1), with j denoting the appropriate spherical Bessel function, is valid for d odd; if d even is needed then $\rho_z(z)$ *etc.*, can be calculated in terms of Bessel functions of a purely imaginary argument [10].

The corresponding result for the kinetic energy density $t_d(z)$ will also be quoted here, again for d odd [10].

$$t_d(z) = t_{d0} + \frac{k_f^2}{2}[\rho_d(z) - \rho_{d0}]$$
$$+ \frac{k_f^{d+2}}{2\pi^2(2\pi)^{(d-3)/2}} \frac{j_{(d+1)/2}(2k_f z)}{(2k_f z)^{(d+1)/2}}, \qquad (2.2)$$

where t_{d0} is the kinetic energy density of the homogeneous electron liquid of number density ρ_{d0}. These non-relativistic results (2.1) and (2.2) will be appealed to later. Before that, the finite square barrier model will be treated in one-dimension, but now *via* Dirac's relativistic wave equation.

3. RELATION BETWEEN KINETIC ENERGY AND ELECTRON DENSITIES IN SQUARE BARRIER MODEL OF A ONE-DIMENSIONAL INHOMOGENEOUS ELECTRON LIQUID TREATED RELATIVISTICALLY

To the writer's knowledge, results for $\rho_d(z)$ and $t_d(z)$ for the finite square barrier model *via* the Dirac equation have, as yet, only been obtained for the one-dimensional ($d = 1$) case [9]. This study of Baltin and March gives $t_1(z)$ and $\rho_1(z)$ quite explicitly, for a finite square

barrier of height V_0 and, as already anticipated in Section 2 above, the ratio $V_0/mc^2 \equiv \nu$ plays a significant role.

Their results for $t_1(z)$ and $\rho_1(z)$ are written as integrals over a variable τ running from 0 to τ_f, where $\tau = \hbar k/mc$. The result for $\rho_1(z)$ will be written only for the region inside the containing energy barrier of height V_0, where the inhomogeneity in density disappears sufficiently far into the bulk electron liquid of uniform density ρ_{10} say. The form of $\rho_1(z)$ is then subsumed in the dimensionless 'displaced charge' $\Delta_1(z)$ (see Eq. (A1) with $d = 1$), which is given by [9]

$$2\nu\tau_f\Delta_1(z) = \int_0^{\tau_f} \left(\frac{\tau^2}{\omega} - 2\nu\right)\cos(2\tau\zeta)d\tau$$
$$+ \int_0^{\tau_f} [1 - (\omega - 2\nu)^2]^{1/2}\tau\frac{\sin(2\tau\zeta)}{\omega}d\tau \qquad (3.1)$$

where $\omega = (1+\tau^2)^{1/2}$ and $\zeta = (mc/\hbar)z$.

The corresponding result for the kinetic energy density $t_1(z)$ is usefully expressed by writing

$$t_1(z, k_f) = t^{\text{homo}}(k_f) + t^{\text{osc}}(z, k_f) \qquad (3.2)$$

where the oscillatory contribution t^{osc} has the form [9]

$$t^{\text{osc}}(z, k_f) = \left(\frac{mc}{\pi\hbar}\right)\frac{mc^2}{\nu}\left[\int_0^{\tau_f} \cos(2\tau\zeta)(\omega - 1)\left(\frac{\tau^2}{\omega} - 2\nu\right)d\tau\right.$$
$$+ \int_0^{\tau_f} \tau\sin(2\tau\zeta)\frac{\omega - 1}{\omega}$$
$$\left.\cdot [1 - (\omega - 2\nu)^2]^{1/2}d\tau\right] \qquad (3.3)$$

and t^{homo} is the homogeneous electron liquid kinetic energy density.

The basic step in relating Eqs. (3.1) and (3.3) is now to differentiate both expressions with respect to τ_f, to find first of all for the electron density the result

$$\frac{\partial}{\partial\tau_f}\{2\nu\tau_f\Delta_1(z)\} = \left(\frac{\tau_f^2}{\omega_f} - 2\nu\right)\cos(2\tau_f\zeta)$$
$$+ [1 - (\omega_f - 2\nu)^2]^{1/2}\tau_f\frac{\sin(2\tau_f\zeta)}{\omega_f} \qquad (3.4)$$

By a similar procedure, one can derive from Eq. (3.3) the result

$$
\frac{\pi\hbar}{mc}\left(\frac{\nu}{mc^2}\right)\frac{\partial t^{\mathrm{osc}}(z,k_f)}{\partial \tau_f} = (\omega_f - 1)\left(\frac{\tau_f^2}{\omega_f} - 2\nu\right)\cos(2\tau_f\zeta)
$$
$$
+ \frac{(\omega_f - 1)}{\omega_f}[1 - (\omega_f - 2\nu)^2]^{1/2}
$$
$$
\cdot \tau_f \sin(2\tau_f\zeta). \tag{3.5}
$$

If one now multiplies Eq. (3.4) throughout by $(\omega_f - 1)$ and subtracts from Eq. (3.5), the remarkably simple relation

$$
\left[\frac{\pi\hbar}{m^2c^3}\right]\frac{\partial t^{\mathrm{osc}}(z,k_f)}{\partial \tau_f} = 2(\omega_f - 1)\left[\tau_f\frac{\partial \Delta_1(z)}{\partial \tau_f} + \Delta_1(z)\right] \tag{3.6}
$$

emerges. Furthermore, it must be stressed that $\nu = V_0/mc^2$ has disappeared explicitly from the relation (3.6), even though, of course, $t^{\mathrm{osc}}(z,k_f)$ and $\Delta_1(z)$ separately depend on the choice of barrier height. It is worthwhile, for taking the non-relativistic limit of Eq. (3.6), to use the definition of ω immediately below Eq. (3.1) to write

$$
(\omega_f - 1) = \tau_f^2/(\omega_f + 1). \tag{3.7}
$$

hence, using Eq. (3.7) in Eq. (3.6):

$$
\frac{\pi\hbar}{m^2c^3}(\omega_f + 1)\frac{\partial t^{\mathrm{osc}}}{\partial \tau_f} = 2\tau_f^2\left[\tau_f\frac{\partial \Delta_1(z)}{\partial \tau_f} + \Delta_1(z)\right]. \tag{3.8}
$$

This Eq. (3.8) is then the desired connection between kinetic energy and electron densities in this square barrier model of an inhomogeneous relativistic electron liquid.

To compare this exact result (3.8) derived *via* Dirac's relativistic wave equation, with a non-relativistic (nr) Schrödinger counterpart, let us next note that $\omega_f \to 1$ as the velocity of light c is allowed to tend to infinity. Then, replacing τ_f in Eq. (3.8) in favour of k_f, one finds the non-relativistic limit to be

$$
\frac{\partial t^{\mathrm{osc}}_{\mathrm{nr}}(z)}{\partial k_f} = \frac{\hbar^2 k_f^2}{\pi m}\left[k_f\frac{\partial \Delta_1^{\mathrm{nr}}(z)}{\partial k_f} + \Delta_1^{\mathrm{nr}}(z)\right]. \tag{3.9}
$$

To conclude this section, let us check Eq. (3.9) in the infinite barrier non-relativistic limit.

3.1. Non-relativistic Infinite Barrier Limit

One has almost immediately the dimensionless displaced charge in terms of the zero-order spherical Bessel function $j_0(x) = \sin x/x$ (compare Eq. (2.1)):

$$\Delta_1^{nr}(z) = -j_0(2k_f z). \tag{3.10}$$

The corresponding result for the non-relativistic kinetic energy in the same limit is given by [9]

$$t_{nr}^{osc}(z) = \frac{k_f^3}{\pi} [\Delta_1^{nr}(z)] + \frac{2k_f^3}{\pi} \frac{j_1(2k_f z)}{2k_f z} \tag{3.11}$$

where the first-order spherical Bessel function $j_1(x)$ is simply [$\sin x - x \cos x$]$/x^2$. But now one has the mathematical identity

$$\frac{d}{dx} j_0(x) = -j_1(x). \tag{3.12}$$

Combining Eqs. (3.10) and (3.12) immediately yields

$$j_1(2k_f z) = \frac{d}{d(2k_f z)} \Delta_1^{nr}(z) \tag{3.13}$$

and hence one can substitute for $j_1(2k_f z)$ in Eq. (3.11) to obtain

$$t_{nr}^{osc}(z) = \frac{k_f^3}{\pi} \Delta_1^{nr}(z) + \frac{k_f}{2\pi z} \frac{\partial}{\partial z} \Delta_1^{nr}(z). \tag{3.14}$$

Introducing the dimensionless change $\Delta t_{nr}(r)$ in the kinetic energy density induced by the barrier, defined by

$$\Delta t_{nr}(z) = t_{nr}^{osc}(z)/t_{10} \tag{3.15}$$

and noting that the homogeneous electron liquid has $t_{10} = k_f^3/3\pi$ for the doubly filled level case under consideration, Eq. (3.14) is readily

rewritten as

$$\Delta t_{\mathrm{nr}}(z) = 3\Delta_1^{\mathrm{nr}}(z) + \frac{3}{2k_f^2 z}\frac{\partial \Delta_1^{\mathrm{nr}}(z)}{\partial z},\qquad (3.16)$$

the d-dimensional generalization of this equation, using the results of Section 2, being recorded in Appendix 1. It is worth stressing here that in non-relativistic theory, Eq. (3.16) affords a direct route to calculate the kinetic energy density from the ground-state electron density. In contrast, the relativistic theory of the inhomogeneous electron liquid generated by the one-dimensional square barrier model has the non-relativistic limit (3.9). It is apparent that, to check Eq. (3.9) in the infinite barrier limit, the LHS can be evaluated directly by inserting Eq. (3.11) while the RHS is determined solely by use of Eq. (3.10) for the displaced charge.

Taking first the RHS of Eq. (3.9), one readily obtains by using Eq. (3.12) the result

$$\mathrm{RHS} = \frac{\hbar^2}{m}\left[-\frac{k_f^2}{\pi}j_0(2k_f z) + \frac{2k_f^3 z}{\pi}j_1(2k_f z)\right].\qquad (3.17)$$

Turning to the evaluation of the LHS of Eq. (3.9), let us first insert Eq. (3.15) to find

$$\left(\frac{m}{\hbar^2}\right)\frac{\partial}{\partial k_f}t_{\mathrm{nr}}^{\mathrm{osc}}(z) = \frac{k_f^2}{\pi}\Delta t_{\mathrm{nr}}(z) + \frac{k_f^3}{3\pi}\frac{\partial \Delta t_{\mathrm{nr}}(z)}{\partial k_f}.\qquad (3.18)$$

One must now use the result (3.16) for $\Delta t_{\mathrm{nr}}(z)$ in Eq. (3.18). Some intermediate steps are supplied in Appendix 2, where two mathematical identities relating spherical Bessel functions, and their derivatives, of different orders are invoked. The first term on the RHS of Eq. (3.18) is then easily written in terms of j_0 and j_1 which are already present in Eq. (3.17):

$$\frac{k_f^2}{\pi}\Delta t_{\mathrm{nr}}(z) = -\frac{3k_f^2}{\pi}j_0(2k_f z) + \frac{3k_f}{\pi z}j_1(2k_f z).\qquad (3.19)$$

The evaluation of the second term on the RHS of Eq. (3.18) after inserting Eq. (3.16) evidently involves second derivatives of $j_0(x)$. After invoking the mathematical identities already referred to one

finds (see Appendix 2)

$$\frac{k_f^3}{3\pi}\frac{\partial \Delta t_{nr}(z)}{\partial k_f} = \frac{2k_f^2}{\pi}j_0(2k_fz) - \frac{3k_f}{\pi z}j_1(2k_fz) + \frac{2k_f^3z}{\pi}j_1(2k_fz), \quad (3.20)$$

after removing $j_2(x)$ in favour of j_0 and j_1. Adding Eqs. (3.19) and
(3.20) leads back precisely to the quantity in the square bracket of
Eq. (3.17). Thus, Eq. (3.9) is verified to hold in the limiting case of
an infinite barrier.

4. SUMMARY AND FUTURE DIRECTIONS

For the finite square barrier model, solved *via* Dirac's relativistic wave
equation in the one-dimensional case, it has been demonstrated that
the kinetic energy density and the ground-state electron density are re-
lated through Eq. (3.8). This finding is in the spirit of relativistic DFT,
in which the calculation of the kinetic energy density directly from the
electron density is a major aim, thereby avoiding four-component Dirac
wave functions. Of course, it is recognized that Eq. (3.8) has been
derived for a pretty specialized model, but it should be reiterated that
in the relation (3.8) the barrier height has disappeared, even though
the electron density and kinetic energy separately depend on V_0/mc^2.

It has then been shown that the non-relativistic limit of (3.9) can be
checked for the infinite barrier model, where it emerges that kine-
tic and electron densities are related directly by Eq. (3.16), the *d*-
dimensional version of which has also been derived in Appendix 1.
Derivatives of Eq. (3.16) with respect to the Fermi wavenumber k_f
lead back, after some manipulation, to Eq. (3.9).

In view of the above findings, it would seem to be of interest for the
future if the results of Baltin and March [9] on the one-dimensional
relativistic square barrier model could be generalized to three dimen-
sions using the Dirac equation. Such a generalization has already
been given by these authors for (two and) three dimensions in the
homogeneous electron liquid.

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APPENDIX 1: *d*-DIMENSIONAL GENERALIZATION OF NON-RELATIVISTIC RELATION BETWEEN KINETIC ENERGY AND ELECTRON DENSITIES FOR SEMI-INFINITE ELECTRON LIQUIDS

The purpose of this Appendix is to generalize the non-relativistic one-dimensional relation (3.16) between kinetic energy and electron densities to d dimensions. Equations (2.1) and (2.2) then afford the appropriate starting point.

Defining the dimensionless quantities

$$\Delta t_d(z) = \frac{t_d(z) - t_{d0}}{t_{d0}} : \quad \Delta_d(z) = \frac{\rho_d(z) - \rho_{d0}}{\rho_{d0}}, \tag{A1.1}$$

Equation (2.1), valid for d odd, takes the form

$$\Delta_d(z) = -2^{(d+1)/2}\left(\frac{1}{2}\cdot\frac{3}{2}\cdots\frac{d}{2}\right)\frac{j_{(d-1)/2}(2k_f z)}{(2k_f z)^{(d-1)/2}}. \tag{A1.2}$$

To relate this d dimensional expression to Eq. (3.11) of the main text, let us put $d = 1$ in Eq. (A1.2), when the spherical Bessel function part reduces to $j_0(2k_f z)$ while the multiplying constant is simply (-1).

Turning to the d dimensional kinetic energy density and using the dimensionless ratio Δt_d defined in Eq. (A1.1), one obtains

$$\Delta t_d(z) = \frac{k_f^2}{2}\frac{\rho_{d0}}{t_{d0}}\Delta_d(z) + \frac{k^{d+2}}{(2\pi^2)(2\pi)^{(d-3)/2}t_{d0}}\frac{j_{(d+1)/2}(2k_fz)}{(2k_fz)^{(d+1)/2}}. \quad (A1.3)$$

One can readily calculate the ratio ρ_{d0}/t_{d0} appearing in Eq. (A1.3) from the results of Ref. [10] as

$$\frac{\rho_{d0}}{t_{d0}} = \frac{2}{k_f^2}\left(\frac{d+2}{d}\right), \quad (A1.4)$$

and therefore the first term on the RHS of Eq. (A1.3) is simply $\{(d+2)/d\}\Delta_d(z)$, which again checks with the result for $d = 1$ in Eq. (3.16).

Thus it only remains to relate the final terms in Eq. (A1.3) to Eq. (A1.2). Using once again the identity (3.21), but now with $\ell + 1 = (d+1)/2$ for d odd, one has immediately

$$-\frac{j_{(d+1)/2}(2k_fz)}{(2k_fz)^{(d-1)/2}} = \frac{1}{2k_f}\frac{\partial}{\partial z}\left[\frac{j_{(d-1)/2}(2k_fz)}{(2k_fz)^{(d-1)/2}}\right]. \quad (A1.5)$$

Substituting this result for $j_{(d+1)/2}$ in Eq. (A1.3) then leads to

$$\Delta t_d(z) = \left(\frac{d+2}{d}\right)\Delta_d(z) - \frac{k_f^{d+2}}{(2\pi^2)(2\pi)^{(d-3)/2}t_{d0}}\frac{1}{4k_f^2z}$$
$$\times\frac{\partial}{\partial z}\left[\frac{j_{(d-1)/2}(2k_fz)}{(2k_fz)^{(d-1)/2}}\right]. \quad (A1.6)$$

Differentiating Eq. (2.1) with respect to z then allows the final term of Eq. (A1.6) to be replaced in favour of the derivative $(\partial/\partial z)\Delta_d(z)$. Using Eq. (2.1), in which the first term on the RHS is ρ_{d0}, and Eq. (A1.4), one can eliminate t_{d0} from Eq. (A1.6) to obtain

$$\Delta t_d(z) = \left(\frac{d+2}{d}\right)\left[\Delta_d(z) + \frac{1}{2k_f^2z}\frac{\partial\Delta_d(z)}{\partial z}\right]. \quad (A1.7)$$

This is the desired non-relativistic d dimensional relation between kinetic energy and electron densities in this class of models. It immediately reduces to Eq. (3.16) of the main text in the special case when $d = 1$.

APPENDIX 2: SOME DETAILS OF DERIVATION OF EQ. (3.20) OF MAIN TEXT

This Appendix will supply some details used in obtaining Eq. (3.20) of the main text. Into the LHS, one first inserts the result (3.16) and then utilizes Eq. (3.13). In terms of the spherical Bessel function j_1, one then finds after a short calculation:

$$\frac{k_f^3}{3\pi} \frac{\partial}{\partial k_f} \Delta t_{nr}(z) = \left[\frac{2k_f^3 z}{\pi} - \frac{k_f}{\pi z} \right] j_1(2k_f z) + \frac{2k_f^2}{\pi} j_1'(2k_f z). \qquad (A2.1)$$

For the derivative j_1', one now appeals to the mathematical identity [11]

$$\frac{d}{dx} [x^{-\ell} j_\ell(x)] = -x^{-\ell} j_{\ell+1}(x) \qquad (A2.2)$$

with $\ell = 1$, and evidently $j_2(2k_f z)$ then enters Eq. (A2.1). This equation then can be re-expressed readily as

$$\frac{k_f^3}{3\pi} \frac{\partial}{\partial k_f} \Delta t_{nr}(z) = \frac{2k_f^3 z}{\pi} j_1(2k_f z) - \frac{2k_f^2}{\pi} j_2(2k_f z). \qquad (A2.3)$$

But one has the further identity [11]

$$j_{\ell-1}(x) + j_{\ell+1}(x) = \frac{(2\ell + 1)}{x} j_\ell(x) \qquad (A2.4)$$

and putting $\ell = 1, j_2(2k_f z)$ can be removed from Eq. (A2.3) in favour of j_0 and j_1. The resulting equation is identical to Eq. (3.20). Using this equation together with Eqs. (3.19) and (3.17) verifies Eq. (3.9) for the infinite barrier model.