Electron and kinetic energy densities from Dirac's equation for a model semi-infinite inhomogeneous electron gas

1987 J. Phys. A: Math. Gen. 20 5517

(http://iopscience.iop.org/0305-4470/20/16/026)

J. Phys. A: Math. Gen. **20** (1987) 5517-5528. Printed in the UK

Electron and kinetic energy densities from Dirac's equation for a model semi-infinite inhomogeneous electron gas

R Baltin† and N H March

Theoretical Chemistry Department, University of Oxford, 1 South Parks Road, Oxford OX1 3TG, UK

Received 22 May 1987

Abstract. Adopting a simple independent 'particle in a box' model with a finite square barrier, Dirac's relativistic wave equation has been used to obtain exact results for the electron density ρ and kinetic energy density t in the semi-infinite inhomogeneous electron-gas limit. By utilising a suitable power series development, one can pass to the non-relativistic limit and subsequently to the limit of an infinite barrier, in which case well established results are regained. Finally, the relation to relativistic Thomas-Fermi theory is discussed.

1. Introduction

The description of a many-electron ground state by its electron density has become of major importance for studying the inhomogeneous electron gas as it exists in atoms, molecules and condensed matter, following the pioneering work of Thomas (1926) and Fermi (1928). This area has by now been extensively reviewed (Banzai and Deb 1981, Lundqvist and March 1983, Callaway and March 1984, Dreizler and da Providencia 1985). While the range of validity of the original Thomas-Fermi theory is now well understood, the same can hardly be said for the relativistic version of that theory, due to Vallarta and Rosen (1932), even though it has been extensively applied to problems in atomic physics (see, for example, Hill *et al* (1987) and references therein).

Therefore, it remains of interest to study the theory of the inhomogeneous electron gas for simple model systems by using relativistic quantum mechanics. The present paper is in this area. Specifically, by considering a simple 'particle in a box' model (though of necessity now with a finite square barrier), the Dirac one-electron wavefunctions appropriate for independent particle motion are used to construct (i) the electron density ρ and (ii) the kinetic energy density t. Explicit relation to the non-relativistic limit is then exhibited by allowing the velocity of light c to tend to infinity, after which the passage to an infinite barrier limit can be correctly made. Though the full solutions for the wavefunctions are available for a 'box' of finite length, the main focus here will be on the semi-infinite inhomogeneous electron gas in which the 'box' length is also allowed to tend to infinity.

Matters discussed on the basis of this admittedly elementary model are (i) the Friedel oscillations induced asymptotically by introducing a localised potential into an initially uniform relativistic electron gas and (ii) the kinetic energy density in relation

† On leave from the Department of Theoretical Chemistry, University of Ulm, West Germany.

0305-4470/87/165517+12$02.50

to the electron density in the uniform gas case. Using (ii), the relation of the Dirac theory to the relativistic Thomas-Fermi theory is exhibited for slowly varying potentials introduced into a homogeneous relativistic electron gas.

2. Eigenspinors and electron density in a one-dimensional finite square-well potential

The usual one-electron Dirac Hamiltonian H

$$H = c\alpha_z p_z + V(z) + \beta mc^2 \tag{2.1}$$

is the basis for what follows. (For general references to Dirac's theory see, e.g., Bjorken and Drell (1964) or Rose (1961)). The square-well potential adopted here for $V(z)$ is defined by

$$V(z) = \begin{cases} 0 & 0 \leq z \leq l \\ V_0 > 0 & z < 0 \text{ or } z > l \end{cases} \tag{2.2}$$

the three regions I-III referring to $z<0$, $0 \leq z \leq l$ and $z>l$, respectively. α_z and β are the customary 4×4 matrices

$$\alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{2.3}$$

One wishes to solve $H\psi = \varepsilon\psi$ for $mc^2 \leq \varepsilon \leq mc^2 + V_0$.

In region II, four independent solutions of Dirac's equation are found to be $\psi_+ = v_+ \exp(ikz)$ with $v_+ = (1, 0, g, 0)$ or $(0, 1, 0, -g)$ and $\psi_- = v_- \exp(-ikz)$ with $v_- = (0, 1, 0, g)$ or $(-1, 0, g, 0)$ where

$$0 \leq c\hbar k \equiv (\varepsilon^2 - m^2c^4)^{1/2} = [\eta(\eta + 2mc^2)]^{1/2} \tag{2.4}$$

and

$$g \equiv \frac{c\hbar k}{\varepsilon + mc^2} = \left(\frac{\eta}{\eta + 2mc^2}\right)^{1/2} \tag{2.5}$$

using $\eta \equiv \varepsilon - mc^2$.

In regions I and III solutions having the same energy and tending to zero as $z \to -\infty$ or $z \to +\infty$, respectively, are given by $\psi = v_{\mathrm{I}} \exp(\kappa z)$ with $v_{\mathrm{I}} = (0, 1, 0, i\gamma)$ or $(-1, 0, i\gamma, 0)$ (region I) and $\psi = v_{\mathrm{III}} \exp(-\kappa z)$ with $v_{\mathrm{III}} = (1, 0, i\gamma, 0)$ or $(0, 1, 0, -i\gamma)$ (region III). Here we have put

$$\begin{aligned} 0 \leq c\hbar\kappa &\equiv [m^2c^4 - (\varepsilon - V_0)^2]^{1/2} \\ &= [(V_0 - \eta)(2mc^2 - V_0 + \eta)]^{1/2} \end{aligned} \tag{2.6}$$

and

$$0 \leq \gamma \equiv \frac{c\hbar\kappa}{\varepsilon - V_0 + mc^2} = \left(\frac{V_0 - \eta}{2mc^2 - V_0 + \eta}\right)^{1/2}. \tag{2.7}$$

Imposing the condition of continuity of ψ at the boundaries between regions I-III leads to the secular equation for the allowed energy levels:

$$2\gamma \cos(kl) + (\gamma^2/g - g)\sin(kl) = 0. \tag{2.8}$$

The current component j^z given by

$$j^z = c\psi^+\alpha_z\psi = c(\psi_1^*\psi_3 + \psi_3^*\psi_1 - \psi_2^*\psi_4 - \psi_4^*\psi_2) \tag{2.9}$$

is evidently continuous at the boundaries if the spinor components are. This is different in non-relativistic Schrödinger theory where current components also involve first-order derivatives of the wavefunction so that continuity of slopes has to be imposed on ψ as another independent condition to make j^z continuous. On the other hand, the Dirac spinors have discontinuous slopes as must be expected because the jump of the potential has to be compensated in the Dirac equation being of first order.

The solutions $\eta = \eta_n$, $n = 1, 2, 3, \ldots$ of equation (2.8) are lying between 0 and V_0 where V_0 has to be restricted to $0 \leq V_0 \leq mc^2$. For $V_0 > mc^2$ unphysical features will occur, e.g. increasing κ (corresponding to stronger falloff of ψ) when the energy η is raised, or even imaginary values of κ are possible for $V_0 > 2mc^2$. These peculiarities are special effects of the Klein paradox.

Since in the non-relativistic limit $c \to \infty$

$$k \to \left(\frac{2m\eta}{\hbar^2}\right)^{1/2} \qquad \gamma \to \frac{1}{c}\left(\frac{V_0 - \eta}{2m}\right)^{1/2} \qquad g \to \frac{1}{c}\left(\frac{\eta}{2m}\right)^{1/2} \tag{2.10}$$

the secular (2.8) is readily shown to reduce to the well known non-relativistic form

$$2[\eta(V_0 - \eta)]^{1/2} \cos\left[l\left(\frac{2m\eta}{\hbar^2}\right)^{1/2}\right] + (V_0 - 2\eta)\sin\left[l\left(\frac{2m\eta}{\hbar^2}\right)^{1/2}\right] = 0. \tag{2.11}$$

2.1. The limit of infinite 'box' length l

Below we shall focus primarily on the semi-infinite inhomogeneous electron gas, corresponding to the 'box' length l tending to infinity such that the number of electrons per unit length, referred to below as the 'electron density', remains finite. For very large l, equation (2.8) has solutions

$$k = k_n = \pi n/l \qquad n = 1, 2, 3, \ldots \tag{2.12}$$

independent of V_0 and correspondingly η can be found to have the allowed values

$$\eta = \eta_n = [m^2c^4 + (c\hbar\pi/l)^2 n^2]^{1/2} - mc^2. \tag{2.13}$$

For $c \to \infty$, $\eta_n \to \frac{1}{2}\hbar^2\pi^2 n^2/(ml^2)$ as required.

The final results for the eigenspinors are that there are two independent degenerate solutions:

$$\psi^{(1)}(z) = D_1\left[\theta(-z)\,\mathrm{e}^{\kappa z}\begin{pmatrix}-1\\0\\\mathrm{i}\gamma\\0\end{pmatrix} + \theta(z)\theta(l-z)\begin{pmatrix}-\cos(kz) - (\gamma/g)\sin(kz)\\0\\-\mathrm{i}g\sin(kz) + \mathrm{i}\gamma\cos(kz)\\0\end{pmatrix}\right.$$

$$\left. -\tfrac{1}{2}\theta(z-l)\exp[\kappa(l-z)]\left(\frac{g}{\gamma} + \frac{\gamma}{g}\right)\sin(kl)\begin{pmatrix}1\\0\\\mathrm{i}\gamma\\0\end{pmatrix}\right] \tag{2.14}$$

and

$$\psi^{(2)}(z) = D_2 \left[\theta(-z)\, \mathrm{e}^{\kappa z} \begin{pmatrix} 0 \\ 1 \\ 0 \\ \mathrm{i}\gamma \end{pmatrix} + \theta(z)\theta(l-z) \begin{pmatrix} 0 \\ \cos(kz) + (\gamma/g)\sin(kz) \\ 0 \\ -\mathrm{i}g\sin(kz) + \mathrm{i}\gamma\cos(kz) \end{pmatrix} \right.$$

$$\left. + \tfrac{1}{2}\theta(z-l)\exp[\kappa(l-z)]\left(\frac{g}{\gamma} + \frac{\gamma}{g}\right)\sin(kl) \begin{pmatrix} 0 \\ 1 \\ 0 \\ -\mathrm{i}\gamma \end{pmatrix} \right]. \tag{2.15}$$

Here $\theta(z)$ denotes the unit step function. $\theta(z)\theta(l-z) = 1$ if $0 \leqslant z \leqslant l$ and is zero otherwise. $\psi^{(1)}$ and $\psi^{(2)}$ differ by their spin, which is $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively, in the z direction.

It turns out that for the normalisation factors $D_1 = D_2 = C$, say, where for large l one finds

$$C = C_n = \left(\frac{\eta_n(\eta_n + 2mc^2)(\eta_n + 2mc^2 - V_0)}{2mc^2 V_0 l(\eta_n + mc^2)} \right)^{1/2}. \tag{2.16}$$

2.2. Electron density $\rho(z, \eta_F)$ in the limit l tending to infinity

We turn to the first aim of using this box model, namely to calculate the electron density as a function of z and the Fermi energy η_F in the limit as the 'box' length l tends to infinity. The density $\rho(z, N)$ including levels $n = 1$ to N is evidently

$$\rho(z, N) = \sum_{n=1}^{N} [\psi_n^{(1)+}(z)\psi_n^{(1)}(z) + \psi_n^{(2)+}(z)\psi_n^{(2)}(z)]. \tag{2.17}$$

For $l \to \infty$ one can replace $\psi_n^{(i)}$ by $\psi^{(i)}(z, \eta)$ being a smooth function of energy η, and consequently one can write

$$\rho(z, \eta_F) = \int_{\eta=0}^{\eta_F} \frac{\partial n}{\partial \eta} [\psi^{(1)+}(z, \eta)\psi^{(1)}(z, \eta) + \psi^{(2)+}(z, \eta)\psi^{(2)}(z, \eta)]\, \mathrm{d}\eta. \tag{2.18}$$

Solving equation (2.13) for n and differentiating with respect to η yields

$$\frac{\partial n}{\partial \eta} = \frac{l}{c\hbar\pi} \frac{\eta + mc^2}{[\eta(\eta + 2mc^2)]^{1/2}} \tag{2.19}$$

and evidently l cancels against the length in $C_n^2 = C^2(\eta)$ in (2.16). The contributions of $\psi^{(1)}$ and $\psi^{(2)}$ to the density are the same, and it follows that

$$\rho(z, \eta_F) = \frac{1}{mc^3\hbar\pi V_0} \int_0^{\eta_F} (\eta + 2mc^2 - V_0)[\eta(\eta + 2mc^2)]^{1/2}$$

$$\times \{\theta(-z)(1+\gamma^2)\, \mathrm{e}^{2\kappa z} + \theta(z)\theta(l-z)[(\cos(kz) + (\gamma/g)\sin(kz))^2$$

$$+ (\gamma\cos(kz) - g\sin(kz))^2] + \theta(z-l)\exp[2\kappa(l-z)](1+\gamma^2)\}\, \mathrm{d}\eta \tag{2.20}$$

where the contents of the curly brackets in (2.20) will be denoted by $R(z, k)$ below. Changing the variable of integration from η to k yields from (2.20) the result

$$\rho(z, k_F) = \frac{\hbar^2}{m\pi V_0} \int_0^{k_F} \left(1 + \frac{mc^2 - V_0}{W(k)}\right) R(z, k) k^2 \, dk \tag{2.21}$$

where $W(k) = [m^2c^4 + (c\hbar k)^2]^{1/2}$.

Focusing attention on the density inside the box, i.e. in region II, one finds after some algebra that

$$\rho_{II}(z, k_F) = \frac{2k_F}{\pi} + \frac{\hbar^2}{\pi m\nu} \int_0^{k_F} \frac{dk}{W} \left(k^2 - \frac{V_0 W}{(c\hbar)^2}\right) \cos(2kz) + \frac{\hbar}{\pi m\nu c} \int_0^{k_F} \frac{k \, dk}{W} [(mc^2)^2 - (W - V_0)^2]^{1/2} \sin(2kz) \tag{2.22}$$

where $\nu \equiv V_0/(2mc^2) \leqslant \frac{1}{2}$.

Finally, it is useful to transform to dimensionless variables

$$\tau \equiv \hbar k/mc \qquad \tau_F \equiv \hbar k_F/mc \qquad \zeta \equiv (mc/\hbar)z \tag{2.23}$$

when one finds the exact limiting electron density for large l to be

$$\rho_{II}(z, k_F) = \frac{2k_F}{\pi} \left[1 + \frac{1}{2\nu\tau_F} \int_0^{\tau_F} \left(\frac{\tau^2}{\omega} - 2\nu\right) \cos(2\tau\zeta) \, d\tau + \frac{1}{2\nu\tau_F} \int_0^{\tau_F} [1 - (\omega - 2\nu)^2]^{1/2} \frac{\tau \sin(2\tau\zeta)}{\omega} d\tau\right] \tag{2.24}$$

with

$$\omega \equiv (1 + \tau^2)^{1/2}. \tag{2.25}$$

Further evaluation seems presently possible by expanding the square roots when $\tau_F \ll 1$ and $\tau_F^2 \ll 2\nu$. One then finds that the integrations can be performed to yield, with $\xi = 2k_F z = 2\tau_F \zeta$,

$$\rho_{II}(z, k_F) = \frac{2k_F}{\pi} \left[1 - j_0(\xi) + \tau_F \left(\frac{1-\nu}{\nu}\right)^{1/2} j_1(\xi) + \frac{\tau_F^2}{2\nu} \left(j_0(\xi) - \frac{2j_1(\xi)}{\xi}\right) - \tau_F^3 \left(\frac{1-\nu}{\nu}\right)^{1/2} \left(\frac{1}{2} + \frac{1-2\nu}{8\nu(1-\nu)}\right) \left(j_1(\xi) - \frac{2}{\xi} j_2(\xi)\right) + O(\tau_F^4)\right]. \tag{2.26}$$

To pass to the non-relativistic limit it is useful to introduce $\lambda \equiv \eta_F/V_0 = \hbar^2 k_F^2/(2mV_0)$, whence it follows that $\nu = \tau_F^2/(2\lambda)$. $\tau_F^2 \ll 4\nu$ then corresponds to $\lambda \ll \frac{1}{2}$ and $\nu \leqslant \frac{1}{2}$ corresponds to $\tau_F^2 \leqslant 2\lambda$. Then the non-relativistic limit $c \to \infty$ corresponds to $\tau_F \to 0$, when one finds

$$\rho_{II}^{nr}(z, k_F) = \frac{2k_F}{\pi} \{1 - j_0(\xi) + 2\lambda^{1/2} j_1(\xi) + 2\lambda[j_0(\xi) - (2/\xi) j_1(\xi)] - \lambda^{3/2}[j_1(\xi) - (2/\xi) j_2(\xi)] + O(\lambda^2)\}. \tag{2.27}$$

The first two terms on the right-hand side of (2.27) give the usual expression for the density for a particle in a 'box' with infinite walls. The 'wall' at $z = 0$ induces long-range Friedel oscillations of wavelength π/k_F in the initially uniform density $2k_F/\pi \equiv \rho_0$. It can be seen from (2.26) that the oscillations remain of the same wavelength when relativity is included.

Having accomplished the first objective of calculating the electron density of this semi-infinite inhomogeneous electron gas from Dirac's equation, the results being given in equation (2.24) and its power series development (2.26), we turn to the second aim, namely to calculate the kinetic energy density for this model.

3. Kinetic energy density in the limit $l \to \infty$

The kinetic energy density associated with a single spinor in the present one-dimensional case can be written

$$t_\psi(z) = \psi^\dagger(z)\, T\psi(z) \tag{3.1}$$

where T is to be taken as the free-particle Dirac Hamiltonian minus the rest-mass energy, i.e.

$$T = H^{(0)} - mc^2 1 = c\alpha_z p_z + mc^2(\beta - 1) \tag{3.2}$$

where 1 denotes the 4×4 unit matrix and $H^{(0)}$ is given by equation (2.1) with $V(z)$ put equal to zero.

Since eigenstates of H will be employed, one finds immediately that

$$\begin{aligned} t_\psi(z) &= \psi^\dagger(z)[H - V(z) - mc^2 1]\psi(z) \\ &= [\eta - V(z)]\psi^\dagger\psi. \end{aligned} \tag{3.3}$$

Therefore the sum over states differs from that in (2.20) merely by the introduction of an additional factor η or $\eta - V_0$ in the integrand depending upon whether z is in region II or not. Using k as the integration variable, with $\eta = W(k) - mc^2$, yields

$$t(z, k_F) = \frac{\hbar^2}{m\pi V_0}\int_0^{k_F} (W - mc^2 - V_0\sigma)\left(1 + \frac{mc^2 - V_0}{W}\right) R(z, k)k^2\, dk \tag{3.4}$$

where $\sigma = 0$ for $z \in [0, l]$ and 1 otherwise.

Again restricting attention to region II one can write

$$t_{II}(z, k_F) = t^{\text{homo}}(k_F) + t^{\text{osc}}(z, k_F) \tag{3.5}$$

with the homogeneous part given explicitly by

$$\begin{aligned} t^{\text{homo}}(k_F) &= \frac{2}{\pi}\int_0^{k_F} [W(k) - mc^2]\, dk \\ &= \left(\frac{mc}{\pi\hbar}\right) mc^2\{\tau_F[(1+\tau_F^2)^{1/2} - 2] + \ln[\tau_F + (1+\tau_F^2)^{1/2}]\}. \end{aligned} \tag{3.6}$$

We will return to this expression below. However, to complete the evaluation of $t_{II}(z, k_F)$ one has the oscillatory part in (3.5) as

$$\begin{aligned} t^{\text{osc}}(z, k_F) = {} & \frac{\hbar^2}{\pi m\nu}\int_0^{k_F} (W - mc^2)\left(k^2 - \frac{V_0 W}{(c\hbar)^2}\right)\frac{\cos(2kz)}{W}\, dk \\ & + \frac{\hbar}{\pi m\nu c}\int_0^{k_F} (W - mc^2)[(mc^2)^2 - (W - V_0)^2]^{1/2}\frac{k\sin(2kz)}{W}\, dk. \end{aligned} \tag{3.7}$$

Again using dimensionless variables, equation (2.23), we obtain

$$t^{\mathrm{osc}}(z, k_{\mathrm{F}}) = \frac{mc}{\pi\hbar}\frac{mc^2}{\nu}\left(\int_0^{\tau_{\mathrm{F}}} \cos(2\tau\zeta)(\omega-1)(\tau^2/\omega - 2\nu)\,\mathrm{d}\tau \right.$$
$$\left. + \int_0^{\tau_{\mathrm{F}}} \tau \sin(2\tau\zeta)\frac{\omega-1}{\omega}[1-(\omega-2\nu)^2]^{1/2}\,\mathrm{d}\tau\right). \tag{3.8}$$

As in equation (2.26) these integrals can be done approximately by expanding the roots under the conditions $\tau_{\mathrm{F}} \ll 1$ and, at the same time, $\tau_{\mathrm{F}}^2 \ll 2\nu$. To be consistent, the homogeneous part, though integrated exactly, is also expanded so that we find for the total kinetic energy density

$$t_{11}(z, k_{\mathrm{F}}) = \frac{2k_{\mathrm{F}}\eta_{\mathrm{F}}}{3\pi}\left[1 - \tfrac{3}{20}\tau_{\mathrm{F}}^2 - 3[j_0 - (2/\xi)j_1] + 3\left(\frac{1-\nu}{\nu}\right)^{1/2}[j_1 - (2/\xi)j_2]\tau_{\mathrm{F}}\right.$$
$$+ \tfrac{3}{2}(\tfrac{1}{2} + 1/\nu)[j_0 - (4/\xi)j_1 + (8/\xi^2)j_2]\tau_{\mathrm{F}}^2$$
$$\left. + 3\left(\frac{1-\nu}{\nu}\right)^{1/2}\left(\frac{2\nu-1}{8\nu(1-\nu)} - \frac{3}{4}\right)[j_1 - (4/\xi)j_2 + (8/\xi^2)j_3]\tau_{\mathrm{F}}^3 + \mathrm{O}(\tau_{\mathrm{F}}^4)\right] \tag{3.9}$$

where the spherical Bessel functions j_n are to be taken at $\xi \equiv 2k_{\mathrm{F}}z$.

To perform the non-relativistic limit it is again convenient to express ν by τ_{F} and by the c-free parameter λ already used. For $c \to \infty$ one then obtains

$$t_{11}^{\mathrm{nr}}(z, k_{\mathrm{F}}) = \frac{2k_{\mathrm{F}}\eta_{\mathrm{F}}}{3\pi}\{1 - 3[j_0 - (2/\xi)j_1] + 6\lambda^{1/2}[j_1 - (2/\xi)j_2]$$
$$+ 6\lambda[j_0 - (4/\xi)j_1 + (8/\xi^2)j_2] - 3\lambda^{3/2}[j_1 - (4/\xi)j_2 + (8/\xi^2)j_3] + \mathrm{O}(\lambda^2)\}. \tag{3.10}$$

Only after $c \to \infty$ is it possible to let $V_0 \to \infty$ which corresponds to $\lambda \to 0$, the result being

$$t_{11}^{\mathrm{nr}}(z, k_{\mathrm{F}})\Big|_{\substack{\text{infinite}\\ \text{wall}}} = \frac{2k_{\mathrm{F}}\eta_{\mathrm{F}}}{3\pi}\{1 - 3[j_0 - (2/\xi)j_1]\}. \tag{3.11}$$

4. Relation to relativistic Thomas–Fermi theory

This is the point at which we want to bring the predictions of Dirac theory into contact with the relativistic Thomas-Fermi theory. In this latter theory, one writes an equation for the chemical potential μ of the electronic charge cloud in the inhomogeneous relativistic electron gas as

$$\mu = (c^2p_{\mathrm{F}}^2 + m^2c^4)^{1/2} - mc^2 + V \tag{4.1}$$

where p_{F} is the Fermi or maximum momentum at the specified position in the electronic cloud while V is the potential energy at this same position.

Returning to the Dirac theory of §§ 2 and 3, consider the constant part of both ρ and t. By elimination of the Fermi wavenumber k_{F} one finds in this homogeneous limit the relation

$$t(\rho) = a\{b\rho[(1 + b^2\rho^2)^{1/2} - 2] + \ln[b\rho + (1 + b^2\rho^2)^{1/2}]\} \tag{4.2}$$

where the superscripts 'homo' are omitted henceforth. The constants are given by

$$a \equiv mc^2(mc/\hbar\pi) \qquad b \equiv \hbar\pi/2mc. \tag{4.3}$$

According to the derivation given in §§ 2 and 3 the range of validity of equation (4.2) seems to be restricted to the interval $0 \leq \tau_F = b\rho \leq 1$. However, as far as the homogeneous parts of ρ and t are concerned, equation (4.2) may be alternatively derived from the Dirac equation using periodic boundary conditions in a space with the potential being zero everywhere. This is shown paradigmatically for the three-dimensional case in § 4.3. In the absence of any potential, no restriction of the range of $b\rho$ can arise so that, in summary, one can state that equation (4.2) is actually valid for any homogeneous density.

It is of interest, first of all, to consider the ratio of $t(\rho)$ given for a homogeneous relativistic electron gas in equation (4.2) with its non-relativistic limit $t_{nr}(\rho)$ given by

$$t_{nr}(\rho) = \frac{\pi^2 \hbar^2}{24m} \rho^3 \tag{4.4}$$

which is easily verified to result also from equation (4.2) in the limit $c \to \infty$. The ratio $f(\rho) \equiv t(\rho)/t_{nr}(\rho)$ is plotted in figure 1.

4.1. Variation principle corresponding to Euler equation (4.1)

It is now a straightforward matter for the non-interacting particle case treated exclusively in the present study based on the Dirac equation, to construct a variation principle having equation (4.1) as its Euler equation. Thus we write for the ground-state energy E (with rest-mass energy not being included) for the inhomogeneous relativistic electron gas of density $\rho(z)$, with non-uniformity induced by a one-body potential energy $V(z)$,

$$E = \int t(\rho)\, dz + \int \rho(z) V(z)\, dz \equiv T + U \tag{4.5}$$

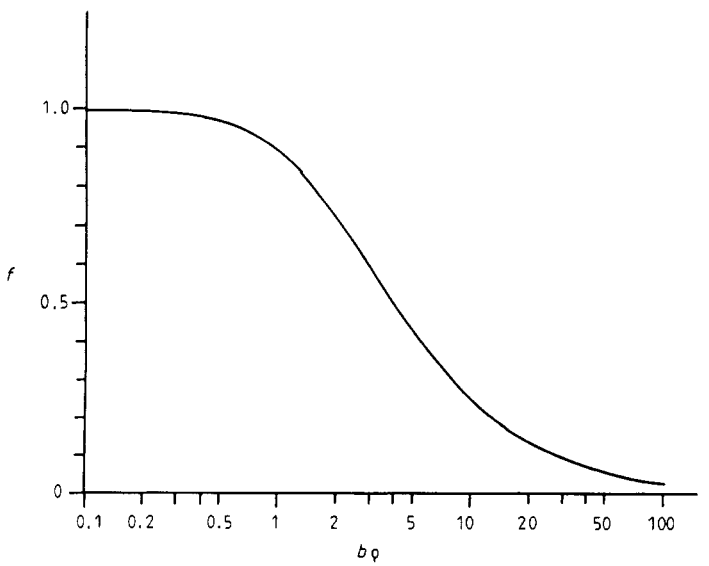

Figure 1. Ratio $f(\rho) = t(\rho)/t_{nr}(\rho)$ where $t(\rho)$ is the relativistic kinetic energy density for the homogeneous electron gas of density ρ in one dimension, equation (4.2). $t_{nr}(\rho)$ is the non-relativistic limit, equation (4.4), of $t(\rho)$.

and hence, introducting as usual μ as the Lagrange multiplier taking care of the normalisation condition,

$$\int \rho(z)\,\mathrm{d}z = N \tag{4.6}$$

through the minimum principle

$$\delta(E-\mu N)=0 \tag{4.7}$$

one finds

$$\mu = \delta T/\delta\rho(z) + V(z). \tag{4.8}$$

Calculating the functional derivative using equation (4.2) is easily shown to lead back to equation (4.1).

4.2. Generalisation to d dimensions (d = 1, 2, 3)

In d dimensions, the phase space relation $\rho(z)=2k_{\mathrm{F}}(z)/\pi$ is replaced by

$$\rho(z) = C_d p_{\mathrm{F}}^d(z) \tag{4.9}$$

with $C_d = 2\pi^{d/2}/[\Gamma(\frac{1}{2}d+1)h^d]$. This can clearly be combined with the chemical potential equation (4.1) to yield the Euler equation of the relativistic Thomas-Fermi theory in d dimensions (March 1985).

One can now attempt, therefore, to set up the analogue of equation (4.2), valid for $d=1$, and for $d=2$ and 3 as well.

When p_{F} is eliminated in equation (4.1) by use of equation (4.9) and when the resulting equation is identified with an Euler equation (4.8) it follows that

$$\frac{\delta T_d}{\delta\rho} = [c^2(\rho/C_d)^{2/d} + m^2c^4]^{1/2} - mc^2 \tag{4.10}$$

where T_d is the kinetic energy of the electron gas in d dimensions.

Since the right-hand side of equation (4.10) does not contain any derivatives of ρ it follows that

$$\delta T_d/\delta\rho = \mathrm{d}t_d/\mathrm{d}\rho \tag{4.11}$$

with t_d being the kinetic energy density in d dimensions.

From the last two equations it readily follows that

$$t_d(\rho) = \int_0^{\rho} \{[c^2(\tilde{\rho}/C_d)^{2/d} + m^2c^4]^{1/2} - mc^2\}\,\mathrm{d}\tilde{\rho}. \tag{4.12}$$

Changing to the integration variable $u=(\tilde{\rho}/C_d)^{1/d}$ yields

$$t_d(\rho) = dC_d \int_0^{p_{\mathrm{F}}(\rho)} [(c^2u^2+m^2c^4)^{1/2} - mc^2]u^{d-1}\,\mathrm{d}u \tag{4.13}$$

where $p_{\mathrm{F}}(\rho)$ is given by equation (4.9).

The integrals (4.13) may be solved exactly, the result being given again by equation (4.2) for $d=1$, and by

$$t_2(\rho) = a_2[(1+b_2\rho)^{3/2} - \tfrac{3}{2}b_2\rho - 1] \tag{4.14}$$

$$t_3(\rho) = a_3\{b_3\rho^{1/3}(\tfrac{1}{2}+b_3^2\rho^{2/3})(1+b_3^2\rho^{2/3})^{1/2} - \tfrac{4}{3}b_3^3\rho - \tfrac{1}{2}\ln[b_3\rho^{1/3} + (1+b_3^2\rho^{2/3})^{1/2}]\} \tag{4.15}$$

with constants

$$a_2 \equiv \frac{1}{3\pi}\left(\frac{mc}{\hbar}\right)^2 mc^2 \qquad b_2 \equiv 2\pi(\hbar/mc)^2 \tag{4.16}$$

and

$$a_3 \equiv \frac{1}{4\pi^2}\left(\frac{mc}{\hbar}\right)^3 mc^2 \qquad b_3 \equiv (3\pi^2)^{1/3}(\hbar/mc). \tag{4.17}$$

The non-relativistic limit of t_1 has already been quoted, equation (4.4). In the cases $d=2$ and $d=3, c\to\infty$ leads to the correct non-relativistic Thomas-Fermi expressions from equations (4.14) and (4.15):

$$t_2^{\mathrm{nr}}(\rho) = (\pi\hbar^2/2m)\rho^2 \tag{4.18}$$

and

$$t_3^{\mathrm{nr}}(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3}(\hbar^2/m)\rho^{5/3}. \tag{4.19}$$

Expressions (4.14) and (4.15) are valid for arbitrary homogeneous densities ρ. This is confirmed from Dirac's equation for $d=3$ in the following subsection.

4.3. The homogeneous electron and kinetic energy densities from Dirac's equation in three dimensions

This last subsection is to provide us from Dirac's equation with an independent derivation of results already obtained from the variation principle of § 4.2. It will be sufficient to consider, as a paradigm, the three-dimensional case.

Dirac's Hamiltonian for a free electron in three dimensions is given by

$$H^{(0)} = c(\boldsymbol{\alpha}\cdot\boldsymbol{p}) + \beta mc^2 = \begin{pmatrix} mc^2 & 0 & cp_z & c(p_x - \mathrm{i}p_y) \\ 0 & mc^2 & c(p_x + \mathrm{i}p_y) & -cp_z \\ cp_z & c(p_x - \mathrm{i}p_y) & -mc^2 & 0 \\ c(p_x + \mathrm{i}p_y) & -cp_z & 0 & -mc^2 \end{pmatrix} \tag{4.20}$$

($\boldsymbol{p} = -\mathrm{i}\hbar\nabla$). It is then readily verified that

$$\psi_{\boldsymbol{k}\uparrow}(\boldsymbol{x}) = D_{\boldsymbol{k}} \begin{pmatrix} \mathrm{e}^{\mathrm{i}\phi} q_+ \\ q_- \\ \mathrm{e}^{\mathrm{i}\phi} g q_+ \\ g q_- \end{pmatrix} \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \tag{4.21}$$

is an eigenspinor of $H^{(0)}$ having its spin parallel to $\boldsymbol{k}$. The energy ε and the function g satisfy equations (2.4) and (2.5), respectively, however, now with $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$. The expressions $q_\pm$ are defined by $q_\pm \equiv [\hbar(k \pm k_z)]^{1/2}$ and $\mathrm{e}^{\mathrm{i}\phi}$ is a phase factor equal to $(k_x - \mathrm{i}k_y)/(k_x^2 + k_y^2)^{1/2}$.

The normalisation constant $D_{\boldsymbol{k}}$ and the level density may be determined after periodic boundary conditions

$$\psi_{\boldsymbol{k}\uparrow}(\boldsymbol{x} + \boldsymbol{R}) \equiv \psi_{\boldsymbol{k}\uparrow}(\boldsymbol{x}) \tag{4.22}$$

have been imposed on ψ. The volume of periodicity is chosen to be a cube with side length l eventually tending to infinity, and $\boldsymbol{R} \equiv (m_x l, m_y l, m_z l)$ with m_x, m_y, m_z being

integers. As in non-relativistic theory, it follows from equations (4.21) and (4.22) that $\boldsymbol{k}$ has to be quantised, $k_j = 2\pi n_j/l$, $j = x, y, z$, with n_j being integers.

Normalisation of $\psi_{k\uparrow}$ over the volume l^3,

$$\int_0^l \int_0^l \int_0^l \psi_{k\uparrow}^+ \psi_{k\uparrow} \, dx \, dy \, dz = 1 \tag{4.23}$$

yields

$$D_k = D_k = \left(\frac{\varepsilon + mc^2}{4\hbar k \varepsilon l^3}\right)^{1/2}. \tag{4.24}$$

From the quantised values of k_j the density of states in $\boldsymbol{k}$ space is obviously given by $(l/2\pi)^3$ so that the number dn of states contained in a spherical shell of radius k and thickness dk is

$$dn = (l/2\pi)^3 4\pi k^2 \, dk. \tag{4.25}$$

Spinors $\psi_{k\downarrow}$ having the same energy differ from $\psi_{k\uparrow}$ by components $(-e^{i\phi}q_-, q_+, e^{i\phi}gq_-, -gq_+)$ yielding the same contribution to densities, namely

$$\psi_{k\uparrow}^+ \psi_{k\uparrow} = \psi_{k\downarrow}^+ \psi_{k\downarrow} = l^{-3} \tag{4.26}$$

so that, from (4.25) and (4.26), it follows that

$$\begin{aligned} \rho(k_F) &= \int_0^{k_F} \frac{dn}{dk} (\psi_{k\uparrow}^+ \psi_{k\uparrow} + \psi_{k\downarrow}^+ \psi_{k\downarrow}) \, dk \\ &= k_F^3/3\pi^2 \end{aligned} \tag{4.27}$$

and

$$\begin{aligned} t(k_F) &= \int_0^{k_F} \frac{dn}{dk} [\varepsilon(k) - mc^2](\psi_{k\uparrow}^+ \psi_{k\uparrow} + \psi_{k\downarrow}^+ \psi_{k\downarrow}) \, dk \\ &= \frac{1}{4\pi^2} mc^2 \left(\frac{mc}{\hbar}\right)^3 \{\tau_F(\tfrac{1}{2} + \tau_F^2)(1 + \tau_F^2)^{1/2} - \tfrac{1}{2} \ln[\tau_F + (1 + \tau_F^2)^{1/2}]\} - mc^2 \rho \end{aligned} \tag{4.28}$$

which leads us back to equation (4.15) when $\tau_F = \hbar k_F/mc$ is eliminated by use of equation (4.27).

5. Summary and conclusion

The main results of the present study of the 'particle in a box' model are as follows.

(i) The electron density $\rho(z)$ as given by equation (2.24). This can be evaluated by a power series expansion as in equation (2.26) and (*a*) the non-relativistic limit $c \to \infty$ taken and (*b*) subsequently the infinite barrier limit $V_0 \to \infty$. The usual 'box' density

$$\rho(z) = \rho_0 \left(1 - \frac{\sin(2k_F z)}{2k_F z}\right)$$

is then regained.

(ii) The long-range Friedel oscillations induced by a localised 'perturbation' in an initially homogeneous relativistic electron gas have wavelength π/k_F as in the non-relativistic limit.

(iii) The kinetic energy density $t(z)$ has the exact form (3.5), (3.6) and (3.7), which expands again to yield the known non-relativistic result in the subsequent passage to the infinite barrier limit.

From the homogeneous electron-gas results implicit in equations (2.24) and (3.6) for $\rho(z)$ and $t(z)$, respectively, the variational principle (4.7) with total energy E given in terms of $\rho(z)$ by equations (4.5) and (4.2) follows.

Moreover, combining relation (4.9) between ρ and the Fermi momentum p_F in d dimensions (March 1985) with the chemical potential, equation (4.1), one obtains an equation which, when identified with an Euler equation, allows for determination of t_d for the homogeneous gas (see equations (4.13)-(4.15)) merely by an integration. On the other hand, these expressions for t_d may also be easily derived from the free-particle Dirac equation as is shown in § 4.3 for $d = 3$.

Needless to say, while the functional relationship between the kinetic energy density t and the electron density ρ can be derived as in equations (4.2), (4.14) and (4.15) for the homogeneous relativistic electron gas, no such derivation is, of course, possible from the simple model of an inhomogeneous electron gas presented here. Nevertheless, this model problem does serve to clarify some points as to (i) the derivation of kinetic energy density of an inhomogeneous electron gas and (ii) it appears possible with this model to make useful progress on the extension to $d = 2$ and 3 dimensions which has already been worked out in the infinite barrier limit of the semi-infinite inhomogeneous electron gas in non-relativistic theory (March 1987).

Acknowledgment

One of us (RB) is indebted to the 'Fonds der Chemischen Industrie' for financial support.

References

Banzai A S and Deb B M 1981 *Rev. Mod. Phys.* **53** 95
Bjorken J D and Drell S D 1964 *Relativistic Quantum Mechanics* (New York: McGraw-Hill)
Callaway J and March N H 1984 *Solid State Physics* vol 38, ed H Ehrenreich and D Turnbull (New York: Academic) p 315
Dreizler R M and da Providencia J 1985 *Density Functional Methods in Physics* (New York: Plenum)
Fermi E 1928 *Z. Phys.* **48** 73
Hill S H, Grout P J and March N H 1987 *J. Phys. B: At. Mol. Phys.* **20** 11
Lundqvist S and March N H (ed) 1983 *Theory of the Inhomogeneous Electron Gas* (New York: Plenum)
March N H 1985 *Int. J. Quantum Chem.* **27** 595
—— 1987 *J. Math. Phys.* submitted
Rose M E 1961 *Relativistic Electron Theory* (New York: Wiley)
Thomas L H 1926 *Proc. Camb. Phil. Soc.* **23** 542
Vallarta M S and Rosen N 1932 *Phys. Rev.* **41** 708