Relativistic virial relations for both homogeneous and spatially varying electron liquids

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RELATIVISTIC VIRIAL RELATIONS FOR BOTH HOMOGENEOUS AND SPATIALLY VARYING ELECTRON LIQUIDS

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Relativistic virial relations are first discussed for a homogeneous electron liquid. The chemical potential is involved in such virial relations, and the approximate effects of electron correlation are studied, using the Quantum Monte Carlo (QMC) data of Kenny *et al.* (S.D. Kenny, G. Rajagopal, R.J. Needs, W.-K. Leung, M.J. Godfrey, A.J. Williamson and W.M.C. Foulkes (1996). *Phys. Rev. Lett.*, **77**, 1099).

Attention is then shifted to inhomogeneous electron liquids. Based on Dirac's relativistic wave equation, an approximate propagator solution using a WKB-like treatment of this equation by Linderberg for central fields is a focal point. This approach, it is demonstrated here, leads back to the exact single-particle kinetic energy of the uniform electron gas and hence to the virial relations referred to above when the central field is switched off. Virial relations are then referred to for the finite central field case. Finally, a local density approximation applied to heavy atoms in intense magnetic fields is briefly treated, and another approximate virial relation is exhibited.

Keywords: Relativistic virial theorem; Electron liquid; Magnetic field

1. BACKGROUND AND OUTLINE

About a decade ago, the relativistic virial was examined by one of us [1] within the context of a local density approximation (LDA) for atoms with and without applied magnetic fields. Here results are presented which, while they relax the constraint of LDA until the penultimate section, are still semiclassical in that they invoke WKB-like approximations to the energy-level spectrum resulting from Dirac's relativistic one-electron equation. Such an approximate treatment has been proposed recently by Linderberg [2]: here its relation to the earlier nonrelativistic study of March and Plaskett [3] on heavy atoms is established. This is then followed by a treatment of atoms in intense magnetic fields, using the theory presented by Hill, Grout and March [4], which again is of semiclassical nature, though now additional approximations are involved beyond invoking WKB-like eigenvalue evaluation. The outline of

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the article is then as follows. In Section 2 immediately below the focal point is the relativistic homogeneous electron liquid. The high-density correlation energy of Needs *et al.* [5] is utilized and from this some approximate consequences of the virial follow, and in particular the correlation kinetic energy is extracted.

The remainder of this investigation is concerned with inhomogeneous electronic assemblies with and without applied magnetic fields. Thus in Section 3 (plus Appendix A) an analysis of a WKB-like treatment, of essentially the propagator resulting from Dirac's theory, is made, the nonrelativistic limit being here shown to lead to an earlier result of March and Plaskett [3]. In the homogeneous limit, the result of Linderberg for the kinetic energy density is shown to reduce to the result earlier obtained by Baltin and March [6]. Section 3.2 constitutes a brief derivation of the virial in terms of the kinetic energy density. In Section 4 attention is then shifted to the case of atomic ions placed in an intense applied magnetic field, such as that that exists at the surface of neutron stars ($\sim 10^{13}$ Gauss). Because of the additional complexity due to the intense applied field we return to LDA and use the (semiclassical) relativistic study of Hill, Grout and March [4] to establish a virial relation. Section 5 constitutes a summary plus some proposals for future investigation in the general area of this article.

2. HOMOGENEOUS RELATIVISTIC ELECTRON LIQUID

The Euler equation of density functional theory reflects the constancy of the chemical potential μ at every point **r** in an inhomogeneous electron assembly. It reads [7]

$$\mu = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + V(\mathbf{r}) \tag{1}$$

where $T_s[\rho]$ is the (as yet unknown) single-particle kinetic energy functional of the ground-state density $\rho(\mathbf{r})$. In Eq. (1), the final term represents the effective one-body potential which is central to current approximations of density functional theory. In turn $V(\mathbf{r})$ is the sum of three terms:

$$V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{es}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}), \tag{2}$$

respectively the external potential, the electrostatic potential created by the density $\rho(\mathbf{r})$, and the exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ given by

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \tag{3}$$

Again, as with $T_s[\rho]$ in Eq. (1), the exchange-correlation energy functional $E_{\text{xc}}[\rho]$ is not known.

Our concern in the present study is with the relativistic counterparts of the above theory. By inclusion of the fine structure constant $\alpha = e^2/\hbar c = 1/137$, the detail in the theory proliferates and it is natural enough therefore to deal first with the relativistic homogeneous electron gas.

2.1   Single-particle Kinetic Energy of a Relativistic Homogeneous Electron Assembly

Unlike the inhomogeneous electron liquid, the noninteracting single-particle kinetic energy density, say $t_\alpha(\rho)$, where ρ is the (now constant) electron density, is known [6], namely:

$$t_\alpha(\rho) = a\left\{\beta\left(\frac{1}{2} + \beta^2\right)\left(1 + \beta^2\right)^{1/2} - \frac{4}{3}\beta^3 - \frac{1}{2}\ln\left(\beta + (1 + \beta^2)^{1/2}\right)\right\} \tag{4}$$

in terms of the basic dimensionless variable $\beta = b\rho^{1/3}$, the constants a and b being given by

$$a = \left(\frac{1}{4\pi^2}\right)\left(\frac{m_0 c}{\hbar}\right)^3 m_0 c^2 \qquad b = (3\pi^2)^{1/3}\left(\frac{\hbar}{m_0 c}\right) \tag{5}$$

Fortunately, as will be shown below, from the form (1), the average of the virial $\langle \mathbf{r}.\mathbf{F}\rangle$ (which simply weights the virial with $\rho(\mathbf{r})$) involves only $\partial t_\alpha(\rho)/\partial\rho$, which has the much simpler form

$$\frac{\partial t_\alpha}{\partial\rho} = \sqrt{c^2 p_f^2 + m_0^2 c^4} - m_0 c^2 \tag{6}$$

where the Fermi momentum p_f is related to the uniform electron density ρ by the usual phase space result [3]

$$\rho = \frac{8\pi}{3h^3}p_f^3 \tag{7}$$

The rest mass energy has been subtracted in Eq. (6) so as to recover the correct nonrelativistic limit, as $c \to \infty$.

2.2   Exchange-correlation energy of a Relativistic Homogeneous Electron Liquid

Using QMC calculations, Kenny *et al.* [5] put forward the following result for the relativistic exchange-correlation energy per electron, say $\epsilon_{xc}^{rel}(r_s)$, (in a.u.)

$$\epsilon_{xc}^{rel}(r_s) = \epsilon_{xc}^{nonrel}(r_s) + \epsilon_x^{HF}(r_s)f(r_s) \tag{8}$$

with the variable r_s defined as usual by

$$\rho = \frac{1}{(4/3)\pi r_s^3} \tag{9}$$

and where $\epsilon_x^{HF}(r_s)$ denotes the relativistic correction to the exchange energy from Hartree–Fock theory which they show to be equal to

$$\epsilon_x^{HF}(r_s) = \frac{9}{8c^2 r_s^3} \tag{10}$$

The function $f(r_s)$ was obtained by Kenny *et al.* [5] by a fit to their discrete data points and is given by

$$f(r_s) = \sum_{n=0}^{4} c_n r_s^n \quad 0.1 \leq r_s \leq 5 \tag{11}$$

$$= a + br_s \quad 5 < r_s \leq 10 \tag{12}$$

The constants in Eqs. (11) and (12) are $c_0 = 0.99818$, $c_1 = -0.29020$, $c_2 = 0.14474$, $c_3 = -0.02573$, $c_4 = 0.001634$, $a = 0.75$, and $b = 0.044$. In the very high-density regime, where $r_s < 0.1$, correlation can be neglected and the relativistic exchange-correlation energy is assumed to be well approximated by the local density approximation to the relativistic exchange-only energy which was first obtained by Akhiezer and Peletminskii [8] (see also [9] and references therein) and is given by

$$\varepsilon_{x\alpha} = \varepsilon_{x0} F(\beta) = -\left(\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\right)\rho^{1/3}\left[1 - \frac{3\{\beta(1+\beta^2)^{1/2} - \ln[\beta + (1+\beta^2)^{1/2}]\}^2}{2\beta^4}\right] \tag{13}$$

with the variable β defined above.

From these results we evaluated the change in the chemical potential, say $\Delta\mu$, due to the relativistic correction to the exchange-correlation energy, i.e. $\partial(\Delta\varepsilon_{xc})/\partial\rho$ where $\Delta\varepsilon_{xc}$ now denotes the change in the exchange-correlation energy density, i.e. $\Delta\varepsilon_{xc} = \rho\Delta\epsilon_{x\alpha} = \rho(\epsilon_{xc}^{rel} - \epsilon_{xc}^{nonrel})$. In Fig. 1 we plot $\partial(\Delta\varepsilon_{xc})/\partial\rho$ *versus* r_s.
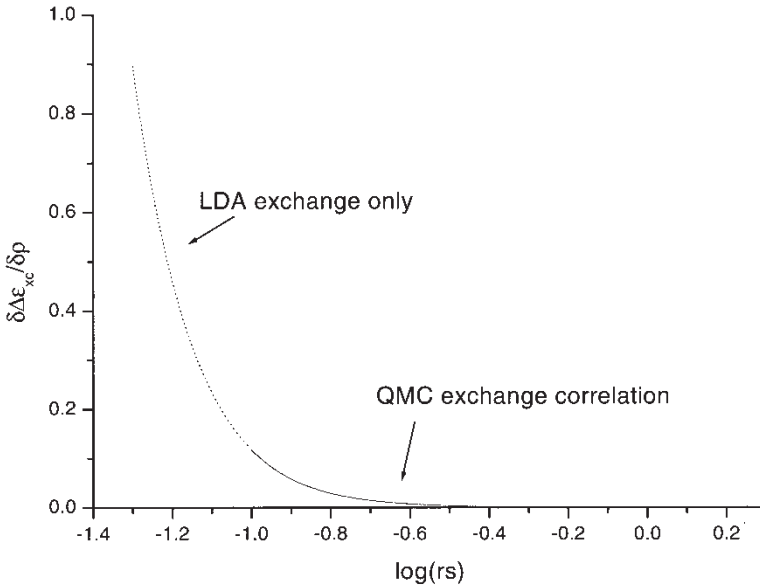
FIGURE 1   Relates to the change in chemical potential, Δ_μ say, due to relativistic correction to the exchange-correlation energy in homogeneous electron liquid. Quantity actually plotted as a function of mean interelectronic spacing r_s is $\partial(\Delta\epsilon_{xc})/\partial\rho$ where $\Delta\epsilon_{xc}$ denotes the change in the exchange-correlation energy density $\Delta\epsilon_{xc} = \rho(\epsilon_{xc}^{rel} - \epsilon_{xc}^{nonrel})$.

3. INHOMOGENEOUS ELECTRON LIQUIDS

3.1 Linderberg's Approximate Solution of the Radial Dirac Equation for a General Central Potential $V(r)$

We turn next, from the homogeneous (thermodynamic limit) assembly above to Linderberg's use of propagator theory for finite central field systems and in particular heavy atoms [2]. Here, this theory yields the electron density in terms of an integral over the residues of the Green function at the poles corresponding to the occupied levels. As Linderberg then shows for a central potential $V(r)$, states with quantum number k are degenerate and the total density resulting from these states is found to be

$$\rho_k(r) = \frac{2|k|}{\pi} \left\{ \left[c - \frac{V(r)}{e^2 c} \right]^2 - c^2 - \left[\frac{k + (1/2)}{r} \right]^2 \right\}^{1/2} \tag{14}$$

This is to be compared with the nonrelativistic result of March and Plaskett [3], who write using semiclassical WKB-like notation (their Eq. (12))

$$p_l(E, r) = \left\{ 2m_0 \left[E - V(r) - \frac{(l + (1/2))^2}{r^2} \frac{\hbar^2}{2m_0} \right] \right\}^{1/2} \tag{15}$$

where p_l is an 'effective momentum' for orbital angular momentum quantum number l. If we introduce atomic units ($m_0 = \hbar = 1$) into the result of March and Plaskett plus the limit (say of the Thomas–Fermi neutral atom) $E \to 0$, it is straightforward to show that the Linderberg result (14) reduces to that of March and Plaskett (15) in the nonrelativisitc limit.

The total density $\rho(r)$ can be obtained by summing over all k-values and evaluating this sum approximately by replacing it with an integration. Linderberg thereby obtained the electron density $\rho(r)$ and to establish a parallel with Eq. (1), one must now find an expression for the kinetic energy density $t_\alpha(r)$ associated with his density $\rho(r)$. In fact, the above parallel is best made after summing over k and then replacing the resultant sum by an (of course approximate) integration. Linderberg then obtains the kinetic energy, including the energy $m_0 c^2$ associated with the rest mass of the electron as

$$t_\alpha(r) = \frac{cr^2}{2\pi} \left[c^2 + \frac{Z^2(0)}{c^2 r^2} \right]^2 \left\{ \frac{\xi(r) + \xi^3(r)}{[1 - \xi(r)^2]^2} - \frac{1}{2} \ln \left(\frac{1 + \xi(r)}{1 - \xi(r)} \right) \right\} \tag{16}$$

As he points out, the quantity $\xi(r)$ in terms of the density $\rho(r)$ is given by

$$\xi(r) = \left\{ \frac{3\pi\rho(r)}{4c^3 r^2} \right\}^{1/3} \bigg/ \left\{ 1 + \frac{Z^2(0)}{c^4 r^2} + \left(\frac{3\pi\rho(r)}{4c^3 r^2} \right)^{2/3} \right\}^{1/2} \tag{17}$$

Here $Z(0)$ reflects the self-consistent potential $V(r)$ in Linderberg's treatment through the equation

$$V(r) = -\frac{Z(r)e^2}{r} \tag{18}$$

where evidently $Z(r)|_{r=0} = Z(0)$.

In Appendix A we show that in the limit of zero external field, the Linderberg expression for $t_\alpha(r)$ in Eq. (16) reduces to the result (4) obtained by Baltin and March [6]. These authors had essentially derived the result (4) for one-dimensional systems only, but reasoned that its validity extended to three-dimensional systems as is confirmed here.

Thus, Linderberg's result has the correct limit given earlier by Baltin and March when the potential driving the inhomogeneity in the density in this approximate propagator theory is switched off. This has encouraged us to briefly summarize how the results from Linderberg's propagator approximation can be used to calculate the virial $\langle \mathbf{r} \cdot \mathbf{F} \rangle$ of the central field problem under consideration.

3.2 Virial Theorem for Finite Central Field Problems from Linderberg's Approximation

The chemical potential in Eq. (1), posed relativistically, now satisfies

$$\mu_\alpha = \frac{\partial t_\alpha}{\partial \rho} + V(r) \tag{19}$$

and we find, by differentiating with respect to r and utilizing the constancy of μ_α, the result that the force $F = -\partial V/\partial r$ is given by

$$-\frac{\partial V}{\partial r} = F(r) = \frac{\partial}{\partial r}\left[\frac{\partial t_\alpha}{\partial \rho(r)}\right] \tag{20}$$

and evidently therefore the average virial $\langle \mathbf{r} \cdot \mathbf{F} \rangle$ is given by

$$\langle \mathbf{r} \cdot \mathbf{F} \rangle = -\int \rho(r) r \frac{\partial V}{\partial r}\, d\mathbf{r} \tag{21}$$

$$= -\int \rho(r) r \frac{\partial}{\partial r}\left[\frac{\partial t_\alpha(r)}{\partial \rho}\right] d\mathbf{r} \tag{22}$$

So in essence, the work of Linderberg provides all the necessary physical quantities to evaluate the virial $\langle \mathbf{r} \cdot \mathbf{F} \rangle$ for an inhomogeneous relativistic central field problem.

While this is a formally correct deduction, we emphasize that whereas the key ingredient to calculate the virial, namely $t_\alpha(r)$, is exact when the external potential is 'switched off', as demonstrated in Appendix A, Eq. (16) for the finite atomic systems now under discussion involves WKB-like approximation plus the modification of Linderberg attributes to Kramers and for which he also refers Kemble's book. We also caution now, in contrast to the exact homogeneous limit in Appendix A, that the self-consistent 'atom' in this approach, as Linderberg also correctly stresses, has

a finite radius for the electron density distribution. As the detail then proliferates, we shall not pursue this matter further.

4. RELATIVISTIC LOCAL DENSITY APPROXIMATION FOR HEAVY ATOMS IN INTENSE MAGNETIC FIELDS

From the relativistic theory of Hill, Grout and March [4], the Euler equation for their local density method reads, in an applied magnetic field of strength B,

$$\mu_{\alpha B} = \left[\frac{c^2 h^4 \rho^2}{4e^2 B^2} + m_0^2 c^4 \right]^{1/2} - m_0 c^2 + V(r) \tag{23}$$

and hence

$$\frac{dt_{\alpha B}}{d\rho} = \left[\frac{c^2 h^4 \rho^2}{4e^2 B^2} + m_0^2 c^4 \right]^{1/2} - m_0 c^2 \tag{24}$$

We now note from Eq. (19) of [1] that one possible definition of the kinetic energy density $t(r)$ is given by

$$t(r) = \rho \frac{\partial t}{\partial \rho} + \frac{1}{3} \rho r \frac{d}{dr} \left(\frac{dt}{d\rho} \right) \tag{25}$$

which obviously lacks uniqueness since any function of r can be added to $t(r)$ which integrates to zero through the whole of space.

But now from the Euler equation (23), it follows since the chemical potential μ is the same at every point in the electron gas that

$$0 = \frac{d}{dr} \frac{dt_{\alpha B}}{d\rho} + \frac{dV}{dr} \tag{26}$$

and therefore, by substitution in Eq. (25)

$$t_{\alpha B}(r) = \rho \frac{\partial t_{\alpha B}}{\partial \rho} - \frac{1}{3} \rho r \frac{\partial V}{\partial r} \tag{27}$$

Thus the average of the virial $\langle \mathbf{r} \cdot \mathbf{F} \rangle$ follows from Eq. (27) as

$$\frac{1}{3} \langle \mathbf{r} \cdot \mathbf{F} \rangle = T_{\alpha B} - \int \rho \frac{\partial t_{\alpha B}}{\partial \rho} \, d\mathbf{r}, \tag{28}$$

where $T_{\alpha B} = \int t_{\alpha b}[r] \, d\mathbf{r}$. Therefore, in the high B theory of Hill, Grout and March [4] the explicit virial relation is given by Eq. (28), with $\partial t_{\alpha B}/\partial \rho$ from Eq. (26).

5. SUMMARY AND FUTURE DIRECTIONS

The main achievements of the present study of relativistic virial relations are for the change in the chemical potential of a homogeneous electron liquid due to the relativistic correction to the exchange-correlation energy, the latter being displayed in Fig. 1 using the QMC data of Kenny *et al.* [5]. Turning to spatially varying densities, the main results reported stem from the approximate propagator solution kindly made available to us by Linderberg [2]. His approach, as demonstrated in Section 3.1 and Appendix A, leads back to the results (4) and (6) given by Baltin and March [6] when the central potential $V(r)$ is 'switched off'. Then in Section 4, heavy atoms in intense magnetic fields such as exist at the surface of neutron stars, but now treated in LDA, are considered, the (now approximate) relativistic virial relation in Eq. (28) then resulting.

It would be of obvious interest for the future if formally exact treatments of the relativistic virial theorem, such as presented for instance in the work of Goldman and Drake [10], who were concerned with a Dirac electron in an arbitrary local potential, could be employed to make contact with the approximate theory of the virial in the case of inhomogeneous electron liquids as discussed especially in Sections 3.2 and 4 above.

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APPENDIX A: HOMOGENEOUS RELATIVISTIC ELECTRON LIQUID LIMIT FROM LINDERBERG'S APPROXIMATE PROPAGATOR THEORY

When we 'switch off' the potential in Linderberg's approximate theory based on the Dirac relativistic wave equation, we find

$$\xi = \frac{b\rho^{1/3}}{(1 + b^2\rho^{2/3})^{1/2}} \tag{A.1}$$

where in Linderberg's units (compare Eq. (5))

$$b = (3\pi^2)^{1/3}/c \tag{A.2}$$

Similarly the kinetic energy density t_α is in this uniform limit given by

$$t_\alpha = \frac{c^5}{8\pi^2}\left[\frac{\xi + \xi^3}{[1 - \xi^2]^2} - \frac{1}{2}\ln\left(\frac{1 + \xi}{1 - \xi}\right)\right] \tag{A.3}$$

Inserting Eq. (A.1) into Eq. (A.3) we obtain after some algebra

$$t_\alpha = \frac{c^5}{4\pi^2}\left\{\beta\left(\frac{1}{2} + \beta^2\right)(1 + \beta^2)^{1/2} - \frac{1}{2}\ln\left(\beta + (1 + \beta^2)^{1/2}\right)\right\} \tag{A.4}$$

The extra term proportional to β^3 appearing in the Baltin–March expression (4) is just the rest mass energy density $m_0 c^2 \rho$ which was explicitly subtracted in their derivation, but is still present in the Linderberg work. Both expressions are thus found to be identical.