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THOMAS-FERMI THEORY OF AN INHOMOGENEOUS ELECTRON LIQUID GENERALIZED TO INCORPORATE DENSITY GRADIENTS

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Motivated by exact results for many closed shells in a bare Coulomb field, a generalization of the Thomas-Fermi statistical model is proposed. This generalization includes density gradients in the density-potential relation, and offers the possibility of avoiding the singularity (of the original method) in the density at an atomic nucleus and of embodying Kato's theorem.

Keywords: Electron liquid; Thomas-Fermi theory; density gradient

1. BACKGROUND

The original Thomas-Fermi (TF) statistical theory [1], the forerunner of modern density functional theory (DFT) [2], is based on a density-potential relation of the form

$$\rho(\vec{r}) = \text{constant} (\mu - V(\vec{r}))^{3/2} \quad (1)$$

with $\rho(\vec{r})$ the ground-state electron density in the inhomogeneous electron liquid generated by the one-body potential energy $V(\vec{r})$. The quantity μ appearing in eqn(1) is the chemical potential of the

inhomogeneous electron cloud. It is constant throughout the entire electron distribution, and in DFT is written formally as the sum of kinetic and potential contributions, each of which depends on the spatial position \vec{r} in the electronic charge cloud. If T_s denotes the single-particle kinetic energy[2], the Euler equation of DFT is customarily written

$$\mu = \frac{\delta T_s}{\delta \rho(\vec{r})} + V(\vec{r}). \quad (2)$$

In a complete theory of atoms and molecules, $V(\vec{r})$ is the sum of a Hartree potential energy $V_H(\vec{r})$ generated by the nuclei together with the electronic charge density $\rho(\vec{r})$ from classical electrostatics, and an exchange plus correlation potential $V_{xc}(\vec{r})$. In the same spirit as the formal kinetic energy functional derivative $\delta T_s/\delta \rho(\vec{r})$ already displayed in eqn(2) $V_{xc}(\vec{r})$ is often written

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}}{\delta \rho(\vec{r})}. \quad (3)$$

As yet, neither $T_s[\rho]$ nor the exchange-correlation energy functional $E_{xc}[\rho]$ is known. However, given an approximate form of $V_{xc}(\vec{r})$ (eg. the so-called local density approximation), $\delta T_s/\delta \rho(\vec{r})$ can be bypassed by solving one-electron Schrödinger equations, the so-called Slater-Kohn-Sham (SKS) equations [3,4], with the approximate potential energy $V(\vec{r}) = V_H(\vec{r}) + V_{xc}(\vec{r})$.

Recently, Holas and March[5] have presented an exact expression for $V_{xc}(\vec{r})$ in terms of low-order density matrices (DMS), both the fully interacting one and two DMS and the analogues (non-interacting) calculated from SKS wave functions being involved. In lowest order, in which the interacting DMS are replaced by their non-interacting analogues, an approximation to the exchange potential energy was obtained which was identical with the result of the work formalism of Harbola and Sahní[6]. Their result was in the form of a (path-dependent) line integral. The full theory [5] of $V_{xc}(\vec{r})$ has been used subsequently by Levy and March[7] to exhibit the 'kinetic correction' to the Harbola-Sahní exchange-only result which restores path independence. Comparing the above approach with the formal

result (3), we conclude that the functional differentiation has in some sense been replaced by a line integral.

The above considerations have prompted us to return to the functional derivative of the single-particle kinetic energy T_s in eqn(2). Then, for large numbers of electrons in atoms and molecules, on which regime all attention focussed below, it is natural to take the original TF theory as starting point. Furthermore, though the theory given below is approximate, we shall invoke some exact relations for closed shells in a bare Coulomb field. Thus, we turn immediately to summarize exact results for this model problem.

2. KINETIC ENERGY FOR CLOSED SHELLS IN BARE COULOMB FIELD

In a recent study, Amovilli and March [8] have studied the kinetic energy density $t_{\mathcal{N}}(r)$ for \mathcal{N} closed shells in hydrogen-like atom in terms of the ground-state density $\rho_{\mathcal{N}}(r)$ and its derivatives, and the Coulomb potential energy $-Z/r$. Their result takes the form

$$\frac{\partial t_{\mathcal{N}}}{\partial r} = \frac{1}{8} \rho_{\mathcal{N}}''' - \frac{3}{4r^2} \rho_{\mathcal{N}}' - \frac{3Z}{2r^2} \rho_{\mathcal{N}}, \quad (4)$$

which can be viewed as a differential form of the virial theorem [8].

We note first of all that if we neglect gradients of $\rho_{\mathcal{N}}$ relative to the $Z\rho_{\mathcal{N}}$ term in eqn(4), then we recover a relation valid in the original form of density functional theory (DFT): namely the TF statistical method [1].

In this method one has

$$t_{TF} = c_k \rho^{5/3} \quad : \quad c_k = \frac{3h^2}{10m} \left(\frac{3}{8\pi} \right)^{2/3} \quad (5)$$

and hence

$$\frac{\partial t_{TF}}{\partial r} = \frac{5}{3} c_k \rho^{2/3} \frac{\partial \rho}{\partial r}. \quad (6)$$

Using the TF density-potential relation(1), eqn(6) is contained in eqn (4) when $\rho_{\mathcal{N}}'''$ and $\rho_{\mathcal{N}}'$ are neglected.

We note further that eqn(6) can be written in a form motivated by density functional theory, as discussed, for example, in the book of Parr and Yang [2],

$$\frac{\partial t_{TF}}{\partial r} = \frac{\partial T_{TF}}{\delta \rho} \frac{\partial \rho}{\partial r}, \quad (7)$$

where the total kinetic energy $T_{TF} = \int t_{TF} d\vec{r} = c_k \int \rho^{5/3} d\vec{r}$.

Below, we shall continue to insist on the applicability of eqn(7), even though we shall retain the gradient terms in eqn(4). Invoking the general form (2), the Euler equation in DFT, we can combine eqns(2), (4) and (7) to reach the result for a bare Coulomb field:

$$\left(\mu + \frac{Z}{r} \right) \rho' = \frac{1}{8} \rho''' - \frac{3}{4r^2} \rho' - \frac{3Z}{2r^2} \rho. \quad (8)$$

We must stress that although we have retained the exact form of eqn(4) in arriving at eqn(8), the 'statistically motivated' form (7) has also been retained, which must be expected to involve approximations, even in the limit of large numbers of electrons (compare regime of Bohr's correspondence Principle). Therefore, let us study at this stage the forms of solution of eqn(8) at small and large distances from the nucleus.

2.1. Large r Solution of eqn(8) for $Z=1$ and $\mu=0$

One useful check of the accuracy of eqn(8) is to bring it into contact with the work of Heilmann and Lieb(HL)[9] (see also Appendix 1 below). These authors calculated $\rho_{\mathcal{N}}(r)$ in eqn(4) in the limit in which the number of closed shells tends to infinity and the chemical potential μ tends to zero. For $Z=1$, their result at large r takes the form

$$\rho_{\infty}(r) = \frac{A}{r^{3/2}}, \quad r \rightarrow \infty: A = \frac{\sqrt{2}}{3\pi^2}. \quad (9)$$

Since $\mu=0$, the LHS of eqn(8) is proportional to $r^{-7/2}$ at large r . On the RHS, the first two terms are readily shown from eqn(9) to be of $O(r^{-9/2})$ at large r . The final term is equal to the LHS, without, however, the need to fix A , the value of which is known from the study of HL and is also recorded in eqn(9).

2.2. Small r Solution: Kato's Theorem and Beyond

One of the major problems associated with the TF density-potential relation (1) is that near an atomic nucleus the density $\rho_{\mathcal{N}}(r)$ diverges. This is, of course, because of the 'local' character of eqn(1), the potential at $r=0$ determining the density there.

We have therefore investigated the solution of eqn(8), still for $\mu=0$ but now for general Z , by Taylor expansion of $\rho_{\mathcal{N}}(r)$ around $r=0$. The following solution is readily generated:

$$\rho_{\mathcal{N}}(r) = \rho(0) \left[1 - 2Zr + \frac{10}{3}(Zr)^2 - \frac{28}{3}(Zr)^3 + O(r^4) \right]. \quad (10)$$

The term in r is easily interpreted: it reflects Kato's theorem [10], or equivalently the electron-nuclear cusp condition:

$$\rho'(r)|_{r=0} = -2Z\rho(0). \quad (11)$$

While it is satisfactory that eqn(8) embodies this result for the bare Coulomb potential energy $-Z/r$, it will presumably need numerical solution of eqn(8) to investigate whether the Taylor expansion (10) valid at small r can be precisely matched to the HL large r asymptotic form (9) corresponding to $Z=1$ and $\mu=0$.

The interpolation approximation $\rho(r) = \rho(0)[1 + (4Z/3)r]^{3/2}$ reproduces the first three terms of the small r series (10), and for $Z=1$ relates $\rho(0)$ to A in eqn(9).

However, the fact that there are physically acceptable solutions of eqn(8) at small and at large r for the bare Coulomb field has encouraged us to generalize this equation to apply when the bare Coulomb potential is replaced by the appropriate Hartree self-consistent field form.

3. GENERALIZATION OF SELF-CONSISTENT TF ATOM

We turn from the bare Coulomb field model of section 2 to the analogous treatment which generalizes the self-consistent TF atom.

Let us put $-\mathcal{V} = \mu + Z/r$ in eqn(8) which becomes

$$\frac{3}{2}\mathcal{V}'\rho - \mathcal{V}\rho' = \frac{1}{8}\rho''' - \frac{3}{4r^2}\rho'. \quad (12)$$

If we neglect the RHS, one can integrate eqn(12) to regain the TF density-potential (1), which can be applied both to the bare Coulomb field model and to the self-consistent TF atom.

Returning to eqn(12) as it stands, one can rewrite it as a first-order linear differential equation for $\mathcal{V}(r)$:

$$\mathcal{V}' - \frac{2}{3}\mathcal{V}\frac{\partial \ln \rho}{\partial r} = \frac{1}{12}\frac{\rho'''}{\rho} - \frac{1}{2r^2}\frac{\rho'}{\rho}. \quad (13)$$

Using the integrating factor $\rho^{-2/3}$, one readily obtains

$$\frac{\partial}{\partial r}[\rho^{-2/3}\mathcal{V}] = \rho^{-2/3}\left[\frac{1}{12}\frac{\rho'''}{\rho} - \frac{1}{2r^2}\frac{\rho'}{\rho}\right]. \quad (14)$$

Integrating eqn(14) yields the desired result

$$\mathcal{V}(r) = \rho^{2/3} \int^r \left[\rho^{-2/3} \left\{ \frac{1}{12} \frac{\rho'''}{\rho} - \frac{1}{2s^2} \frac{\rho'}{\rho} \right\} \right] ds. \quad (15)$$

Hence, from the Euler eqn(2), one has for the functional derivative of the single-particle kinetic energy

$$\frac{\delta T_s}{\delta \rho(\vec{r})} = -\rho^{2/3} \int^r \left[\rho^{-2/3} \left\{ \frac{1}{12} \frac{\rho'''}{\rho} - \frac{1}{2s^2} \frac{\rho'}{\rho} \right\} \right] ds. \quad (16)$$

As with $V_{xc} = \delta E_{xc}/\delta \rho(\vec{r})$ discussed earlier, it may be noted that a line integral is again involved in eqn(16), when correcting the TF method for atoms.

Next we impose Hartree self-consistency on the above atomic theory, via Poisson's equation

$$\nabla^2 \mathcal{V} = -4\pi\rho(r), \quad (17)$$

or in spherical symmetry

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial \mathcal{V}}{\partial r} \right] = -4\pi\rho(r). \quad (18)$$

Simultaneous solution of eqns(13) and (18) should yield a self-consistent potential energy \mathcal{V} and corresponding ground-state density ρ transcending the original self-consistent TF atom. The boundary conditions evidently include \mathcal{V} and ρ both tending to zero at infinity, $\mathcal{V} \rightarrow -Z/r$ as $r \rightarrow 0$, and if possible the Kato result (11) at $r=0$ on the density ρ .

3.1. Self-consistency Imposed on $\delta T_s / \delta \rho(\vec{r})$

Returning to the general Euler eqn.(2) of DFT, we note that for Hartree self-consistency embodied in the Poisson equation (17)

$$\nabla^2 \frac{\delta T_s}{\delta \rho(\vec{r})} = 4\pi\rho(r). \quad (19)$$

While eqn(19) is formally exact if we neglect the exchange-correlation potential, which is asymptotically correct in sufficiently heavy atoms treated by non-relativistic Schrödinger theory, we shall below combine this equation with the approximate functional derivative of the single-particle kinetic energy T_s given in eqn(16). This is the approximation at the heart of the present study. Forming from eqn(16) the derivatives $\partial/\partial r[\delta T_s/\delta \rho(\vec{r})]$ and $\partial^2/\partial r^2[\delta T_s/\delta \rho(\vec{r})]$ required in eqn(19), one finds after some calculation

$$\begin{aligned} \frac{2}{3} \frac{\delta T_s}{\delta \rho(\vec{r})} \left[\frac{\rho''}{\rho} - \frac{1}{3} \left(\frac{\rho'}{\rho} \right)^2 + \frac{2\rho'}{r\rho} \right] &= 4\pi\rho + \frac{\rho^{IV}}{12\rho} - \frac{\rho''' \rho'}{36\rho^2} \\ &+ \frac{1}{6} \left(\frac{\rho'}{r\rho} \right)^2 - \frac{\rho''}{2r^2\rho} - \frac{\rho'''}{6r\rho}. \end{aligned} \quad (20)$$

Thus, in the approximate self-consistent atomic theory at the symmetrized Hartree level, one has achieved a basic aim of DFT in

expressing $\delta T_s/\delta\rho(\vec{r})$ solely in terms of $\rho(\vec{r})$ and its derivatives (up to and including $\rho''V$ in this approximation).

Alternatively, if one replaces $\delta T_s/\delta\rho(\vec{r})$ in eqn(20) by $(\mu - V)$ from the Euler equation (2), one has a density potential relation for heavy atoms which has been designed to transcend the TF relation (1).

4. SUMMARY

Equation (4) is an exact result relating kinetic energy $t(r)$ and electron density $\rho(\vec{r})$ for an arbitrary number \mathcal{N} of closed shells in a bare Coulomb field. Combining this result (4) with the 'statistically motivated' approximation (7), one is led to the density-potential relation (8) for closed shells in a bare Coulomb potential energy $-Z/r$. Eqn(8) has been solved in the limit $\mu \rightarrow 0$ at small (eqn(10)) and large (eqn(9)) r . The large r result is consistent with the exact study of $\rho_\infty(r)$ by HL, while the small r solution correctly embodies Kato's theorem.

From eqn(8), an approximate expression (16) for the functional derivative of the single-particle kinetic energy $\delta T_s/\delta\rho(\vec{r})$ has been obtained (see also Appendix 2), which transcends the TF result by including density gradients. Whereas eqn(8) involves a line integral when one invokes Hartree self-consistency through Poisson's equation, one reaches the explicit, though somewhat complicated, form (20) for $\delta T_s/\delta\rho(\vec{r})$. Probably therefore the simplest generalization for future numerical study of the self-consistent TF atom is to solve simultaneously eqns(13) and (18).

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APPENDIX 1. SINGULARITIES IN THE ATOMIC SCATTERING FACTOR $f_{\infty}(k)$

HL give the integral representation for the hydrogenic density, for $Z = 1$, $\rho_{\infty}(r)$, as

$$\rho_{\infty}(r) = \frac{1}{\pi^2(2r)^{3/2}} \int_0^{\infty} x e^{-x} \phi(x) \int_0^{\pi} W(x, \theta) J_3(2\phi(x)[2rW(x, \theta)]^{1/2}) d\theta dx. \quad (\text{A.1})$$

Here J_3 is a Bessel function and

$$\phi(x) = [x/(1 - e^{-x})]^{1/2} \quad (\text{A.2})$$

while

$$W(x, \theta) = 1 + e^{-x} - 2e^{-x/2} \cos \theta. \quad (\text{A.3})$$

The asymptotic expansion of eqn(A.1) is also known from the study of HL:

$$\rho_{\infty}(r) = \left(\frac{1}{\pi^2 2^{1/2}} \right) r^{-3/2} \left[\sum_{j=0}^{\infty} a_j (8r)^{-j} - \sin(\sqrt{32}r) \sum_{j=1}^{\infty} b_j (8r)^{-j} + \cos(\sqrt{32}r) \sum_{j=1}^{\infty} c_j (8r)^{-j-1/2} \right]. \quad (\text{A.4})$$

HL give the first few coefficients in eqn(A.4). It is relevant to note that a second integral representation of $\rho_{\infty}(r)$ is given by HL in their equation (2.14) [9].

One of the noteworthy points about the asymptotic expansion (A.4) of the exact form (A.1) of $\rho_\infty(r)$ is that it can, at least in principle, be used to define the singularities of the atomic scattering factor $f_\infty(k)$, defined as usual by the Fourier transform of $\rho_\infty(r)$:

$$f_\infty(k) = \int \rho_\infty(r) \exp(i\vec{k} \cdot \vec{r}) d\vec{r}. \quad (\text{A.5})$$

As $k \rightarrow 0$, evidently $f_\infty(k)$ must diverge, since $\rho_\infty(r)$ integrated over all space must diverge. This is due to the slow fall-off given by equation(9) at sufficiently large r , and leads to the form

$$\lim_{k \rightarrow 0} f_\infty(k) = \frac{B}{k^{3/2}} : B = \frac{1}{3\pi^{3/2}}. \quad (\text{A.6})$$

Also, at large r , $f_\infty(k) \propto k^{-4}$, again from Fourier transform 'singularity' theory, where the coefficient is determined from Kato's theorem by the product $Z\rho(0)$.

These results are from singular behaviour at $k=0$ and $r=0$. The presence of the terms $\sin(\sqrt{32r})r^{-5/2}$ and $\cos(\sqrt{32r})r^{-3}$ in eqn (A.4) herald further singularities of $f_\infty(k)$ in \vec{k} space, probably away from $\vec{k} = 0$. The approximate equation(8) for $\mu=0$ reflects faithfully the $k=0$ singularity but not any away from $\vec{k} = 0$.

APPENDIX 2. PROPOSED RELATION BETWEEN $\delta T/\delta\rho(\vec{r})$ AND DERIVATIVE $t'(r)$ OF KINETIC ENERGY DENSITY $t(r)$

Let us write the kinetic energy functional $T[\rho]$ in the form

$$T[\rho] = \int_0^\infty dr f(\rho; r) \int_0^\infty ds H(s, r) g(\rho, \rho', \rho'', \rho''', \rho^{IV}; s) \quad (\text{A.7})$$

where $H(r, s) = 1$ for $r > s$, and is zero for $r < s$ and $f(\rho; r) = r\rho(\vec{r})$, which is motivated by the work of Amovilli and March [8].

Then the functional derivative $\delta T/\delta\rho(\vec{r})$ takes the form

$$\frac{\delta T}{\delta\rho(\vec{r})} = \frac{\partial f}{\partial\rho} \int_r^\infty ds g(s) + G \int_0^r ds f(s) \quad (\text{A.8})$$

where G is defined by

$$G = \left[\frac{\partial g}{\partial \rho} - \frac{d}{dr} \frac{\partial g}{\partial \rho'} + \frac{d^2}{dr^2} \frac{\partial g}{\partial \rho''} - \frac{d^3}{dr^3} \frac{\partial g}{\partial \rho'''} + \frac{d^4}{dr^4} \frac{\partial g}{\partial \rho^{(4)}} \right]. \quad (\text{A.9})$$

A 2.1. Transcending 'Statistically Motivated' Approximation Relating $\delta T/\delta \rho(\vec{r})$ and $t'(r)$

Writing

$$T = 4\pi \int_0^\infty t(r) r^2 dr \quad (\text{A.10})$$

one finds from eqn(A.7)

$$t'(r) = -\frac{\rho g}{4\pi r} + \left[\frac{\rho'}{4\pi r^2} - \frac{\rho}{4\pi r^3} \right] \frac{\delta T}{\delta \rho(\vec{r})} - \frac{\rho' G}{4\pi r^2} \int_0^r s \rho(s) ds + \frac{\rho G}{4\pi r^3} \int_0^r s \rho(s) ds. \quad (\text{A.11})$$

For the Coulomb field case, and an arbitrary number of closed shells, $t'(r)$ is known explicitly in terms of ρ , its derivatives and the potential energy $-Z/r$. But in addition, one can insert in eqn(A.11) $(\mu + Z/r)$ for the functional derivative $\delta T/\delta \rho(\vec{r})$. Hence one is led to an integro-differential equation for the density $\rho(\vec{r})$. This presumably transcends the approximate differential equation of the main text. In particular, eqn(A.11) should reproduce well the HL density obtained in the limit when the number of closed shells tends to infinity.

A 2.2. One-level Case

In contrast to the approximate development above, the one-level case can be treated exactly. Thus

$$T = \frac{\hbar^2}{8m} \int \frac{(\vec{\nabla} \rho)^2}{\rho} d\vec{r} \quad (\text{A.12})$$

and hence the kinetic energy density t (now proportional to $(\vec{\nabla}\psi)^2$ in wave function language) is given by

$$t(r) = \frac{\hbar^2}{8m} \frac{(\vec{\nabla}\rho)^2}{\rho}. \quad (\text{A.13})$$

Thus, in spherically symmetric problems

$$t(r) = \frac{\hbar^2}{8m} \frac{\rho'^2}{\rho}, \quad (\text{A.14})$$

and hence its derivative is given by

$$t'(r) = \frac{\hbar^2}{8m} \left[\frac{2\rho\rho'\rho'' - \rho'^3}{\rho^2} \right] \quad (\text{A.15})$$

or

$$\frac{t'(r)}{\rho'} = \frac{\hbar^2}{4m} \left[\frac{\rho''}{\rho} - \frac{1}{2} \left(\frac{\rho'}{\rho} \right)^2 \right]. \quad (\text{A.16})$$

But from eqn(8)

$$\frac{\delta T}{\delta\rho(\vec{r})} = \frac{\hbar^2}{8m} \left[\left(\frac{\vec{\nabla}\rho}{\rho} \right)^2 - 2 \frac{\nabla^2\rho}{\rho} \right] = \frac{\hbar^2}{8m} \left[\left(\frac{\rho'}{\rho} \right)^2 - 2 \frac{\rho''}{\rho} - \frac{4}{r} \frac{\rho'}{\rho} \right]. \quad (\text{A.17})$$

Using eqn(A.16) in eqn(A.17) yields in this one-level example with spherical symmetry:

$$\frac{\delta T}{\delta\rho(\vec{r})} = -\frac{t'}{\rho'} - \frac{\hbar^2}{2mr} \frac{\rho'}{\rho}. \quad (\text{A.18})$$

Using eqn(A.14), one can eliminate the last term in eqn(A.18) in favour of t , to find

$$\frac{\delta T}{\delta\rho(\vec{r})} = -\frac{t'}{\rho'} - \frac{4t}{r\rho'}. \quad (\text{A.19})$$

Combining eqn(A.19) with the Euler equation

$$\frac{\delta T}{\delta \rho(\vec{r})} = \mu - V(r) \quad (\text{A.20})$$

yields

$$\rho'[\mu - V(r)] = -\left[t' + \frac{4t}{r}\right]. \quad (\text{A.21})$$

Of course, eqn(A.21) must be equivalent to the Schrödinger equation for the density amplitude $\rho^{1/2}$ in this one-level example.

APPENDIX 3. KINETIC ENERGY TENSOR FOR COULOMB FIELD

A further result of the present study concerns the kinetic energy tensor T_{ij} . In a general central field, we have

$$T_{ij} = t(r) \frac{r_i r_j}{r^2} + F(r) \left[\frac{3r_i r_j}{r^2} - \delta_{ij} \right], \quad (\text{A.22})$$

where $t(r)$ is the trace of T_{ij} (the kinetic energy density tensor) and $F(r)$ is a further function entering through a null-trace tensor.

Applying the differential form of the virial theorem, namely

$$\sum_j \frac{\partial T_{ij}}{\partial r_j} = -\frac{1}{2} \rho \frac{\partial V}{\partial r_i} + \frac{1}{8} \frac{\partial}{\partial r_i} \nabla^2 \rho \quad (\text{A.23})$$

we obtain

$$t' + 2F' = \frac{\rho'''}{8} + \frac{\rho''}{4r} - \frac{\rho'}{4r^2} - \frac{Z\rho}{2r^2}. \quad (\text{A.24})$$

Using the explicit result for t' in a Coulomb field, one finds an equation for F' , namely

$$F' = \frac{\rho''}{8r} + \frac{\rho'}{4r^2} + \frac{Z\rho}{2r^2} \quad (\text{A.25})$$

which, on integration, completes the determination of the kinetic energy tensor T_{ij} in eqn(A.22) for the case of the bare Coulomb field.