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Inhomogeneous Relativistic Electron Systems: a Density Functional Formalism.

Munagala Venkata Ramana

Louisiana State University and Agricultural & Mechanical College

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INHOMOGENEOUS RELATIVISTIC ELECTRON SYSTEMS: A DENSITY
FUNCTIONAL FORMALISM

The Louisiana State University and Agricultural and Mechanical Col. PH.D. 1981

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INHOMOGENEOUS RELATIVISTIC ELECTRON SYSTEMS:
A DENSITY FUNCTIONAL FORMALISM

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Physics and Astronomy

by
Munagala V. Ramana
M.Sc. University of Delhi, Delhi, India, 1975
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ABSTRACT

The correlation energy of an unpolarized relativistic electron gas is numerically calculated by summing ring diagrams due to both the longitudinal and transverse photon contributions. From this a local relativistic correlation potential is deduced which appears in the density functional theory of inhomogeneous systems where relativistic effects make important contributions. The nonrelativistic gas results are found to be significant underestimates.

A fitted form of the correlation energy and potential were used in a self-consistent calculation of energies of atoms of large Z . Trends of the correlation contribution across the periodic table are evaluated and discussed. Correlation contributions to the $K\alpha_1$ and $K\alpha_2$ lines are compared to the differences between accurate computations, without correlation, and experimental values.

The role of the Breit interaction in a local approximation is evaluated through self-consistent atomic calculations. It is found that the full transverse interaction is underestimated by about an atomic unit in the systems investigated. Comparison with previous non-local Dirac-Fock calculations indicate that non-local effects may be important.

The problem of the relativistic spin polarized electron gas is considered. The Green function is deduced and used to calculate the particle density, magnetization,

exchange energy and potentials. In the ultrarelativistic limit the magnetization is found to be one-third its non-relativistic value. States of uniform magnetization do not appear as ground states in the Hartree-Fock approximation. The exchange energy is found to change sign over a range of values of the relativistic parameter $\beta (= \hbar k_F / mc)$ and magnetization. Effective one particle equations for the inhomogeneous polarized gas are given. The effective one particle potentials that appear in this equation are calculated in a local density scheme and their significance discussed.

CHAPTER I

A. Notations, Orders of Magnitude, and the Need For Relativistic Treatment

Our notations are as in Björken and Drell (1965) and the work of Rajagopal and Callaway (1973). We use relativistic units $\hbar = 1 = c$. We still have a choice of one parameter. Since our interest lies in atomic and solid state systems we choose our unit of length as the Bohr radius of the hydrogen atom: $a_0 = \frac{\hbar^2}{me^2} = 1$. In these units the electromagnetic coupling constant $e^2 = \alpha$ ($= 1/137.037$). Then the energy of the first level of the hydrogen atom ($e^4 m/2\hbar^2$), the Rydberg $= \frac{1}{2} e^2$ relativistic units. In the solid state context the velocity of the electron at the Fermi surface is a typical electronic velocity in the system and so our relativistic parameter is chosen to be β ($= k_F/m$). It is related to the more conventional density parameter r_s (viz. $1/\frac{4}{3}\pi r_s^3 a_0^3 = k_F^3/3\pi^2$) by $\beta = (9\pi/4)^{1/3} 1/\alpha r_s \approx 1/71.4 r_s$. A density of $\beta = 1$, where relativistic effects are expected, correspond to $r_s \approx 0.014$. This may be compared with the region of "high density" in the nonrelativistic electron gas theory for which $r_s < 1$. The corresponding electronic densities are $n_0 \approx 6.15 \times 10^{29} \text{ cm}^{-3}$ ($r_s \approx 0.014$) and $n_0 \approx 1.69 \times 10^{24} \text{ cm}^{-3}$ ($r_s \approx 1$).

To get some physical idea of what is involved we may expect relativistic effects to show up when the Fermi momentum $\hbar k_F \approx mc$, where m is the electronic rest mass and c is the velocity of light. Using the charge density at the nucleus provided by Janak et al. (1978) for Indium ($Z = 49$) as $8 \times 10^4 / (\text{Bohr radius})^3$ and that $k_F^3 / (3\pi^2 n)^{1/3}$ gives $\beta = \hbar k_F / mc \approx 1$. Another estimate could be arrived at by calculating the density of two electrons in a sphere of volume a_0/Z . The condition $\beta \approx 1$ gives $Z \approx 57$. In any case these estimates give us an idea of where to expect relativistic effects.

In what follows we briefly discuss what may be expected due to relativistic effects. A more detailed review of relativistic effects in atoms, molecules and solids with extensive references is the one due to Pyykkö (1978).

The most easily observed relativistic effect even in light atoms is the fine structure of the spectral lines due to spin-orbit splitting. This was first explained by Sommerfeld (1916) using the old quantum theory. As we move up in Z there are other relativistic effects apart from those of spin. The relativistic motion of the core electron increases its mass and since the mass appears in the denominator of the Bohr radius the orbit shrinks. All other s orbitals which must remain orthogonal to the core shrink as much. The inner p orbitals are similarly

affected. Pyykkö estimates this contraction to be as much as 20% in mercury ($Z = 80$). These two effects, the spin-orbit splitting and the relativistic contraction of the core, are called direct effects. Because of the contraction of the s and p levels the nucleus is better shielded from the outer electrons. This leads to an indirect effect, namely the expansion of the outer valence shells. The order of magnitude of the expansion is expected to be as large as the contraction. For the inner shells of large Z atoms QED effects become important. Vacuum polarization effects due to the nuclear charge, including higher order corrections, were calculated by Huang et al. (1976) and contribute about 1.5 a.u. to the 1s shell in mercury. Electron self energy terms due to the zero point oscillations of the electromagnetic field contribute about 7 a.u. to the 1s shell as calculated by Huang et al. (1976). Correlation effects are expected to contribute a few electron volts.

In the following we briefly survey some earlier calculations which bear out the above expectations. We will see that relativity plays a significant role in atomic properties, in chemical bonding and in the properties of solids. More detailed accounts are to be found in several review articles: Grant (1970), Pyykkö (1978) Pyykkö and Desclaux (1979), Pitzer (1979), Desclaux (1980), Andersen (1980).

To get some idea of the role of relativity consider the case of gold where relativistic effects exhibit themselves most strikingly dominating other competing effects like shell structure expansion, Lanthonoid contraction, etc. (Pyykkö, 1978). (For example in cesium these effects cancel each other making it the largest atom in nature). Its properties are quite different from what can be expected from its lighter analogues Ag and Cu. For example the first ionization energy for gold at 9.22 eV is higher than that of Ag (7.574) or Cu (7.724). This is attributed to the relativistic contraction of the ns shell in gold.

Further effects which may be explained by this contraction are the electron affinity of gold which is much higher and which allows it to form the Au^- ion in CsAu and RbAu, which are semiconductors, unlike Ag and Cu, the dissociation energy in Au_2 is higher, the bond lengths in the hydrides are shorter. The self consistent field (SCF) expansion of the outer d-orbital may serve to explain why the second ionization energy of gold is smaller than Ag or Cu, its trivalency and pentavalency and its yellow color. This expansion places the 5d to Fermi-level transitions at around 2.3 eV. Thus gold absorbs strongly in blue and violet and reflects red and yellow. It is interesting to note at this point that non-relativistic calculations predict very similar

properties for silver and gold while relativistic calculations gives qualitative agreement with experiment (Pyykkö (1978) and references therein). While gold is the most spectacular in its exhibition of relativistic effects, the difference in behavior between fifth row elements and the corresponding sixth row elements may be largely understood on the basis of these effects.

Relativistic calculations in atoms have been attempted since 1940. These have increased in sophistication and complexity since then culminating in the multiconfiguration Dirac-Fock (MCDF) calculations. Such calculations are large even for atomic systems and in the case of molecules and solids the size and complexity of the calculations become prohibitive. An alternative, reliable method of dealing with inhomogeneous many electron systems with reasonable computational effort is available in the density functional scheme. This theory was developed by Hohenberg and Kohn (1964), Kohn and Sham (1965) and Sham and Kohn (1966). In the local approximation it has been greatly successful in dealing with a wide variety of nonrelativistic inhomogeneous systems. The accuracies are no better than 1% (Kohn and Vashishta, 1981). These methods have not been tried very widely in relativistic systems. This, we believe, was due to the lack of proper treatment for exchange and correlation in the relativistic density

functional theory (RDFT). The aim of this thesis is to provide such a treatment. In the next section we summarize the work done so far for relativistic systems.

B. Survey of Earlier Work for Relativistic Many-Electron Systems

In the nonrelativistic theory two electrons interact via the Coulomb potential and the treatment of such interacting fermion system has become the electron gas theory. In the relativistic case, Breit (1929) derived a relativistic two electron interaction beside the usual Coulomb interaction. So, a relativistic generalization requires not only the use of Dirac formalism but also a proper theory of interactions. In the early development, the electron interactions were taken to be Coulombic and the Breit interaction was treated as a perturbation.

Swirles (1935) was the first to suggest that the Dirac one-electron equation may be used instead of the nonrelativistic Schrodinger equation in the self consistent field method of Hartree, to gauge the relativistic effects in heavy atoms. Williams (1940) first followed her proposal, omitting exchange, for the Cu^+ ion and reported contractions of the inner shell charge densities but no changes in the energy. Copper was too light an atom to show relativistic effects. Much later, Mayers (1957) for Hg and Cohen (1960) for Hg, Hg^{++} , W, Pt and U reported

results of relativistic calculations again omitting exchange and showed substantial improvements over the non-relativistic calculations. In most of the preceding work, only Coulomb interaction between the electrons was used.

Since then there has been a rapid burgeoning of relativistic calculations for atoms, molecules and solids. The Dirac-Fock method was used by Grant (1961) and Mann (1967), a Dirac-Slater method by Liberman (1965) using the non-relativistic Slater type exchange and a multi-configuration Dirac-Fock (MCDF) by Desclaux (1975). Mann and Johnson (1971) have made an extensive evaluation of the role of the Breit interaction and various forms of it (see for example Bethe and Salpeter 1957) including the full transverse interaction in the Dirac-Fock scheme. Huang et al. (1976) have done almost complete calculations of atomic binding energies for atoms of $2 \leq Z \leq 106$, though they use Breit interaction and omit correlation. Their calculations compared with experimental results of Deslattes et al. (1980) and the earlier nonrelativistic estimates of Cowan (1967) suggest that correlation corrections to binding energies may be a few eV. To our knowledge no systematic calculation of the correlation contribution in atoms in the relativistic case has been reported.

The most recent relativistic molecular calculations were reported for Au complexes by Guenzenberger and Ellis (1980), using a statistical exchange model. No full MCDF

or DF calculations, we believe, have been carried out for molecules. Almost all nonrelativistic band structure schemes have been generalized to the relativistic case. The earliest one was by Callaway et al. (1957). Recent calculations are by Skriver et al. (1978), Glotzel (1978), Schwarz and Herzig (1978), Andersen et al. (1980) and MacDonald et al. (1981). For reviews one may see the excellent overview by Pyykkö (1978) and references therein, Grant (1970), Desclaux (1980) and the recent "Proceedings of the International Conference on the Physics of Actinides and Related 4f Materials (1980)".

C. The Density Functional Formalism in Relativistic Systems

The density functional (DF) formalism of Hohenberg and Kohn (1964) and the local density version of Kohn and Sham (1965), Sham and Kohn (1966) and their generalizations (Mermin (1965) and recently Gupta and Rajagopal (1980) for finite temperature, von-Barth and Hedin (1972) for spin polarized cases, Pant and Rajagopal (1972) for spin polarized situations, Rajagopal and Callaway (1973) for spins in a relativistic theory, and Gunnarsson and Lundqvist (1976) for spin polarized cases have met with great success in providing a theoretical framework and basis for practical applications in dealing with systems of many interacting electrons. A recent review by Rajagopal (1980)

neatly summarizes the current status of the theory. A fundamental limitation of the DF formalism, viz. its inability to deal adequately with relativistic systems, was removed by Rajagopal and Callaway (1973) and Rajagopal (1978) and independently by MacDonald and Vosko (1979). In a local scheme, using the exchange energy of a uniform relativistic electron gas, the exchange part of the effective potential was deduced. Using this exchange only approximation, for uranium and some atoms of the lithium isoelectronic sequence, an effective one particle Dirac equation was solved self-consistently by Das et al. (1980) and Das (1980) (for fermium). The contribution to the exchange term due to the transverse photon interaction, left out by Ellis (1978) in his treatment, was found to be significant. It must be mentioned that prior to this the non-relativistic Kohn-Sham exchange was used in a one particle Dirac equation (Lieberman et al., 1971). The Breit interaction and its non-local generalization of Mann and Johnson (1971), (which corresponds to our transverse interaction), were evaluated perturbatively by Mann and Johnson (1971) in the Dirac-Fock scheme. They found that the Breit interaction as an approximation to the full transverse interaction was larger by about a Rydberg in mercury. The Breit interaction is obtained from the full transverse interaction by dropping a term in the denominator which represents the energy transfer by the transverse

photon. We perform a similar evaluation in the case of the local approximation in density functional theory.

In the following we further develop the relativistic density functional scheme. We do this in two directions. We calculate the correlation part of the exchange correlation potential, based on a calculation of the ground state energy of the homogeneous electron gas, within a ring diagram sum approximation which is a generalization of the non-relativistic result of Gell-Mann and Brueckner (1957) (GB) and apply this to an atomic case. We extend the non-relativistic spin density functional (SDF) formalism of von-Barth and Hedin (1972) to the relativistic case, based on the theorems proved by Rajagopal and Callaway (1973). We deal here with the problem of spin not being a good quantum number. We present the exchange potentials for the inhomogeneous polarized electron gas derived from the calculation of the exchange energy for the uniform polarized gas.

In the non-relativistic formalism, it is known that the correlation contribution to the exchange correlation potential is important, and that it profoundly affects the behavior of systems with uncompensated spin (Gunnarsson and Lundqvist (1976)). In relativistic systems correlations were not studied in any serious way. Some correlation was included in some MCDF calculations. Freedman et al. (1972) and Fricke et al. (1972) using an extrapolation of the non-relativistic GB result estimate the

correlation effects in fermium to be less than 1 eV. We show from our calculation that this contribution, by omitting relativistic effects, is underestimated and in fact may be of the order of 10 eV.

D. Spin Density Functional (SDF) Formalism in Relativistic Systems

In non-relativistic systems with uncompensated spin it is known that the application of the DF scheme, with the results of the unpolarized gas as input give results seriously in error. The SDF scheme greatly improves this, Gunnarsson and Lundqvist (1976). In relativistic systems too, where there is uncompensated spin, we expect the need for an SDF scheme. While the required theorems have been proved for a relativistic density functional (RSDF) by Rajagopal and Callaway (1973) and the effective one particle equations were written down by MacDonald and Vosko (1979), to our knowledge no calculation of the effective one particle potentials have been reported. We therefore fill this gap. Using the results of the relativistic homogeneous spin polarized gas as input in an exchange only approximation we calculate the effective one particle potentials in a local density scheme. While dealing with the relativistic spin polarized gas we encounter some novel and interesting conceptual problems.

In the second chapter we develop the theory for calculating the correlation contribution to the relativistic

case. We outline a many-electron field theoretic formalism so that the proper interactions and other approximations can be clearly brought out. We point out the approximations and renormalizations involved. We present explicitly the longitudinal and transverse parts of the correlation energy and potential. In the third chapter we present and discuss the numerical results and compare with the approximations of Jancovici (1962) and we report the results of an actual self-consistent calculation for various atoms with correlation included. Since a calculation with the full exchange has already been published a comparison would enable us to assess the correlation contribution. In passing we also evaluate the Breit interaction vis-a-vis the full transverse interaction in the local approximation. We find, upon comparison with the results of Mann and Johnson (1971) that non-local effects may be important.

In Chapter IV, the second part of the thesis, we discuss the spin polarized homogeneous relativistic electron gas and develop its Feynmann propagator. We use this propagator to calculate some interesting physical quantities of the homogeneous gas and discuss their significance. We follow this with the effective one particle equation for the inhomogeneous system and calculate the effective potentials. In Chapter V we summarize our results.

E. A Note on Renormalizations

In relativistic many body theory there are two kinds of renormalizations that we have to deal with. The first is the usual many body renormalizations due to interacting particles in the Fermi sea. The second that we encounter is the quantum electrodynamic renormalizations due to the infinite Dirac sea. We are interested in the former while the latter has been dealt with adequately in the literature even in the context of relativistic many particle systems. See, for example, the references in the beginning of Section II.B. Essentially in our formal calculations we encounter terms involving electron density (Fermi function) and terms which are divergent and independent of the density, where we assume that the infinite negative energy sea is filled. The latter terms give rise to QED renormalizations and may be dropped if we use the physical charge and mass. For further discussion see MacDonald (1978).

CHAPTER II

A. Density Functional Theory for the Inhomogeneous Relativistic Electron System

The Hamiltonian for our system is

$$\begin{aligned}
 H = & \int d\vec{r} \bar{\psi}(x) [\vec{\gamma} \cdot \vec{p} + m(1 - \gamma_0)] \psi(x) + H_{\text{rad}}^{\text{tr}} \\
 & + \frac{1}{2} \iint d\vec{r} d\vec{r}' \frac{e^2}{|\vec{r} - \vec{r}'|} : \bar{\psi}(x') \gamma_0 \psi(x) : \bar{\psi}(x') \gamma_0 \psi(x') : \\
 & - e \int d\vec{r} : \bar{\psi}(x) \gamma_i \psi(x) : : A_{\text{tr}}^i(x) : \\
 & - e \int d\vec{r} : \bar{\psi}(x) \gamma_\mu \psi(x) : A_{\text{ext}}^\mu(r)
 \end{aligned} \tag{2.1}$$

The notations are as in Björken and Drell (1965) and Rajagopal and Callaway (1973). In (2.1) the ψ 's are the four component second quantized Dirac spinor operators, the γ 's are the 4x4 Dirac matrices, $H_{\text{rad}}^{\text{tr}}$ is the Hamiltonian for the transverse radiation field. In the first term the rest mass m of the electron has been subtracted out so that the energies are measured relative to the rest mass. The usual Coulomb interaction between electrons appears explicitly in the third term because we use the radiation gauge, $\vec{\nabla} \cdot \vec{A} = 0$. The colons represent normal ordering where all creation operators appear to the left of all destruction operators; this eliminates the infinite mass and charge of the vacuum. The fourth term represents the

interaction of the current with the transverse radiation field, a contribution which is negligible in the non-relativistic theory. It is this which leads to additional electron interactions due to relativity. As a general convention any repeated indices are summed over with Roman indices running from 1 through 3 and Greek indices running from 0 through 3. In the last term we represent the interaction of the system with our external probe A_{ext}^μ , which is a classical entity independent of time, A_{ext}^μ may represent the field generated by the background positive charge for example.

The generalization of the Hohenberg-Kohn theorem as proved in Rajagopal and Callaway may now be stated.

Theorem: The non-degenerate ground state energy per unit volume of the system described by the Hamiltonian of (2.1) is a functional of the ground-state expectation value of the four current density, $J_\mu(\vec{r}) = \langle \bar{\psi}(x) \gamma_\mu \psi(x) \rangle$:

$$\frac{\langle H \rangle}{\Omega} = F[J_\mu] + \frac{e}{\Omega} \int d\vec{r} J_\mu(\vec{r}) A_{\text{ext}}^\mu(\vec{r}) \equiv E_{A_{\text{ext}}^\mu}[J_\mu] \quad (2.2)$$

where $F[J_\mu]$ is a universal functional independent of A_{ext}^μ . The correct J_μ minimizes $E_{A_{\text{ext}}^\mu}[J_\mu]$ subject to the condition

$$\partial^\mu J_\mu = 0 \quad (2.3)$$

and the total number of electrons is a given constant,

$$\int d\vec{r} J_0(\vec{r}) = eN . \quad (2.4)$$

The continuity Eq. (2.3), is a reflection of the gauge invariance of the Hamiltonian (2.1). The expectation value in the ground state of any operator θ is $\langle \theta \rangle$ Ω is the volume of the system. The proof of this theorem, Rajagopal and Callaway (1973), is a straightforward generalization of the proof of Hohenberg and Kohn (1964). The theorem of Kohn and Sham (1965) can also be generalized and we can write down the effective one-particle Dirac equation of the system which must be solved self-consistently to determine the ground state of the system. As in the non-relativistic case we introduce a functional

$$\begin{aligned} F[J_\mu] = T[J_\mu] + \frac{1}{2\Omega} \iint d^3r d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|} n(\vec{r})n(\vec{r}') \\ - e \int \langle \vec{J}(\vec{r}) \rangle \cdot \vec{A}_{tr}(\vec{r}) d^3r + E_{xc}[J_\mu] \end{aligned} \quad (2.5)$$

where the kinetic energy functional

$$T[J_\mu] = \frac{1}{\Omega} \int d^3r \langle \bar{\psi}(x) [\vec{\gamma} \cdot \vec{p} + m(1-\gamma_0)] \psi(x) \rangle , \quad (2.5a)$$

and $E_{xc}[J_\mu]$ is the exchange correlation contribution from the Coulomb interaction and the transverse photon interaction of the electrons and the energy of the transverse photons. Thus

$$\begin{aligned}
E_{xc}[J_\mu] &= \frac{1}{2\Omega} \iint d^3r d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|} \\
&<:\bar{\psi}(x)\gamma_0\psi(x): : \bar{\psi}(x')\gamma_0\psi(x'): \\
&- <:\bar{\psi}(x)\gamma_0\psi(x):><:\bar{\psi}(x')\gamma_0\psi(x'):> \\
&- \frac{e}{\Omega} \iint d^3r d^3r' <:\bar{\psi}(x)\gamma_i\psi(x): : A_{tr}^i(x): \\
&- <:\bar{\psi}(x)\gamma_i\psi(x):><:A_{tr}^i(x):> \\
&+ \frac{1}{\Omega} <H_{rad}^{tr}> \quad . \quad (2.6)
\end{aligned}$$

The second theorem is then:

A Dirac equation for a set of spinors $\{\phi_i(r)\}$ can be defined such that

$$(-i\vec{\alpha}\cdot\vec{\nabla}-m(1-\beta) + V_{eff}[r;J_\mu])\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}) \quad (2.7)$$

where

$$\begin{aligned}
V_{eff}[\vec{r};J_\mu] &= -\left(v_{ext}(\vec{r}) + e^2 \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' + \frac{\delta E_{xc}}{\delta n(r)}\right) \\
&- e\vec{\alpha}\cdot\left(\vec{A}_{ext}(\vec{r}) + e \int \frac{\vec{J}(r')d^3r'}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{xc}}{\delta \vec{J}(\vec{r})}\right)
\end{aligned} \quad (2.8)$$

The ground state particle and current densities are given by

$$n(\vec{r}) = \sum_{i(\text{occ})} \text{Tr}(\phi_i^*(\vec{r})\phi_i(\vec{r})) \quad , \quad (2.9)$$

and

$$J_k(\vec{r}) = \sum_{i(\text{occ})} \text{Tr}(\phi_i^*(r)\alpha_k\phi_i(\vec{r})) \quad . \quad (2.10)$$

Here Tr denotes a trace over the spinors. The construction preserves the continuity equation $\vec{\nabla} \cdot \vec{J} = 0$. The equations (2.7-10) have to be solved self-consistently.

The problem now is to find an expression for E_{xc} so that V_{eff} may be used in an actual calculation. There have been several such practical schemes as discussed in detail by Rajagopal (1980). One of the more successful schemes is the local scheme in the non-relativistic theory, where E_{xc} is calculated for a homogeneous electron gas and used as input for a real system with a "slowly" varying density. It may be assumed in such systems that the density is locally homogeneous. In practice the scheme has been extremely successful, along with its spin generalized version, even for atoms and molecules. We now discuss the local scheme for the relativistic case.

B. The Relativistic Electron Gas

The problem of the uniform relativistic electron system was studied from various viewpoints before because this model is of great interest in many fields--nuclear physics (Chin (1977)), astrophysics (Akhieser and Peletminskii (1960)), many-electron physics (Fradkin (1967)), Bowers et al. (1973)) and plasma physics (Tsytovich (1961), Bezzeridis and DuBois (1972)).

In calculations in a local scheme prior to 1980, for relativistic systems of interest an ad hoc use of the results of non-relativistic gas for E_{xc} was employed (Connolly (1977)). The results of Rajagopal (1978), MacDonald and Vosko (1979) for the exchange contribution of E_{xc} yielded reasonable results for heavy atomic systems (Das et al. 1980). In the following we outline the derivation of the result of the exchange only approximation and follow it with a calculation of the correlation contribution, the first of the two main results of this thesis.

To evaluate Eq. (2.6) we have to resort to approximation schemes as in the non-relativistic theory. In the non-relativistic case where the velocity of light is infinite the only expansion parameter is $1/a_0 k_F = n e^2 / k_F$ and the theory is good at high densities. In the relativistic case where the densities are much higher the electromagnetic coupling constant $e^2 = 1/137$ is still small and is a natural expansion parameter as in quantum

electrodynamics. The theory is therefore valid for all densities such that $me^2/k_F \ll 1$ (Jancovici, 1962). We may state that for high densities $\gtrsim 6.2 \times 10^{29} \text{ cm}^{-3}$, one needs a relativistic theory as indicated in Chapter I.A.

In the ground state of the system there are no free photons present so that the last term in (2.6) is zero. The exchange only approximation to the lowest order is easily accomplished by using the plane wave expressions for the Dirac spinors $\bar{\psi}(x)$ and $\psi(x)$ and calculating the ground state expectation values. The contribution of the Coulomb term is calculated exactly as in the non-relativistic theory, the only additional complication being a trace to be taken over the Dirac γ matrices. The contribution of the transverse photon interaction is similarly evaluated; A_{tr}^i may be expressed, using the wave equation with a source term, as an integral over the transverse photon-propagator for the free field (to be defined later) and a Dirac current. We have only outlined the derivation since the details have appeared elsewhere (Rajagopal (1978), MacDonald and Vosko (1979)). Since the currents are order $1/c$, at low densities, i.e. the non-relativistic limit, the transverse contribution is negligible and of order $1/c^2$. It may be pointed out here that these same terms lead to relativistic interactions of the Breit type as we will show presently. To this order, we thus arrive at the relativistic Hartree-Fock (exchange contributions) approximation.

If now, in an effort to calculate the correlation energy which is defined as

$$E_c = E_{\text{exact}} - E_{\text{Hartree Fock}} \quad (2.11)$$

by taking the next term in the perturbation expansion we are faced with a bad divergence due to the long range of the Coulomb interactions. The same situation occurs in the non-relativistic theory and was circumvented by Gell-Mann and Brueckner (GB) (1957). They found that a class of divergent diagrams may be resummed to give a finite value. This was the famous sum of ring diagrams also known as the random phase approximation. We may try such a summation in the relativistic case too. At this point we may define a model Hamiltonian such as Bohm-Pines collective electron theory which will generate the set of ring diagrams and using the Lindhard dielectric function formalism calculate the correlation energy as was done by Jancovici (1962) for the relativistic electron gas. We however follow the Green function method and use the Dyson-Schwinger approach to calculate the correlation energy. This approach was originally used to derive the well-known renormalized electrodynamic theory of the electron to which our theory reduces in the limit of zero electron density. Thus the Schwinger method applied to our problem will give the renormalizations due to both electrodynamic and density-dependent effects.

To this end we define several quantities that appear in our calculations.

The free Dirac operators $\psi(x)$ and $\psi^+(x)$ have the momentum space expansions (Bjorken and Drell (1965))

$$\begin{aligned}\psi(\vec{x}, t) &= \sum_{\pm s} \int \frac{d^3 p}{(2\pi)^{3/2}} \sqrt{\frac{m}{E_p}} \left[b(p, s) u(p, s) e^{-ip \cdot x} \right. \\ &\quad \left. + d^+(p, s) v(p, s) e^{ip \cdot x} \right] \\ \psi^+(x, t) &= \sum_{\pm s} \int \frac{d^3 p}{(2\pi)^{3/2}} \sqrt{\frac{m}{E_p}} \left[b^+(p, s) \bar{u}(p, s) \gamma_0 e^{ip \cdot x} \right. \\ &\quad \left. + d(p, s) \bar{v}(p, s) \gamma_0 e^{-ip \cdot x} \right] \quad (2.11)\end{aligned}$$

here

$$E_p = p_0 = + \sqrt{|\vec{p}|^2 + m^2}$$

$$p \cdot x = p_\mu x^\mu \equiv p^\mu x_\mu = E_p t - \vec{p} \cdot \vec{x}$$

$$\bar{u} \equiv u^\dagger \gamma_0, \quad \bar{v} \equiv v^\dagger \gamma_0.$$

The spin vector s has components in the rest frame $s = (0, \hat{n})$, where $\hat{n}$ is a unit vector in the direction of spin. The positive and negative energy spinors u , $\bar{u}$ and v , $\bar{v}$ satisfy the Dirac equations

$$\begin{aligned}
(\not{p}-m)u(p,s) &= 0 & \bar{u}(p,s)(\not{p}-m) &= 0 \\
(\not{p}+m)v(p,s) &= 0 & \bar{v}(p,s)(\not{p}+m) &= 0 .
\end{aligned} \tag{2.12}$$

for any four vector a , $\not{a} = \gamma \cdot a$. They have the orthogonality relations

$$\begin{aligned}
\bar{u}(p,s)u(p,s') &= \delta_{ss'} = -\bar{v}(p,s)v(p,s') \\
u^\dagger(p,s)u(p,s') &= \frac{E_p}{m} \delta_{ss'} = v^\dagger(p,s)v(p,s') \\
\bar{v}(p,s)u(p,s') &= 0 = v^\dagger(p,s)u(-p,s')
\end{aligned} \tag{2.13}$$

The notation $u(-p,s)$ means $u(\sqrt{p^2+m^2}, -\vec{p}, s)$. They satisfy the completeness relations

$$\begin{aligned}
\sum_{\pm s} [u_\alpha(p,s)\bar{u}_\beta(p,s) - v_\alpha(p,s)\bar{v}_\beta(p,s)] &= \delta_{\alpha\beta} \\
\sum_{\pm s} u_\alpha(p,s)\bar{u}_\beta(p,s) &= \left(\frac{\not{p}+m}{2m}\right)_{\alpha\beta} \equiv (\Lambda_+(p))_{\alpha\beta} \\
-\sum_{\pm s} v_\alpha(p,s)\bar{v}_\beta(p,s) &= \left(\frac{m-\not{p}}{2m}\right)_{\alpha\beta} \equiv (\Lambda_-(p))_{\alpha\beta}
\end{aligned} \tag{2.14}$$

where α, β are spinor indices. The Fock space operators $b(p,s)$ ($b^\dagger(p,s)$) annihilate (create) electrons of a momentum p spin s and $d(p,s)$, ($d^\dagger(p,s)$) annihilate (create) positrons of momentum p and spin s . They satisfy the anti-commutation relations

$$\begin{aligned}
\{b(p,s), b^+(p',s')\} &= \delta_{ss'} \delta^3(p-p') \\
\{d(p,s), d^+(p',s')\} &= \delta_{ss'} \delta^3(p-p') \\
\{b(p,s), b(p',s')\} &= 0 = \{d(p,s), d(p',s')\} \\
\{b^+(p,s), b^+(p',s')\} &= 0 = \{d^+(p,s), d^+(p',s')\} \\
\{b(p,s), d(p',s')\} &= 0 = \{b(p,s), d^+(p',s')\} \\
\{d(p,s), b(p',s')\} &= 0 = \{d(p,s), b^+(p',s')\} . \quad (2.15)
\end{aligned}$$

The anticommutation relations for the fields follow

$$\begin{aligned}
\{\psi_\alpha(x,t), \psi_\beta^+(x',t)\} &= \delta^3(\vec{x}-\vec{x}') \delta_{\alpha\beta} \\
\{\psi(x,t), \psi(x',t)\} &= 0 = \{\psi^+(x,t), \psi^+(x',t)\} . \quad (2.16)
\end{aligned}$$

Notice that these relations are defined only at equal times.

The interacting field satisfies the equation

$$\{(i\not{\partial} - mc)\psi(x) = 0 \quad (2.17)$$

where the electromagnetic field A appears through the minimum coupling. The electromagnetic field itself satisfies the equation

$$(\partial^\mu A^\nu - \partial^\nu A^\mu) = \frac{4\pi}{c} \{j^\mu(x) + j_{\text{ext}}^\mu(x)\} \quad (2.18)$$

$j_{\text{ext}}^\mu(x)$ is a c-number external current designed to probe the system which is set equal to zero at the end of the calculation. We define the Green function for the electron system (Fradkin, 1967; Bowers et. al 1973; Chin, 1977)

$$S_F(1,2) = - \frac{i}{\hbar} \langle T(\psi(1)\bar{\psi}(2)) \rangle \quad (2.19)$$

where for brevity we have indicated the space-time point $x_1 \equiv 1$. T indicates the usual time ordering where for fermions

$$T(\psi(1)\bar{\psi}(2)) = \psi(1)\bar{\psi}(2)\theta(t_1-t_2) - \bar{\psi}(2)\psi(1)\theta(t_2-t_1) \quad (2.20)$$

the minus sign appears because of the anti-commutativity of the fermion fields. θ is the usual step function

$$\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0 \end{cases} \quad (2.21)$$

We define two other functions

$$S_F^>(1,2) = \langle \psi(1)\psi^+(2) \rangle$$

and

$$S_F^<(1,2) = -\langle \psi^+(2) \psi(1) \rangle \quad (2.22)$$

which are related to the Green function in an obvious way.

The induced current is then

$$j^\mu(1) = -ie\hbar \text{tr}\{\gamma^\mu S_F(1,1^+)\} \quad (2.23)$$

where t_1^+ is an infinitesimally later time than t_1 . We also define the photon field correlation functions

$$\frac{4\pi}{c} D^{\mu\nu}(12) = \frac{1}{i\hbar c} \left[\langle T(A^\mu(1)A^\nu(2)) \rangle - \langle A^\mu(1) \rangle \langle A^\nu(2) \rangle \right] \quad (2.24)$$

We make use of the following identity due to Schwinger (Kadanoff and Baym, 1963 and Rajagopal, 1964). For any operator O in the presence of an external probe

$$\frac{\delta \langle O(1) \rangle_{\text{ext}}}{\delta j_v^{\text{ext}}(2)} = \frac{1}{i\hbar c} \left[\langle T(O(1)A^\nu(1)) \rangle - \langle O(1) \rangle \langle A^\nu(1) \rangle \right] . \quad (2.25)$$

Applying this to the field A^μ , we find

$$\frac{\delta \langle A^\mu(1) \rangle}{\delta j_v^{\text{ext}}(2)} = \frac{4\pi}{c} D^{\mu\nu}(12) \quad (2.26)$$

The electron propagator, $S_F(12)$ satisfies the equation

$$[i\hbar \not{\partial}_1 - mc] S_F(12) - \frac{e}{ic\hbar} \langle T(\not{A}(1)\psi(1)\bar{\psi}(2)) \rangle = \delta(12) \quad (2.27)$$

as can be verified by using (2.17) and (2.19). The last term in (2.27) can be expressed in terms of S_F and variational derivatives

$$\frac{\delta}{\delta j_{\text{ext}}^{\nu}(1)} \langle T(\psi(1)\bar{\psi}(2)) \rangle / i\hbar =$$

$$\frac{1}{ic\hbar} \frac{1}{i\hbar} \langle T(A_{\nu}(1)\psi(1)\bar{\psi}(2)) \rangle - \frac{1}{i\hbar} \langle A_{\nu}(1) \rangle \langle T(\psi(1)\bar{\psi}(2)) \rangle$$

so that

$$\frac{1}{i\hbar} \langle T(A_{\nu}(1)\psi(1)\bar{\psi}(2)) \rangle = ic\hbar \left\{ \frac{\delta}{\delta j_{\text{ext}}^{\nu}(1)} + \langle A_{\nu}(1) \rangle \right\} S_F(12)$$

using this in (2.27)

$$[(i\hbar \not{\partial} - \frac{e}{c} \not{A}(1)) - mc] S_F(12) - \gamma^{\mu} \frac{ie\hbar}{c} \frac{\delta}{\delta j_{\text{ext}}^{\mu}(1)} S_F(12)$$

$$= \delta(12) \quad (2.28)$$

The response of the induced currents j^μ to the fields A^λ is described by the polarizability tensor

$$\frac{4\pi}{c} \frac{\delta \langle j^\mu(1) \rangle}{\delta \langle A^\lambda(2) \rangle} \equiv Q_\lambda^\mu \quad (2.29)$$

using (2.23)

$$Q_\lambda^\mu(1,2) = - \frac{4\pi e}{c} \text{tr} \left\{ \gamma^\mu i c \not{A} \frac{\delta S_F(11^+)}{\delta \langle A^\lambda(2) \rangle} \right\} \quad (2.30)$$

Now,

$$\begin{aligned} \frac{\delta S_F(12)}{\delta j_\mu^{\text{ext}}(1)} &= \int \frac{\delta S_F(12)}{\delta \langle A^\lambda(3) \rangle} \frac{\delta \langle A^\lambda(3) \rangle}{\delta j_\mu^{\text{ext}}(1)} d^4 3 = \\ &= \frac{4\pi}{c} \int D^{\lambda\mu}(31) d^4 3 \frac{\delta S_F(12)}{\delta \langle A^\lambda(3) \rangle} \end{aligned} \quad (2.31a)$$

We may now make use of the definition of the inverse Green function, S_F^{-1} ,

$$\int S_F(12) S_F^{-1}(22') d^4 2 = \int S_F^{-1}(12) S_F(22') d^4 2 = \delta(12') \quad (2.32)$$

to get

$$\int \left[\frac{\delta S_F(1\bar{2})}{\delta \langle A^\lambda(3) \rangle} S_F^{-1}(\bar{2}\bar{2}') + S_F(1\bar{2}) \frac{\delta S_F^{-1}(\bar{2}\bar{2}')}{\delta \langle A^\lambda(3) \rangle} \right] d\bar{2} = 0$$

and

$$\frac{\delta S_F(12)}{\delta \langle A^\lambda(3) \rangle} = - \int S_F(1\bar{1}) \frac{\delta S_F^{-1}(\bar{1}\bar{2})}{\delta \langle A^\lambda(3) \rangle} S_F(\bar{2}2) d^4\bar{1} d^4\bar{2} .$$

This equation along with (2,31) may be used in (2.28)

$$\begin{aligned} & \{ (i\hbar \not{\partial}_\mu - \frac{e}{c} \langle A_\mu(1) \rangle - mc) S_F(12) \\ & + ie\hbar \frac{4\pi}{c} \gamma_\mu \int D^{\lambda\mu}(\bar{3}1) S_F(1\bar{1}) \frac{\delta S_F^{-1}(\bar{1}\bar{2})}{\delta \langle A^\lambda(\bar{3}) \rangle} S_F(\bar{2}2') \\ & = \delta(12') \end{aligned} \quad (2.33)$$

multiplying both sides by $i \int S_F^{-1}(2'2) d^4 2'$ gives an expression for S_F^{-1}

$$\begin{aligned} S_F^{-1}(12) &= [i\hbar \not{\partial}_1 - \frac{e}{c} \langle A \rangle - mc] \delta(12) + \frac{4\pi e\hbar}{c} i\gamma^\mu \\ & \frac{4\pi e\hbar}{c} i\gamma^\mu \int S_F(1\bar{1}) \frac{\delta S_F^{-1}(\bar{1}\bar{2})}{\delta \langle A^\lambda(\bar{2}) \rangle} D^{\lambda\mu}(\bar{2}1) d^4\bar{1} d^4\bar{2} \end{aligned} \quad (2.34)$$

In the lowest order

$$\begin{aligned} \frac{\delta S_F^{-1}(\bar{1}\bar{2})}{\delta \langle A^\lambda(\bar{2}) \rangle} &= - \frac{e}{c} \gamma_\lambda \delta(\bar{1}\bar{2}) \delta(\bar{1}2) , \\ S_F^{-1}(12) &\approx [i\hbar \not{\partial} - \frac{e}{c} \langle A \rangle - mc] \delta(12) \\ & - \frac{4\pi e^2 \hbar}{c^2} i \gamma_\mu S_F(12) \gamma_\lambda D^{\lambda\mu}(21) \end{aligned} \quad (2.35)$$

We now turn our attention to the electromagnetic propagator. Let $D_O^{\lambda\mu}(12)$ represent the non-interacting electromagnetic propagator. We may define its inverse as in (2.32). Then from (2.18)

$$\int d2 D_O^{\lambda\mu}(12)^{-1} \langle A_\mu(2) \rangle = \frac{4\pi}{c} \left\{ \langle j^\lambda(1) \rangle + j_{\text{ext}}^\lambda(1) \right\} \quad (2.36)$$

or

$$\int d2 D_O^{\lambda\mu}(12)^{-1} D_{\mu\nu}(23) = \frac{\delta \langle j^\lambda(1) \rangle}{\delta j_{\text{ext}}^\nu(3)} + \delta(13) \delta_\nu^\lambda \quad (2.37)$$

upon taking the functional derivative of (2.36) w.r.t $j_\nu^{(\text{ext})}(3)$. Now

$$\begin{aligned} \frac{\delta \langle j^\lambda(1) \rangle}{\delta j_{\text{ext}}^\nu(3)} &= \int d^4\bar{2} \frac{\delta \langle j^\lambda(1) \rangle}{\delta \langle A^k(\bar{2}) \rangle} \frac{\delta \langle A^k(\bar{2}) \rangle}{\delta j_{\text{ext}}^\nu(3)} \\ &= \int Q_k^\lambda(1\bar{2}) D_\nu^k(\bar{2}3) d\bar{2} \\ \int d2 D_O^{\lambda\mu}(12)^{-1} D_{\mu\nu}(23) &= \int Q_k^\lambda(1\bar{2}) D_\nu^k(\bar{2}3) d\bar{2} + \delta(13) \delta_\nu^\lambda \end{aligned} \quad (2.38)$$

which gives us the Dyson equation for the photon propagator in the position space.

$$D^{\lambda\mu}(12) = D_O^{\lambda\mu}(12) + \int D_O^{\lambda\kappa}(1\bar{1}) Q_{\kappa\nu}(\bar{1}\bar{2}) D^{\nu\mu}(\bar{2}2) d\bar{1}d\bar{2} \quad (2.39)$$

We may express both (2.35) and (2.39) formally in momentum space

$$S_F^{-1}(p) = (\not{p} - mc) - \frac{4\pi e^2 \hbar}{c^2} i \int \frac{d^4 k}{(2\pi\hbar)^4} \gamma_\mu S_F^{(0)}(k+p) \gamma_\lambda D^{\lambda\mu}(k) \quad (2.40)$$

and

$$D^{\lambda\mu}(q) = D_O^{\lambda\mu}(q) + D_O^{\lambda\kappa}(q) Q_{\kappa\nu}(q) D^{\nu\mu}(q) . \quad (2.41)$$

The third term in (2.40) and the second term in (2.41) represent the self-energies, due to interactions, of the electron and photon respectively. This leads us to the problem of evaluating the polarizability tensor $Q_{\kappa\nu}$. To the lowest order

$$Q_{\kappa\nu}^{(0)}(q) = - \frac{4\pi e^2 \hbar}{c} i \int \frac{d^4 p}{(2\pi\hbar)^4} \text{tr}(\gamma_\kappa S_F^{(0)}(p+q) \gamma_\nu S_F^{(0)}(p)) \quad (2.42)$$

where $S_F^{(0)}$ is the non-interacting fermion propagator. $S_F^{(0)}$

may be easily evaluated using the plane wave expansions for the spinor fields, or from (2.40) by dropping the last term representing interactions and doing some algebra

$$S_F^{(0)}(p) = \frac{(\not{p}_+ + m)}{2E_p} \left(\frac{n_F(|\vec{p}|)}{p_0 - E_p - i\eta} + \frac{1 - n_F(|\vec{p}|)}{p_0 - E_p + i\eta} \right) - \frac{(\not{p}_- + m)}{2E_p} \left(\frac{1 - \bar{n}_F(p)}{p_0 + E_p - i\eta} + \frac{\bar{n}_F(p)}{p_0 + E_p + i\eta} \right)$$

$$\not{p}_+ = \{+E_p, \vec{p}\} \quad , \quad \not{p}_- = \{-E_p, \vec{p}\} \quad . \quad (2.43)$$

where $n_F(|\vec{p}|)$ is the Fermi function for positive energy particles and $\bar{n}_F(|\vec{p}|)$ for negative energy particles

$$\bar{n}_F(|\vec{p}|) = 1 - n_F(|\vec{p}|) \quad (2.44)$$

In our model the negative energy Dirac Sea is completely filled so that $\bar{n}_F(p) = 0$ and we have ($\hbar=c=1$)

$$S_F^0(p) = \frac{(\not{p}_+ + m)}{2E_p} \left\{ \frac{n_F(p)}{p_0 - E_p - i\epsilon} + \frac{1 - n_F(p)}{p_0 - E_p + i\epsilon} \right\} - \left\{ \frac{1}{p_0 + E_p - i\epsilon} \right\} \frac{(\not{p}_- + m)}{2E_p} \quad (2.45)$$

The first term in this expression for the propagator describes positive energy particles and the second term positive energy holes or "Fermi holes" which should be

distinguished from holes in the Dirac Sea which are the positrons. The last term without a Fermi function leads to divergent integrals of QED and is eliminated by re-normalizing the charge and mass. We accomplish this by using the physical charge and physical mass for the electron. We still have our familiar many-body re-normalizations. Using (2.45) in (2.42) we have

$$\begin{aligned}
Q_{\lambda\mu}^0(q) = & -4\pi e^2 i \int \frac{d^3 p}{(2\pi)^4} \frac{\text{tr}[\gamma_\lambda (\not{p} + \not{q} + m) \gamma_\mu (\not{p} + m)]}{4E_{\vec{p}} E_{\vec{p}+\vec{q}}} \bigg|_{\substack{p_0 = E_{\vec{p}} \\ p_0 + q_0 = E_{\vec{p}+\vec{q}}}} \\
& \left\{ \frac{1 - n_F(|\vec{p} + \vec{q}|)}{p_0 + q_0 - E_{\vec{p}+\vec{q}} + i\eta} + \frac{n_F(|\vec{p} + \vec{q}|)}{p_0 + q_0 - E_{\vec{p}+\vec{q}} - i\eta} \right\} \left\{ \frac{1 - n_F(|\vec{p}|)}{p_0 - E_{\vec{p}} + i\eta} + \frac{n_F(|\vec{p}|)}{p_0 - E_{\vec{p}} - i\eta} \right\} \\
& + 4\pi e^2 i \int \frac{d^4 p}{(2\pi)^4} \frac{\text{tr}[\gamma_\lambda (\not{p} + \not{q} + m) \gamma_\mu (\not{p} + m)]}{4E_{\vec{p}} E_{\vec{p}+\vec{q}}} \bigg|_{\substack{p_0 = E_{\vec{p}} \\ p_0 + q_0 = -E_{\vec{p}+\vec{q}}}} \\
& \left\{ \frac{1 - n_F(|\vec{p}|)}{p_0 - E_{\vec{p}} + i\eta} + \frac{n_F(|\vec{p}|)}{p_0 - E_{\vec{p}} - i\eta} \right\} \frac{1}{[p_0 + q_0 + E_{\vec{p}+\vec{q}} - i\eta]} \\
& + 4\pi e^2 i \int \frac{d^4 p}{(2\pi)^4} \frac{\text{tr}[\gamma_\lambda (\not{p} + \not{q} + m) \gamma_\mu (\not{p} + m)]}{4E_{\vec{p}} E_{\vec{p}+\vec{q}}} \bigg|_{\substack{p_0 = -E_{\vec{p}} \\ p_0 + q_0 = E_{\vec{p}+\vec{q}}}}
\end{aligned}$$

$$\begin{aligned}
& \left\{ \frac{1-n_F(|\vec{p}+\vec{q}|)}{p_0+q_0-E_{\vec{p}+\vec{q}}+i\eta} + \frac{n_F(|\vec{p}+\vec{q}|)}{p_0+q_0-E_{\vec{p}+\vec{q}}-i\eta} \right\} \frac{1}{(p_0+E_p-i\eta)} \\
& - 4\pi e^2 i \int \frac{d^4 p}{(2\pi)^4} \frac{\text{tr}[\gamma_\lambda (\not{p}+\not{q}+\not{m}) \gamma_\mu (\not{p}+\not{m})]}{4E_p E_{\vec{p}+\vec{q}}} \Bigg|_{\substack{p_0=-E_p \\ p_0+q_0=-E_{\vec{p}+\vec{q}}}} \\
& \frac{1}{(p_0+q_0+E_{\vec{p}+\vec{q}}-i\eta)} \frac{1}{(p_0+E_p-i\eta)} \quad (2.46)
\end{aligned}$$

In evaluating the contour integrals in the above expression the terms for which the two simple poles occur on the same side of the real axis are zero. This is because the contour can be closed in the other half plane.

$$\begin{aligned}
Q_{\lambda\mu}^{(0)}(q) &= 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{\text{tr}[\gamma_\lambda (\not{p}+\not{q}+\not{m}) \gamma_\mu (\not{p}+\not{m})]}{4E_p E_{\vec{p}+\vec{q}}} \Bigg|_{\substack{p_0=E_p \\ p_0+q_0=E_{\vec{p}+\vec{q}}}} \\
& \left\{ \frac{(1-n_F(|\vec{p}+\vec{q}|))n_F(|\vec{p}|)}{+E_p-E_{\vec{p}+\vec{q}}+i\eta} - \frac{n_F(|\vec{p}+\vec{q}|)(1-n_F(|\vec{p}|))}{+E_p-E_{\vec{p}+\vec{q}}-i\eta} \right\} \\
& + 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{\text{tr}[\gamma_\lambda (\not{p}+\not{q}+\not{m}) \gamma_\mu (\not{p}+\not{m})]}{4E_p E_{\vec{p}+\vec{q}}} \Bigg|_{\substack{p_0=E_p \\ p_0+q_0=-E_{\vec{p}+\vec{q}}}}
\end{aligned}$$

$$\begin{aligned}
& \frac{(1-n_F(|\vec{p}|))}{(\omega+E_{\vec{p}}+E_{\vec{p}+\vec{q}}-i\eta)} \\
& - 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{\text{tr}[\gamma_\lambda (\not{p}+\not{q}+m) \gamma_\mu (\not{p}+m)]}{4E_{\vec{p}} E_{\vec{p}+\vec{q}}} \Big|_{\substack{p_0 = -E_{\vec{p}} \\ p_0 + q_0 = -E_{\vec{p}+\vec{q}}}} \\
& \frac{(1-n_F(|\vec{p}+\vec{q}|))}{\omega-E_{\vec{p}}-E_{\vec{p}+\vec{q}}+i\eta} \tag{2.47}
\end{aligned}$$

Upon evaluating the traces, we have

$$\begin{aligned}
\text{Re}(Q_{\lambda\mu}^{(o)}(q)) &= 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{[(p+q)_\lambda p_\lambda + (p+q)_\mu p_\mu - g_{\lambda\mu} p \cdot q]}{E_{\vec{p}} E_{\vec{p}+\vec{q}}} \Big|_{\substack{p_0 = E_{\vec{p}} \\ q_0 = E_{\vec{p}+\vec{q}} - E_{\vec{p}}}} \\
& \quad \frac{n_F(p) - n_F(|\vec{p}+\vec{q}|)}{\omega+E_{\vec{p}}-E_{\vec{p}+\vec{q}}} \\
& + 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{[(p+q)_\lambda p_\mu + (p+q)_\mu p_\lambda - g_{\lambda\mu} p \cdot q]}{E_{\vec{p}} E_{\vec{p}+\vec{q}}} \Big|_{\substack{p_0 = E_{\vec{p}} \\ q_0 = -E_{\vec{p}} - E_{\vec{p}+\vec{q}}}} \\
& \quad \frac{1-n_F(|\vec{p}|)}{\omega+E_{\vec{p}}+E_{\vec{p}+\vec{q}}}
\end{aligned}$$

$$\begin{aligned}
& - 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{[(p+q)_\lambda p_\mu + (p+q)_\mu p_\lambda - g_{\lambda\mu} p \cdot q]}{E_p E_{\vec{p}+\vec{q}}} \bigg|_{\substack{p_0 = -E_p \\ q_0 = E_p + E_{\vec{p}+\vec{q}}}} \\
& \frac{1 - n_F(|\vec{p}+\vec{q}|)}{\omega - E_p - E_{\vec{p}+\vec{q}}} \quad (2.48)
\end{aligned}$$

We now compute $Q_{00}^{(o)}(q)$ and $Q_{ij}^{(o)}(q)$ from the above expression. Since we are ultimately interested in $Q_{\mu\nu} D^{\nu\mu}$ and $D^{i0} = 0 = D^{0i}$ in the Coulomb gauge we need not calculate Q_{0i} . We can write $Q_{ij}^{(o)}$ in terms of longitudinal and transverse components. The only symmetric tensors that are available are $q_i q_j$ and δ_{ij} . Therefore

$$Q_{ij}^{(o)}(q) = \frac{q_i q_j}{|\vec{q}|^2} Q_L^{(o)}(q) + \left(\delta_{ij} - \frac{q_i q_j}{|\vec{q}|^2} \right) Q_T^{(o)}(q) \quad (2.49)$$

where

$$Q_L^{(o)}(q) = \frac{q_i q_j}{|\vec{q}|^2} Q_{ij}^{(o)}(q) \quad (2.50a)$$

and

$$Q_T^{(o)}(q) = \frac{1}{2} \left(\delta_{ij} - \frac{q_i q_j}{|\vec{q}|^2} \right) Q_{ij}^{(o)}(q) \quad (2.50b)$$

Now consider the Dyson equation for $D_{\mu\nu}$. In the Coulomb gauge,

$$D_{io}^{(o)} = 0 = D_{oi}^{(o)}$$

and

$$D_{oo}^{(o)}(k) = \frac{\hbar^2}{|\vec{k}|^2}$$

$$D_{ij}^{(o)}(k) = - \frac{\hbar^2}{k_o^2 - |\vec{k}|^2} \left(\delta_{ij} - \frac{k_i k_j}{|\vec{k}|^2} \right) \quad (2.51)$$

Then

$$D_{oo}(q) = D_{oo}^{(o)}(q) + D_{o\lambda}^{(o)} Q^{(o)\lambda\kappa}(q) D_{\kappa o}(q)$$

$$= D_{oo}^{(o)}(q) + D_{oo}^{(o)} Q^{(o)o\kappa}(q) D_{\kappa o}(q)$$

and

$$D_{oo}(q) = D_o^{(o)}(q) + D_{oo}^{(o)}(q) Q_{oo}^{(o)}(q) D_{oo}(q) \quad (2.52)$$

Where in going to the last line we have used the condition

$$D_{io} = 0$$

$$D_{oo}(q) = \frac{\hbar^2}{|\vec{q}|^2} \cdot \frac{1}{[1 - \frac{\hbar^2}{|\vec{q}|^2} Q_{oo}^{(o)}]} \quad (2.53)$$

This is just the Coulomb interaction, appropriately screened by the longitudinal dielectric function of the medium.

$$\begin{aligned}
D_{ij}(q) &= D_{ij}^{(o)}(q) + D_{i\lambda}^{(o)}(q) Q^{(o)\lambda\kappa}(q) D_{\kappa j}(q) \\
&= D_{ij}^{(o)}(q) + D_{i\ell}^{(o)}(q) Q^{(o)\ell\kappa}(q) D_{\kappa j}(q)
\end{aligned}$$

and again using $D_{i\ell}^{(o)} q^\ell = 0$

$$D_{ij}(q) = D_{ij}^{(o)}(q) + D_{i\ell}^{(o)}(q) Q^{(o)\ell m}(q) D_{mj}(q) \quad (2.54)$$

Using $D_L(q) = 0$ we may write this in terms of transverse contributions only.

$$D_T(q) = D_T^{(o)}(q) + D_T^{(o)}(q) Q_T^{(o)}(q) D_T(q)$$

or

$$D_T(q) = \frac{D_T^{(o)}}{(1 - D_T^{(o)} Q_T^{(o)}(q))} \quad (2.55)$$

This is the additional effective two-electron interaction arising from the electron-transverse photon interaction, which is appropriately screened by the system of electrons. In the literature, the various polarizabilities appearing here have been defined in slightly different ways and the final results appear different. But these expressions are all equivalent, as they must, as is demonstrated in Appendix A.

C. The Calculation of Exchange-Correlation Energy

We now calculate the interaction energy of the system using the Pauli trick (Fetter and Walecka (1972)) appropriately generalized to the relativistic case:

$$\langle H \rangle = \langle H_0 \rangle + \int_0^e \frac{de'}{e'} \langle H_{\text{int}} \rangle_{e'} \quad (2.56)$$

where $\langle H_0 \rangle$ is the kinetic energy in the non-interacting ground state and $\langle H_{\text{int}} \rangle_{e'}$ is the interaction energy for an arbitrary value of the coupling constant e' . Thus

$$E_{\text{xc}} = \int_0^e \frac{de'}{e'} \langle H_{\text{int}} \rangle_{e'} - E_{\text{Hartree}} \quad (2.57)$$

$$\langle H_{\text{int}} \rangle_{e'} = e' \int d^3r_1 \langle \bar{\psi}(1) \gamma_\mu \psi(1) A^\mu(1) \rangle_{e'} \quad (2.58)$$

Using (2.23) and (2.25) this may be written as

$$\begin{aligned} \frac{\langle H_{\text{int}} \rangle_{e'}}{e'} &= i \int Q_{\nu\mu}(12) D^{\mu\nu}(21^+) d^4x_2 d^3r_1 \\ &+ \frac{1}{c} \int d^3r_1 \langle j_\nu(1) \rangle \langle A^\nu(1) \rangle \end{aligned} \quad (2.59)$$

$$E_{xc} = \frac{1}{N} \langle H_{int} \rangle - E_{Hartree} =$$

$$\frac{1}{2} \int_0^{e^2} \frac{de'^2}{e'^2} Q_{\nu\mu}^{(0)}(q) D^{\mu\nu}(q) \frac{d^4 q}{(2\pi)^4}$$

In the Coulomb gauge

$$E_{xc} = \frac{i}{2} \int_0^{e^2} \frac{de'^2}{e'^2} \int Q_{00}(q) D^{00}(q) \frac{d^4 q}{(2\pi)^4} +$$

$$i \int_0^{e^2} \frac{de'^2}{e'^2} Q_T^{(0)} D_T \frac{d^4 q}{(2\pi)^4} \quad (2.60)$$

Notice the second term, the transverse photon-electron interaction energy, carries a factor unity in contrast to half going with the Coulomb interaction energy. We have using (2.55), (2.53) and doing the e^2 integration

$$E_{xc} = \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \log[1 + \frac{4\pi e^2}{q} Q_{00}(q, \omega)]$$

$$+ \int \frac{d^3 q}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \log[1 - \frac{8 e^2}{q^2 + \omega^2} Q_T(q, \omega)] \quad (2.61)$$

where in going from (2.60) to (2.61), ω has been replaced by $i\omega$, which follows on shifting the real ω -line integral in (2.60) into the imaginary- ω line integral. Q_{00} and Q_T may be evaluated using (2.48) and (2.50)

$$Q_{00}(q, \omega) = \int_{k < k_F} \frac{d^3 k}{(2\pi)^3} \left[\frac{(E_{\vec{k}+\vec{q}} - E_{\vec{k}}) [(E_{\vec{k}+\vec{q}} + E_{\vec{k}})^2 - q^2]}{E_{\vec{k}} E_{\vec{k}+\vec{q}} [(E_{\vec{k}+\vec{q}} - E_{\vec{k}})^2 + \omega^2]} + \frac{(E_{\vec{k}+\vec{q}} + E_{\vec{k}}) [(E_{\vec{k}+\vec{q}} - E_{\vec{k}})^2 - q^2]}{E_{\vec{k}} E_{\vec{k}+\vec{q}} [(E_{\vec{k}+\vec{q}} + E_{\vec{k}})^2 + \omega^2]} \right] \quad (2.62a)$$

$$Q_T(q, \omega) = \int_{k < k_F} \frac{d^3 k}{(2\pi)^3} \left[\frac{(E_{\vec{k}+\vec{q}} - E_{\vec{k}}) [E_{\vec{k}+\vec{q}} E_{\vec{k}} - \frac{(\vec{k} \cdot \vec{q})^2}{q^2} - (\vec{k} \cdot \vec{q}) - m^2]}{E_{\vec{k}} E_{\vec{k}+\vec{q}} [(E_{\vec{k}+\vec{q}} - E_{\vec{k}})^2 + \omega^2]} - \frac{(E_{\vec{k}+\vec{q}} + E_{\vec{k}}) [E_{\vec{k}+\vec{q}} E_{\vec{k}} + \frac{(\vec{k} \cdot \vec{q})^2}{q^2} + (\vec{k} \cdot \vec{q}) + m^2]}{E_{\vec{k}} E_{\vec{k}+\vec{q}} [(E_{\vec{k}+\vec{q}} + E_{\vec{k}})^2 + \omega^2]} \right] \quad (2.62b)$$

finally scaling

$$\vec{k} = k_F \vec{x}; \quad \vec{q} = k_F \vec{y}; \quad \omega = k_F y u; \quad E_{\vec{k}} = m E_x \equiv m \sqrt{1 + \beta^2 x^2}$$

$$E_{xc} = \frac{3Nk_F}{8\pi} \int_0^\infty y^3 dy \int_{-\infty}^\infty du \ln \left\{ 1 + \frac{e^2 \beta}{\pi y^2} \tilde{Q}_{00}^{(0)}(y, u) \right\} + \frac{3Nk_F}{4\pi} \int_0^\infty y^3 dy \int_{-\infty}^\infty du \ln \left\{ 1 - \frac{2e^2 \beta}{\pi y^2 (1+u^2)} Q_{00}^{(0)}(y, u) \right\} \quad (2.63)$$

where

$$Q(k_F \vec{y}, k_F y u) = \frac{k_F^3}{4\pi^2 m} \tilde{Q}(y, u) .$$

In the limit $\beta \rightarrow 0$ the expression (2.6a) goes over to the $Q_Q(u)$ of GB and (2.62b) is of order $O(\beta^2)$. The statement that the GB result is accurate in the high density limit is true only in the non-relativistic theory.

The exchange correlation potential is then given by

$$V_{xc} = \frac{\partial E_{xc}^{(Total)}}{\partial n} = \frac{\pi^2}{k_F^2} \frac{\partial E_{xc}}{\partial k_F} \quad (2.64)$$

Separating out the exchange part, which is linear in e^2 we may express the correlation energy and potential as

$$E_c^{(Rings)} = E_c^{(c)}(Rings) + E_c^{(tr)}(Rings) \quad (2.65a)$$

and

$$V_c^{(Rings)} = V_c^{(c)}(Rings) + V_c^{(tr)}(Rings) \quad (2.65b)$$

where

$$\frac{E_c^{(c)}(\text{Rings})}{N} = \frac{3k_F}{8\pi} \int_0^\infty y^3 dy \int_{-\infty}^\infty du \left\{ \ln \left[1 + \frac{e^2 \beta}{\pi y^2} \tilde{Q}_{OO}(y, u) \right] - \frac{e^2 \beta}{\pi y^2} \tilde{Q}_{OO}(y, u) \right\} \quad (2.66a)$$

$$\frac{E_c^{(tr)}(\text{Rings})}{N} = \frac{3k_F}{4\pi} \int_0^\infty y^3 dy \int_{-\infty}^\infty du \left\{ \ln \left[1 - \frac{2e^2 \beta}{\pi y^2 (1+u^2)} \tilde{Q}_T(y, u) \right] + \frac{2e^2 \beta}{\pi y^2 (1+u^2)} \tilde{Q}_T(y, u) \right\} \quad (2.66b)$$

and

$$V_c^{(c)}(\text{Rings}) = \frac{e^2 \beta k_F}{8\pi^2} \int_0^\infty y dy \int_{-\infty}^\infty du \tilde{Q}_{OO}^{(1)}(y, u) \left\{ \frac{1}{1 + \frac{e^2 \beta}{\pi y^2} \tilde{Q}_{OO}(y, u)} - 1 \right\} \quad (2.67a)$$

$$V_c^{(tr)}(\text{Rings}) = \frac{e^2 \beta k_F}{2\pi^2} \int_0^\infty y dy \int_{-\infty}^\infty \frac{du}{1+u^2} Q_T^{(1)}(y, u) \left\{ \frac{1}{1 - \frac{2e^2 \beta}{\pi y^2 (1+u^2)} \tilde{Q}_T(y, u)} - 1 \right\} \quad (2.67b)$$

where

$$\frac{\partial Q_{oo}(q, \omega)}{\partial k_F} = \frac{k_F^2}{4\pi^2 m} \tilde{Q}_{oo}^{(1)}(y, u)$$

$$\frac{\partial Q_T(q, \omega)}{\partial k_F} = \frac{k_F^2}{4\pi^2 m} \tilde{Q}_T^{(1)}(y, u) \quad (2.68)$$

Here $\tilde{Q}^{(1)}(y, u)$ is the same as $\tilde{Q}(y, u)$ except that the integrand is evaluated at $x=1$ and the integral over the angle remains.

Expressions for $Q_{\lambda\mu}(q; \omega)$ were given in different forms by the authors quoted earlier in this chapter and their mutual equivalence demonstrated in Appendix A. The forms (2.66a) and (2.66b) were given by Jancovici (1962).

TABLE CAPTION

Table I. The values of correlation energy and potential in Rydbergs are given for a set of β -values of interest to heavy atomic system. $\epsilon_c^{(T)} = \epsilon_c^{(c)} + \epsilon_c^{(tr)}$ and $v_c^{(T)} = v_c^{(c)} + v_c^{(tr)}$. For comparison we have also given the von-Barth-Hedin results.

β	$-\varepsilon_c^{(vBH)}$	$-\varepsilon_c^{(c)}$	$-\varepsilon_c^{(tr)}$	$-\varepsilon_c^{(T)}$	$-\nu_c^{(vBH)}$	$-\nu_c^{(c)}$	$-\nu_c^{(tr)}$	$-\nu_c^{(T)}$
0.007	0.1234	0.1235	-	0.1235	0.140	0.1389	-	0.1389
0.014	0.1573	0.1574	-	0.1574	0.173	0.174	-	0.174
0.25	0.3252	0.3262	0.0036	0.3298	0.347	0.3453	0.0064	0.3517
0.50	0.3739	0.3924	0.0075	0.3999	0.399	0.4209	0.0131	0.4340
0.75	0.4046	0.4370	0.0369	0.4739	0.430	0.4918	0.0586	0.5504
1.0	0.4269	0.4997	0.0595	0.5592	0.453	0.5721	0.0967	0.6688
1.25	0.4442	0.5546	0.0828	0.6374	0.470	0.6581	0.1218	0.7799
1.5	0.4581	0.6188	0.1062	0.7250	0.483	0.7489	0.1530	0.9019
1.75	0.4697	0.6857	0.1292	0.8149	0.494	0.8336	0.1825	1.0161
2.0	0.4794	0.7545	0.1519	0.9164	0.503	0.9373	0.2119	1.1492
2.25	0.4878	0.8249	0.1740	0.9989	0.511	1.0356	0.2409	1.2765
2.5	0.4951	0.8965	0.1964	1.0929	0.518	1.1339	0.2695	1.4034
2.75	0.5015	0.9690	0.2182	1.1872	0.523	1.2329	0.2979	1.5308

Table I

FIGURE CAPTIONS

- Fig. 1 The correlation energy expressed in Rydbergs vs. β ($=\hbar k_F/mc$). $\epsilon_C^{(c)}$ stands for the Coulomb, $\epsilon_C^{(tr)}$ for the transverse-photon contributions. The full-line curves are our results for $\epsilon_C^{(c)}$ and $\epsilon_C^{(tr)}$; the long dashed curves are the result of Eq. (11) and the short-dashed curves are the $e^4 \ln e^2$ approximation of Jancovici. The non-relativistic answer is labelled vBH.
- Fig. 2 The total correlation energy in Rydbergs as a function of $\log n$ where $n = \text{density} \times a_0^3$, a_0 being the Bohr radius. vBH is the corresponding non-relativistic result.
- Fig. 3 The correlation potential in Rydbergs vs. β . $v_C^{(c)}$, $v_C^{(tr)}$ and vBH stand for Coulomb, transverse-photon, and von-Barth Hedin results. The scale on the right should be used for $v_C^{(tr)}$.
- Fig. 4 The total correlation potential vs. $\ln n$; vBH is the corresponding non-relativistic approximation.
- Fig. 5a Plot of $\epsilon_x^{(tr)}(\text{Breit})$ vs β in Rydbergs.
- Fig. 5b Plot of $v_x^{(tr)}(\text{Breit})$ vs β in Rydbergs.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5a

Fig. 5b

CHAPTER III

A. Numerical Evaluation of the Correlation Energies

In the previous chapter we derived the expressions for the correlation contribution to the energy and potential. In this chapter we carry out these integrations numerically and compare the results with non-relativistic ones and some approximations of Jancovici.

As in the non-relativistic theory the major contributions to the correlation energy are from regions of small energy and momentum transfers ($q < k_F$, $\omega < E_F$). If such an approximation is made we find (see Appendix B) the following expression for ϵ_c

$$\begin{aligned} \epsilon_c^{(\text{Rings})} &\equiv \frac{E_c^{(\text{Rings})}}{N} \sim \frac{3(k_F^2/m)}{32\pi\sqrt{1+\beta^2}} \int_{-\infty}^{\infty} dv \left\{ \ln(1+R_L(v)) \right. \\ &\quad \left. - R_L(v) - (R_L(v))^2 \left(\ln(1+R_L(v)) - \ln R_L(v) \right) \right\} \\ &\quad + \frac{3k_F}{16\pi} \int_{-\infty}^{\infty} dv \left\{ \ln(1+R_{tr}(v)) - R_{tr}(v) \right. \\ &\quad \left. - (R_{tr}(v))^2 \left(\ln(1+R_{tr}(v)) - \ln R_{tr}(v) \right) \right\} \quad (3.1) \end{aligned}$$

where

$$R_L(v) = \frac{4e^2 \sqrt{1+\beta^2}}{\pi\beta} \left(1 - v \tan^{-1} \frac{1}{v}\right) \quad (3.2a)$$

$$R_{tr}(v) = \frac{2e^2\beta}{\pi\sqrt{1+\beta^2}(1+v^2)} \left[-v^2 \frac{\beta^2+1}{\beta^2} + v \frac{\sqrt{1+\beta^2}}{\beta} \right. \\ \left. \left(1 + \frac{v^2(\beta^2+1)}{\beta^2}\right) \tan^{-1} \left(\frac{\beta}{v\sqrt{\beta^2+1}}\right) \right] \quad (3.2b)$$

and

$$v_c^{(Rings)} = \epsilon_c^{Rings} + \frac{\beta}{3} \frac{\partial}{\partial \beta} \epsilon_c^{(Rings)} \quad (3.3)$$

These integrals are evaluated numerically. For $\beta \ll 1$, they reduce to the correct non-relativistic expressions and $\epsilon_c^{(Rings)} \sim \epsilon_c^{(GB)}$. Jancovici makes a further approximation keeping only terms to the order $e^4 \ln e^2$ and gets

$$\epsilon_c^{(c)} = \frac{(1 - \ln 2)}{\pi^2} \sqrt{1+\beta^2} m e^4 \ln e^2 \quad (3.4a)$$

and

$$\epsilon_c^{(tr)} = \frac{3m}{4\pi^3} \frac{\beta^3 e^4 \ln e^2}{(1+\beta^2)} \int_{-\infty}^{\infty} \frac{du}{(1+u^2)^2} \\ \left\{ -\frac{u^2(1+\beta^2)}{\beta^2} + \frac{u\sqrt{1+\beta^2}}{\beta} \left[1 + \frac{u^2}{\beta^2} (1+\beta^2) \right] \right. \\ \left. \tan^{-1} \left(\frac{\beta}{u\sqrt{1+\beta^2}} \right) \right\}^2 \quad (3.4b)$$

We have plotted the correlation energy contributions per particle as a function of β in Fig. 1. The full line curves are our integrals computed numerically and the non-relativistic result of von-Barth and Hedin (1972). The short dashed curves are the $e^4 \ln e^2$ approximation of Jancovici and the long dashed curves are without such an approximation. The Jancovici approximation (JGB) is in the same spirit as the Gell-Mann and Brueckner (1957) (GB) one involving a small q -approximation for the Q_0 , Q_T but retaining the ω -dependence.

From the figure it can be seen that our numerically integrated result merges smoothly with the vBH curve for $\beta < 0.25$. The JGB approximation intersects our curve at about $\beta = 1.6$ lying above it for larger β and below it for smaller values. The disagreement ranges from 15% at $\beta = 0.25$ to 8% at $\beta = 2.75$. The q -dependence is not as important as the non-relativistic case where the GB results differ by 20-30% from vBH answers at low densities. However, for the transverse part of the correlation energy the JGB lies above our result for the entire β range. Thus for the total correlation energy the q -dependence is not as important as in the non-relativistic case. The $e^4 \ln e^2$ approximation on the other hand lies below our curve for both $\epsilon_C^{(c)}$ (8% for $\beta = 2.75$ and 3% for $\beta = 2.75$) and $\epsilon_C^{(tr)}$ (21% for $\beta = 2.75$) in the entire β -range. At low densities the

$e^4 \ln e^2$ scheme and (JGB) does not go to the vBH answer. However, the JGB goes into the GB as it should. The potential behaves like the energy and similar remarks apply to it. We show our results for the potential in Fig. 3.

The relativistic result begins to deviate from the non-relativistic one for $\beta > 0.25$. While the vBH answer rises logarithmically the relativistic answer is linear for large β . We have plotted in Fig. 2, the total correlation energy per particle versus $\log_{10} n$, where n is the electron density in atomic units (density $\times a_0^3$). The correlation potential as a function of β is given in Fig. 3 where the individual Coulomb and transverse contributions are plotted separately as well as the vBH answer for comparison. In Fig. 4, the total correlation potential as a function of $\log_{10} n$ is given. The departure from the non-relativistic result begins at $\beta > 0.25$ as in the energy case. It should be pointed out for both energy and potential, the transverse photon contribution though small, is found to be significant.

In Table I, we have given the numerical values for energy per particle and the potential for some values of β along with the results of von Barth and Hedin. As a useful numerical check we have calculated the correlation energy and potential for very small values of β ($\beta = 0.007, 0.014 \neq r_s = 2, 1$ respectively) using our full

relativistic expressions and find that they compare very well with the non-relativistic result of vBH. We also give the separate Coulomb and transverse contributions in the table. Unlike the case of exchange (Rajagopal, 1978) where the transverse contribution was opposite in sign to the Coulomb and large enough to cancel it, the transverse correlation contribution is of the same sign as the Coulomb part. The correlation contribution to the potential for the electron gas is about 5% of the total exchange at $\beta = 2.5$ and drops to half this value at $\beta = 1$. In the next subsection we incorporate our potentials in a self-consistent relativistic atomic calculation and compare our results with some previous estimates.

Before doing this however we report on the results of an atomic calculation to assess the contribution of the Breit interaction versus the full transverse interaction. This has been done in the case of Dirac-Fock calculations by Mann and Johnson (1971) but not for the local scheme to our knowledge.

If in the calculation of the transverse energy the energy transfer by the photon is assumed negligible then we obtain the Breit energy. That the transverse photon interaction reduces to the Breit interaction was shown by MacDonald (1978). The integrals involved may be done analytically (see Appendix C) with the results

$$\epsilon_x^{(\text{Breit})} = \frac{3}{4\pi} \beta \left\{ 1 + \frac{2}{\beta^4} [\ln(\beta + E_F)]^2 - \frac{4E_F}{\beta^4} [\beta \ln(E_F + \beta) - E_F \ln \beta] \right\} \quad (3.5)$$

$$v_x^{(\text{Breit})} = \frac{\beta}{\pi} \left\{ 1 - \frac{2}{\beta E_F} \ln(\beta + E_F) + \frac{2}{\beta^2} \ln E_F \right\} \quad (3.6)$$

It may be noted here that $\epsilon_x^{(\text{Breit})} < \epsilon_x^{(\text{tr})}$ because the neglect of the energy denominator in the expression for $\epsilon_x^{(\text{tr})}$ decreases the integrand. We plot ϵ_x^{tr} and $\epsilon_x^{\text{Breit}}$ in Rydbergs in Fig. 5a and $v_x^{(\text{tr})}$ and $v_x^{(\text{Breit})}$ in Fig. 5b. We may also break up the full transverse interaction into the magnetic part and a part giving corrections to the Coulomb interaction due to retardation effects. Mann and Johnson (1962) and Johnson (1981).

$$\epsilon_m = \frac{3}{4\pi} \beta \left\{ -\frac{1}{2} + \frac{E_F}{2\beta} \ln(E_F + \beta) + \frac{9}{8\beta^4} [\beta E_F - \ln(E_F + \beta)]^2 \right\} \quad (3.7)$$

$$\epsilon_{\text{ret}} = \frac{3}{4\pi} \beta \left\{ \frac{1}{3} + \frac{1}{3} \beta^2 + \frac{1}{6} \frac{E_F}{\beta} \ln(E_F + \beta) - \frac{2}{3} \frac{E_F^4}{\beta^4} \ln(E_F) - \frac{1}{8\beta^4} [\beta E_F - \ln(E_F + \beta)]^2 \right\} \quad (3.8)$$

In the non-relativistic limit $\beta \rightarrow 0$

$$\epsilon^{\text{tr}} = \frac{3}{4\pi} \left(\frac{5}{9} \beta^2 \right) = \epsilon^{\text{Breit}} \quad (3.9a)$$

$$\epsilon_m = \frac{3}{4\pi} \left(\frac{2}{3} \beta^2 \right) \quad (3.9b)$$

$$\epsilon_{Ret} = \frac{3}{4\pi} \left(-\frac{1}{9} \beta^2 \right) \quad (3.9c)$$

B. A Self-Consistent Atomic Calculation For Mercury and Fermium

We have modified the relativistic Dirac-Slater program due to Liberman et al. (1971) to include the full relativistic Coulomb and transverse exchange as given by Rajagopal (1978) and MacDonald and Vosko (1979). Our tabulated values (Ramana and Rajagopal, 1981a) for the total relativistic correlation energy per particle and the total correlation potential were fit to a cubic spline as a function of β for calculation at any density. We also integrated numerically the expressions of von Barth and Hedin (1972), for the paramagnetic gas and fit the values to a cubic spline as well. The correlation contribution to the total energy of ^{80}Hg and ^{100}Fm and to the 1s binding energy in the frozen orbital approximation were evaluated both in the full SCF and perturbatively (Ramana and Rajagopal, 1981c). The SCF contribution of the correlation to the 1s binding energy is

$$E_{c,SCF}^{1s} = \{E(N) - E(N-1)\} - \{E^O(N) - E^O(N-1)\} \quad (3.10)$$

The first term in the braces is the frozen orbital binding energy with correlation included in the SCF scheme while the second term in braces is the binding energy without correlation. The contribution to the total energy is as usual

$$E_c^{\text{SCF}} = \int \epsilon_c(\rho) \rho(\vec{r}) d^3r \quad (3.11)$$

where ρ is the full self-consistent charge density. The perturbative contribution to the binding energy is given by

$$E_{c;\text{pert}}^{\text{ls}} = \int \epsilon_c(\rho_N^0) \rho_N^0(\vec{r}) d^3r - \int \epsilon_c(\rho_{N-1}^0) \rho_{N-1}^0(\vec{r}) d^3r \quad (3.12)$$

where ρ_N^0 is the SCF charge density without correlation for N electrons. The perturbative contribution to the total energy is

$$E_{c;\text{pert}} = \int \epsilon_c(\rho^0) \rho^0(\vec{r}) d^3r \quad (3.13)$$

Expressions similar to (3.10-3.13) were used for the transverse contributions and the Breit contributions.

In Table II we show the results of our correlation calculation for mercury and fermium. In the first three rows we list the correlation contribution to the total energy and in the last three, the contribution to the 1s binding energy. There is hardly any difference between the perturbative and SCF calculation for the contribution to the total energy. However, for the 1s binding energy SCF changes the perturbative result by about 0.09 a.u. The total correlation contribution in the local density scheme is seen to be much larger than that estimated by Cowan (1967). At this point we must recall the remarks of Cowan (1967) and also of Tong (1971). Because of the highly localized nature of atomic electrons, correlation effects calculated using the free electron gas results in local scheme are much over-estimated and we expect this to be more so in the inner electrons of heavy atomic systems. That this may be the case is also seen from the excellent agreement between DF (Dirac-Fock) results including Lamb shift and vacuum polarization corrections of Huang et al. (1976) and highly accurate experimental data of Bearden and Burr (1967) and Deslattes (1980). The systematic difference in that case is less than 10 eV.

A comparison of the relativistic and non-relativistic correlation energies shows that in the case of mercury the

relativistic correlation contribution is about -0.2 a.u. to the total energy and about -0.4 a.u. for fermium. This contribution is in the right direction since the relativistic correlation energy per particle and potential lie below their non-relativistic counterparts at high densities for the homogeneous electron gas (Ramana and Rajagopal, 1981). In the case of the $1s$ binding energies (rows 4 and 5 in Table II) the relativistic correlation contribution is ≈ -0.08 a.u. for mercury which grows to ≈ -0.15 a.u. for fermium. The relativistic contribution to the correlation energy is not large due to the fact that only a very small number of inner electrons are relativistic.

In Figures 6a and 6b we have plotted our correlation contribution to the K_{α_1} and K_{α_2} lines versus the square root of the K_{α_1} and K_{α_2} energies respectively expressed in KeV. The straight line is a linear regression fit of differences between the theoretical calculations of Huang et al. (1976) and the experimental results of Deslattes et al. (1980). The correlation contribution is not large enough to explain the discrepancies or even the trend. The improvements (Deslattes et al. 1980) being carried out in the theoretical calculations of Huang et al. (1976) like using the transverse interaction instead of the Breit and including it in the SCF, using a more realistic nuclear charge distribution, and the

experimental remeasurements may give a clearer picture of the actual correlation contributions. In Table III we give our values for the correlation contributions to the K_{α_1} and K_{α_2} energies and the total energy for various values of Z . In Fig. 7 we plot the correlation contribution in a.u. to the total energy versus Z . The function $0.058 Z^{1.18}$ fits this curve within 1.5%.

Table IV presents the Breit and transverse contributions to the 1s binding energy in mercury and fermium. In the first column we show the 1s binding energy and in the next four columns we show the results of the perturbative calculation of the transverse, Breit, magnetic contribution to the transverse and the retarded contribution to the transverse exchange energy respectively. The sixth column is the perturbative result of the DF calculation of Mann and Johnson (1971). The last two columns are the Breit and transverse contributions in the SCF calculation. A comparison of the transverse and Breit contributions in mercury shows that the frequency dependence contributes about 1 a.u. in both perturbation theory and SCF, while SCF reduces the perturbative result by about 0.8 a.u. These effects are larger in fermium. The major contribution to the transverse energy is from the magnetic part of which a relatively small amount is cancelled by the negative retardation

correction to the Coulomb interaction. A comparison of our result with that of Mann and Johnson (1971) shows a difference of almost ~ 3.6 a.u. This difference is much larger in the case of the transverse contribution to the total energy which is displayed in Table V. The frequency dependence contributes about 1.6 a.u. in mercury and about 5.2 a.u. in fermium. The SCF contributes very little. A comparison of the results of Mann and Johnson (1971) for magnetic and retardation energy contributions to the total energy in perturbation theory shown in the last two columns with our perturbative theory results shown in the sixth and seventh columns shows our result to be almost 1.7 times as large. This difference persists for all the heavy atoms investigated. We believe that the difference is due to non-local effects. However, the total energies in LDS lie above those of DF values as they should be. In the non-relativistic limit the ratio $E'_{\text{ret}}/E'_m \sim -\frac{1}{6}$ as remarked by Mann and Johnson (1971) while their calculations give $\sim -1/10$. This ratio goes to -1 for $\beta \gg 1$. We get for our two cases a value close to $\sim -1/5$. In Mann and Johnson's (1971) DF calculations, the Breit energy is larger than their transverse interaction energy, in contrast to our local results, as remarked earlier after (3.6).

(i) We have calculated the correlation contribution for mercury and fermium using our previous results (Ramana and ajagopal, 1981). We find that the correlation contributions are much larger than previously estimated. We may have however overestimated the effect of correlation since our relativistic LD calculation shares the same objections of the non-relativistic ones. We find that the contributions to correlation due to relativistic effects quite small in an actual atom even though the correlation energies and potentials for the relativistic and non-relativistic electron gas show dramatic differences. We suggest that this is due to the small number of electrons that are relativistic even in an atom such as Fm.

We have plotted the trends, across the period table of the correlation contributions to the K_{α} energies and to the total energy. The correlation contribution to the K_{α} lines is roughly half the discrepancy between accurate theoretical and experimental results. Even the trends are different.

(ii) Breit versus transverse interaction. We calculated the contributions of Breit and transverse interaction energies in mercury and fermium and compared our results with those of Mann and Johnson's (1971) DF calculations. We found that the LD estimate for the transverse term about ~ 1.7 times larger than the DF result.

We attribute this difference to non-local effects. This may be seen even in the non-relativistic case for the exchange term (Perdew and Zunger, 1981). Huang et al. (1976) using a single determinant constructed out of the self-consistent wave functions from a local density calculation (using $\rho^{1/3}$ potential) evaluate the expectation value of the full Hamiltonian and get results in closer agreement to those of Mann and Johnson (1971) than ours. We find that the Breit term gives the major part of the transverse contribution but that the frequency dependence is important if comparison is to be made with experiment. Even though this calculation is not variational it points to the fact that non-local effects may indeed be significant.

(iii) SCF versus perturbation theory. We have also assessed the importance of SCF for the transverse and correlation contributions and found that SCF makes a difference in the contributions to the binding energy but practically no difference was found between SCF and perturbation theory results for the contributions to the total energy. This is because the levels are more sensitive to the changes in potential in SCF.

(iv) Other effects. Our calculation has not included relaxation effects which are important for the binding energies and effects due to the finite nuclear size which are important for the inner electrons. Lamb

shift and vacuum polarization contributions are much larger than correlation contributions for the inner shells and have been tabulated by Huang et al. (1976). All these effects have to be included if a comparison is to be made with experiment. We expect a local spin density functional formalism to give a better description as in the non-relativistic case.

TABLE CAPTIONS

Table

- II Relativistic (R) and non-relativistic (NR) contributions in atomic units to the total energy and to the 1s binding energy both in SCF and perturbation (pert) theory. The binding energies are obtained using frozen orbitals.
- III Correlation contribution in eV to the K_{α} energies and in a.u. to the total energy.
- IV Breit and transverse (magnetic plus retarded) contributions in atomic units to the 1s binding energy. The first column is the 1s binding energy including the transverse term, the next four columns are from perturbative calculations while the last two are SCF contributions.
- V Breit and transverse (tr) contributions in atomic units to the total energy (first column) in SCF and perturbation (pert) theory. Perturbative contribution is $\int \epsilon_{\mathbf{x}}^{\text{tr}} \rho^{\circ}(\mathbf{r}) d^3\mathbf{r}$ where ρ° is calculated without the transverse potential. For Hg and Fm the ratio of $E'_{\text{ret}}/E'_m \sim -1/5$. The last two columns are from Ref. 4.

	Hg	Fm
$-E_{C;R}^{(pert)}$	10.3502	13.5236
$-E_{C;NR}^{(pert)}$	10.1597	13.1073
$-E_{C;R}^{(SCF)}$	10.3537	13.5274
$-E_{C;R}^{1s(pert)}$	0.292	0.375
$-E_{C;NR}^{1s(pert)}$	0.215	0.228
$-E_{C;R}^{1s(SCF)}$	0.203	0.277

Table II.

	$E_{\text{cr}}[K_{\alpha}] - E[K_{\alpha}]$		$-E_{\text{cr}}(\text{a.u.})$
	$K_{\alpha_2}(\text{eV})$	$K_{\alpha_1}(\text{eV})$	
Ne	0.3102	0.3129	0.8982
Ca	0.5714	0.5742	1.9568
Zn	0.7646	0.7755	3.2819
Zr	0.9034	0.9224	4.4985
Sn	1.1211	1.1565	5.8903
Nd	1.4231	1.4939	7.2465
Yb	1.8014	1.9211	8.8092
Hg	2.2667	2.4545	10.3537
U	3.0259	3.3389	12.1466
Fm	3.6001	4.1362	13.5274

Table III.

	E^{ls}	E_x^{tr}	E_x^{Breit}	E'_m	E'_{Ret}	$E^{tr}(MJ)$	$E^{ls;Breit}$	$E^{ls;tr}$
Hg	-3058.8097	15.02	14.03	18.93	-3.91	11.3742	13.26	14.21
Fm	-5236.9692	31.58	28.52	41.24	-9.66	-	26.98	29.89

Table IV.

	E_{LD}	$E_x^{tr;SCF}$	$E_x^{Breit;SCF}$	$E_x^{tr;pert}$	$E_x^{Breit;pert}$	$E'_m(pert)$	$E'_{ret}(pert)$	$E'_m(MJ)$	$E'_{ret}(MJ)$
Hg (full SCF)	-19602.26	34.00	---	---	---	---	---	---	---
Hg (Tr or Br in Pertn Th)	-19636.39	---	32.48	34.25	32.69	42.47	-8.23	24.50	-2.33
Em (full SCF)	-34801.74	78.32	---	---	---	---	---	---	---
Fm (Tr or Br in Pertn Th)	-34880.41		73.12	79.02	73.69	100.33	-21.31	---	---

Table V.

FIGURE CAPTIONS

- Fig. 6a Correlation contribution in eV to the K_{α_1} line plotted versus the square root of energy in KeV. The straight line is from Ref. 15.
- Fig. 6b Same as a, for K_{α_2} line.
- Fig. 7 Plot of the correlation contribution in a.u. to the total energy as a function of atomic number Z . The trend is not linear in Z but has an exponent of 1.18 ($\sim 0.058 Z^{1.18}$).

Fig. 6a

Fig. 6b

Fig. 7

CHAPTER IV

A. Relativistic Spin Density Functional Formalism

Consider again the system given by the Hamiltonian (2.1). We are now interested in the effects of spin polarization of the electron gas (Ramana and Rajagopal 1981b). In the relativistic theory however spin is closely coupled to the kinetic motion of the particle and is not a good quantum number (see for example Sakurai 1973). To study the effects of the spin we take the viewpoint discussed by MacDonald and Vosko (1979). Instead of an external interaction term of the form $j^\mu A_\mu^{(\text{ext})}$ which contains all the electrodynamics of electronic systems, the non-relativistic viewpoint is taken in that the external fields are those which couple to the particle and spin densities only:

$$H_{\text{ext}} = e \int d^3r \quad : \bar{\psi}(x) \gamma_0 \psi(x) : A_{\text{ext}}^0(x) \\ - : \bar{\psi}(x) \sigma_{\mu\nu} \psi(x) : F_{\text{ext}}^{\mu\nu}(x)$$

The field $F_{\text{ext}}^{\mu\nu}$ is a purely fictitious field which couples to the spin only and serves to lift the spin degeneracy.

In principle, specification of A_{ext}^μ fixes $F_{\text{ext}}^{\mu\nu}$. But we would like to deal with them as given classical objects. As examples one may cite the $A_\mu^{(\text{ext})}$ arising

from the nuclei leading to the hyperfine interaction, Coulomb interaction etc., (Harriman, 1978). In this case the non-degenerate ground state energy is a functional of the expectation values of the four-current density and the magnetization density and the correct densities minimize the ground state energy for a given external potential. The result of Kohn-Sham (1965) can also be generalized and an effective one-particle Dirac equation for an inhomogeneous electron system may be written down. (For details see Rajagopal (1980)).

$$\begin{aligned}
 & [-i\vec{\alpha} \cdot \vec{\nabla} - m(1-\beta) + V_{\text{eff}}(\vec{r}, \vec{J}_\mu, \vec{m}) + \vec{\Sigma} \cdot \vec{W}_{\text{eff}}(\vec{r}, \vec{J}_\mu, \vec{m})] \phi_i(\vec{r}) \\
 & = \epsilon_i \phi_i(\vec{r})
 \end{aligned} \tag{4.1}$$

where

$$\begin{aligned}
 V_{\text{eff}} = & - \left(V_{\text{ext}}(\vec{r}) + e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' + \frac{\delta E_{\text{xc}}}{\delta n(\vec{r})} \right) \\
 & - e\vec{\alpha} \cdot \left(\vec{A}_{\text{ext}} + \int \frac{\vec{J}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' + \frac{\delta E_{\text{xc}}}{\delta \vec{J}(\vec{r})} \right)
 \end{aligned} \tag{4.2}$$

$$W_{\text{eff}} = -e \left(\vec{B}_{\text{ext}} + \frac{\delta E_{\text{xc}}}{\delta \vec{m}(\vec{r})} \right) \tag{4.3}$$

where $\vec{\alpha}$, β and $\vec{\Sigma}$ matrices are related to the Dirac matrices by $\vec{\gamma} = \beta \vec{\alpha}$, $\gamma_0 = \beta$ and $\Sigma^k \equiv \sigma^{ij} = \frac{1}{2} (\gamma^i \gamma^j - \gamma^j \gamma^i)$, i, j, k cyclic and in the ground state the particle density

$$n(\vec{r}) = \sum_{i(\text{occ})} \text{tr}(\phi_i^*(\vec{r}) \phi_i(\vec{r})) , \quad (4.4a)$$

the current density

$$J_k(\vec{r}) = \sum_{i(\text{occ})} \text{tr}(\phi_i^*(\vec{r}) \alpha_k \phi_i(\vec{r})) \quad (4.4b)$$

and the magnetization density

$$m_k(\vec{r}) = \sum_{i(\text{occ})} \text{tr}(\phi_i^*(\vec{r}) \Sigma_k \phi_i(\vec{r})) \quad (4.4c)$$

and E_{xc} is the exchange correlation contribution to the ground state energy of the system. It is a functional, in general, of J_μ , and $\vec{m}$. As a convenient scheme, one often evaluates E_{xc} for an interacting homogeneous electron gas, which then gives rise to a "local" effective potential. In this scheme E_{xc} is a functional of n and $|\vec{m}|$ only since the currents $J_k = 0$ in the ground state.

The Green function for this N -electron system is defined in the usual way

$$S_F(x, x') = -i \langle T(\psi(x) \bar{\psi}(x')) \rangle \quad (4.5)$$

where T is the usual time ordering symbol, and $\langle \dots \rangle$ is the ground state expectation value. We now construct this Green function in momentum space for the non-interacting system, allowing explicitly for the appearance of spin.

In the formulation of the theory for a relativistic-spin-polarized gas we are faced with a difficulty not found in the non-relativistic theory in that the spin of the particle is not decoupled from its kinetic motion.

To resolve this difficulty we assume that each electron in its rest frame has its spin oriented along a fixed unit vector $\hat{n}$. In a frame at rest relative to a uniform positive background this electron has a momentum $\vec{p}$ and energy $p_0 = \sqrt{\vec{p}^2 + m^2} \equiv E_p$ in units of $\hbar = c = 1$ which we use throughout. The spin vector $(0, \hat{n})$ is then boosted to this frame such that (Björken and Drell, 1965)

$$s_\mu s^\mu = -1 \quad \text{and} \quad s_\mu p^\mu = 0 \quad (4.6)$$

which gives

$$s_0 = \frac{\hat{n} \cdot \vec{p}}{m}, \quad \vec{s} = \hat{n} + \left(\frac{E_p}{m} - 1 \right) \frac{(\vec{p} \cdot \hat{n}) \vec{p}}{|\vec{p}|^2}. \quad (4.7)$$

Using (4.5) and the standard plane wave expansions of Björken and Drell (1965) for $\psi(x)$,

$$\psi(x) = \sum_{\pm s} \int \frac{d^3 \vec{p}}{(2\pi)^3} \sqrt{\frac{m}{E_p}} \left[b(p, s) u(p, s) e^{-ip \cdot x} \right. \\ \left. + d^\dagger(p, s) v(p, s) e^{ip \cdot x} \right]$$

and that

$$\langle b^\dagger(p', s') b(p, s) \rangle = (2\pi)^3 \delta_{\vec{p}', \vec{p}} \delta_{s', s} n_{F_s}(p)$$

for electrons and similarly for positrons, we then obtain the Feynman propagator in momentum space

$$S_{F\alpha\beta}(p) = \sum_{\pm s} \left\{ \frac{(\not{p}_+ + m)(1 + \gamma_5 \not{s}_+)}{4E_p} \right\}_{\alpha\beta} \left\{ \frac{n_{F_s}(p)}{p_0 - E_p - i\eta} + \frac{1 - n_{F_s}(p)}{p_0 - E_p + i\eta} \right\} \\ - \sum_{\pm s} \left\{ \frac{(\not{p}_- + m)(1 + \gamma_5 \not{s}_-)}{4E_p} \right\}_{\alpha\beta} \left\{ \frac{1 - \bar{n}_{F_s}(p)}{p_0 + E_p - i\eta} - \frac{\bar{n}_{F_s}(p)}{p_0 + E_p + i\eta} \right\} \quad (4.8)$$

where

$$p_+^\mu = (E_p, \vec{p}) \quad , \quad s_+^\mu = (s_0, \vec{s}) \quad , \\ p_-^\mu = (-E_p, \vec{p}) \quad , \quad s_-^\mu = (-s_0, \vec{s}) \quad , \quad \not{s} = s^\mu \gamma_\mu, \quad \not{p} = p^\mu \gamma_\mu \quad (4.9)$$

and $n_F(\vec{p})$ is the Fermi function for the positive energy electrons and $\bar{n}_F(\vec{p})$ for the positrons. When $k_F = 0$, that is zero density, Equation (13) reduces to the familiar Feynman propagator. In our zero temperature theory the negative energy states are assumed filled ($\bar{n}_F = 0$) and there are no electrons above the Fermi level, $n_F(\vec{p}) = \theta(k_F - |\vec{p}|)$, where k_F is the Fermi momentum of the positive energy electrons of spin s . The density independent term in the second sum of Eq. (4.8) merely contributes to renormalizations and we may safely drop it and use the physical mass and charge (Bowers et al. (1973) and Jancovici (1962)). By this procedure we take care of the quantum electrodynamical renormalizations only. We still have the familiar density renormalizations of the ordinary many-body-theory. The above is a generalization of (2.43) with spin polarization incorporated. In the non-relativistic limit, $m \gg k_F$, it is seen that the propagator reduces to

$$S_F(p) \approx \sum_{\hat{n}} \left(\frac{1 + \vec{\sigma} \cdot \hat{n}}{2} \right) \left\{ \frac{n_{Fn}(\vec{p})}{p_0 - E_p - i\eta} + \frac{1 - n_{Fn}(\vec{p})}{p_0 - E_p + i\eta} \right\} \quad (4.10)$$

which is the usual non-relativistic limit of Rajagopal et al. (1967). $\vec{\sigma}$ here is the Pauli (2x2) spinor.

(i) The number of particles with momentum p is

$$N_p = \int \frac{dp_0}{2\pi i} \text{Tr}(S_F^<(p)\gamma_0) \quad (4.11)$$

where Tr stands for the trace over the γ -matrices. Using Eq. (4.8) we obtain

$$N_p = n_{F\uparrow}(E_p) + n_{F\downarrow}(E_p) \quad (4.12)$$

where $\uparrow$ and $\downarrow$ now refer to $\hat{n}$ and $-\hat{n}$. The total number of particles is then (Ω is the volume of the system)

$$\int \frac{d^3p}{(2\pi)^3} N_p = \frac{N}{\Omega} = n. \quad (4.13)$$

(ii) The spin-magnetization of the system is given by

$$\vec{M}_p = \int \frac{dp_0}{2\pi i} \text{Tr}(\gamma_0 \vec{\Sigma} S_F^<(p)) . \quad (4.14)$$

Here $\vec{\Sigma}$ is the usual spin operator, the k th component of which is $(\gamma_i\gamma_j - \gamma_j\gamma_i)/2$, where i, j and k are cyclic. Using Eq. (4.8) we obtain, upon performing the trace over the γ -matrices,

$$\vec{M}_p = (m\vec{s}/E_p) (n_{F\uparrow}(E_p) - n_{F\downarrow}(E_p)) . \quad (4.15)$$

The total magnetization is then

$$\frac{\vec{m}}{\Omega} = \int \frac{d^3 p}{(2\pi)^3} \vec{M}_p = \int \frac{d^3 p}{(2\pi)^3} \frac{m\vec{s}}{E_p} (n_{F\uparrow}(E_p) - n_{F\downarrow}(E_p)) . \quad (4.16)$$

This has an interesting consequence. $\vec{m}$ can be shown to be in the direction of $\hat{n}$. In the non-relativistic limit, $m\vec{s}/E_p \approx \vec{n}$ and we obtain the well known result (see Rajagopal et al. 1967) that $m_{NR} = (\hat{n}/\Omega)(N_{\uparrow} - N_{\downarrow})$, where $N_{\uparrow}$ and $N_{\downarrow}$ are the total number of electrons aligned parallel and antiparallel to $\hat{n}$. One often defines, in this limit, a parameter ζ called the relative magnetization:

$$\zeta = |m_{NR}|/N = (n_{\uparrow} - n_{\downarrow})/(n_{\uparrow} + n_{\downarrow}) \quad (4.17)$$

which varies between 0 and 1. For non-interacting electrons, we can perform the integrations in Eq. (4.16) upon introducing ζ now as a parameter. Defining

$$\xi = |m|/n$$

we obtain

$$\xi = \frac{1}{2\beta^3} \left\{ \left[\frac{1}{3} \beta^3 x^3 + \beta x (1 + \beta^2 x^2)^{1/2} - \sinh^{-1}(\beta x) \right] - [x \rightarrow y] \right\} \quad (4.18)$$

where $x = (1+\zeta)^{1/3}$, $y = (1-\zeta)^{1/3}$ and $\beta = k_F/m(\hat{M} k_F/mc)$. Thus $\xi_{NR} \rightarrow \zeta$. In the ultra-relativistic limit ($\beta \gg 1$), one obtains

$$\xi_{UR} \rightarrow \frac{1}{3} \zeta . \quad (4.19)$$

The factor $1/3$ is easily understood, if we go back to Eq. (4.16) and note that helicity is a good quantum number, and that $p(p \cdot \hat{n})$ integrated over the Fermi sphere leads to the average of $\cos^2 \theta$ over a unit sphere giving the factor $1/3$. This is an interesting feature of the relativistic theory.

Equipped with the propagator, we now compute the ground state energy of the many-electron system whose Hamiltonian includes, besides the static Coulomb interaction, the transverse photon contribution, in the Hartree-Fock approximation. We are led to the expression

$$\langle H \rangle_{HF}/\Omega = T + E_C^{(x)} + E_{tr}^{(x)} \quad (4.20)$$

where T is the average kinetic energy, $E_C^{(x)}$ is the exchange energy arising from the bare Coulomb interaction between electrons, and $E_{tr}^{(x)}$ is the contribution to the exchange energy from the transverse photon-electron interactions. The actual expressions involved contain traces over γ -matrices and integrals over momenta. We

FIGURE CAPTION

Fig. 8 Plot of the magnetization of the polarized relativistic gas versus the parameter ζ .

Fig. 8

can evaluate T explicitly and it is given by

$$T = (3/\beta^5) n E_F \left\{ (\beta x/8) (2x^2 \beta^2 + 1) (\beta^2 x^2 + 1)^{1/2} - \frac{1}{3} \beta^3 x^3 - \frac{1}{8} \sinh^{-1}(\beta x) + (x+y) \right\} \quad (4.21)$$

where $E_F = k_F^2/2m$ and $n = k_F^3/3\pi^2$.

B. Exchange Energy in a Homogeneous Spin-Polarized Electron Gas

The contribution to the Coulomb part of the exchange energy is

$$E_x^{(c)} = -2\pi e^2 \iint \frac{d^3 p d^3 p'}{(2\pi)^6} \frac{1}{|p-p'|^2} \iint \frac{dp_o dp_o'}{(2\pi)^2} \text{tr}[\gamma_o S_F^<(p) \gamma_o S_F^<(p')] \quad (4.22)$$

$$= -2\pi e^2 \sum_{n,n'} \iint \frac{d^3 p d^3 p'}{(2\pi)^6} \frac{1}{|p-p'|^2} \frac{1}{16E_p E_{p'}} n_{Fn}^{\wedge}(E_p) n_{Fn'}^{\wedge}(E_{p'})$$

$$\text{Tr}[\gamma_o (\not{p}+m) (1+\gamma_5 \not{s}) \gamma_o (\not{p}'+m) (1+\gamma_5 \not{s}')] .$$

The trace may be carried out to give

$$\begin{aligned}
E_x^{(c)} = & \frac{-e^2}{(2\pi)^3} k_F^4 \sum_{\hat{n}, \hat{n}'} \iint \frac{d^3x d^3x'}{(4\pi)^2} \frac{1}{|\vec{x} - \vec{x}'|^2} \frac{1}{E_x E_{x'}} \\
& \left\{ (1 + E_x E_{x'} + \vec{x} \cdot \vec{x}') (1 + s_O s_O' + \vec{s} \cdot \vec{s}') - s_O s_O' E_x E_{x'} \right. \\
& \left. - s_O E_x (\vec{s}' \cdot \vec{x}) - s_O' E_{x'} (\vec{s} \cdot \vec{x}') - (\vec{x} \cdot \vec{s}') (\vec{s} \cdot \vec{x}') \right\}
\end{aligned}
\tag{4.23}$$

Similarly for the transverse term we have

$$\begin{aligned}
E_x^{(tr)} = & -2\pi e^2 \iint \frac{d^3p d^3p'}{(2\pi)^6} \iint \frac{dp_O dp_O'}{(2\pi)^2} \mathcal{D}_T^{ij}(p-p') \\
& \text{tr}[\gamma_i S_F^<(p) \gamma_j S_F^<(p')]
\end{aligned}
\tag{4.24}$$

where $\mathcal{D}_T^{ij}(p-p')$ is the transverse photon propagator given by Bjorken and Drell (1965) and p, p' are energy momentum four vectors

$$\begin{aligned}
E_x^{(tr)} = & -2\pi e^2 \sum_{\hat{n}, \hat{n}'} \iint \frac{d^3p d^3p'}{(2\pi)^6} \frac{[\delta_{ij} - q_i q_j / q^2]}{[(E_p - E_{p'})^2 - (\vec{p} - \vec{p}')^2]} \frac{1}{16 E_p E_{p'}} \\
& n_{F\hat{n}}(E_p) n_{F\hat{n}'}(E_{p'}) \text{Tr}[\gamma_i (\not{p} + m) (1 + \gamma_5 \not{s}) \gamma_j (\not{p}' + m) (1 + \gamma_5 \not{s}')]
\end{aligned}
\tag{4.25}$$

The traces over the γ -matrices were evaluated and the resulting expressions are given in Appendix A. A look at the various terms in Equations A1 and A2 in the Appendix shows that their structure is similar to the various spin-spin, spin-own orbit, spin-other orbit, etc. interactions which appear in two electron theory (Harriman, 1978).

In the non-relativistic limit

$$E_{\text{xNR}}^{(c)} \approx - \frac{e^2}{(2\pi)^3} k_F^4 [x^{4/3} + y^{4/3} - \frac{1}{9} \beta^2 (x^6 + y^6)] \quad (4.26)$$

and

$$\begin{aligned} E_{\text{xNR}}^{(\text{tr})} \approx & \frac{e^2}{(2\pi)^3} k_F^4 \left(\frac{2}{3} \beta^2 \right) \left\{ \frac{5}{18} (x^6 + y^6) \right. \\ & + \frac{1}{9} x^3 y^3 + \frac{1}{2} (xy^5 + x^5 y) \\ & \left. + \frac{1}{4} (x^2 y^4 + x^4 y^2 - x^6 - y^6) \ln \left| \frac{x+y}{x-y} \right| \right\} \quad (4.27) \end{aligned}$$

The transverse term is of order β^2 in the low β limit as it should be. Also, when we set $\lambda=0$ we recover the old nonmagnetic results.

We have plotted in Fig. 9 the total energy per particle which includes the kinetic and Coulomb and transverse exchange as a function of the magnetization parameter ζ

FIGURE CAPTIONS

- Fig. 9 Curves for the total energy/particle scaled to the relativistic Fermi energy versus the polarization parameter ζ for various values of $\beta (=k_F/m = 1/71.4r_S)$.
- Fig. 10 Plot of β_c versus ζ_c such that $E_x^{(c)}(\beta_c, \zeta_c) + E_x^{(tr)}(\beta_c, \zeta_c) = 0$. The total exchange energy is positive above this curve and negative below it.

Fig. 9

Fig. 10

for various values of β . The energy per particle is scaled to the relativistic Fermi energy $(k_F^2 + m^2)^{1/2} - m$. At the very low density of $\beta = 0.001$ we see that the ground state is fully polarized in this approximation which is the non-relativistic result.

At higher densities the kinetic energy is the dominant term and the ground state is a state of zero polarization in the absence of a magnetic field. In the unpolarized case the transverse and Coulomb parts of the exchange cancel each other at $\beta = 2.533$. We reproduce this cancellation with our numerical integration. This cancellation persists for non-zero values of ζ at larger densities. Figure 10 is a plot of this critical density and polarization parameter. The exchange is positive above this curve and negative below it. In Table VI we present a list of values for the total exchange energy as a function of density and the magnetization parameter ζ .

C. Effective Exchange Potentials of the Relativistic Spin Density Functional Theory

In a local spin density approximation, the potentials V_{xc} and W_{xc} may be computed from our expressions for E_{xc} in the usual way

TABLE CAPTION

Table VI. Representative values of the total exchange energy/particle $E_x(\beta, \zeta) = E_x^{(c)}(\beta, \zeta) + E_x^{(tr)}(\beta, \zeta)$ scaled to the relativistic kinetic energy $\sqrt{k_F^2 + m^2} - m$ at the Fermi level.

$\beta \backslash \zeta$	0.0	0.2	0.4	0.6	0.8	1.0
0.01	-0.348	-0.351	-0.361	-0.377	-0.402	-0.439
0.1	-0.0347	-0.0350	-0.0360	-0.03776	-0.0401	-0.0438
0.5	-0.00631	-0.00642	-0.00672	-0.00716	-0.00775	-0.00856
1.0	-0.00241	-0.00259	-0.00298	-0.00350	-0.00410	-0.00475
1.5	-0.00106	-0.00110	-0.00191	-0.00263	-0.00342	-0.00423
2.0	-0.000392	-0.000790	-0.00157	-0.00249	-0.00346	-0.00440
2.533	0.0	-0.000522	-0.00150	-0.00259	-0.00365	-0.00461
3.0	+0.000215	-0.000382	-0.00162	-0.00278	-0.00362	-0.00412

Table VI.

$$V_{xc} = \frac{\delta E_{xc}}{\delta n} = \frac{\delta E_{xc}^{(c)}}{\delta n} + \frac{\delta E_{xc}^{(tr)}}{\delta n} \equiv V_{xc}^{(c)} + V_{xc}^{(tr)} \quad (4.28)$$

$$W_{xc} = \frac{\delta E_{xc}}{\delta |\vec{m}|} = W_{xc}^{(c)} + W_{xc}^{(tr)} \quad (4.29)$$

However, since E_{xc} is most simply expressed in terms of $k_{F\uparrow}$ and $k_{F\downarrow}$, which are the Fermi momenta of "up" and "down" spin electrons related to the particle and magnetization densities as given in I, we have

$$\frac{\delta E_{xc}}{\delta n} = \frac{\delta E_{xc}}{\delta k_{F\uparrow}} \left(\frac{\partial k_{F\uparrow}}{\partial n} \right)_{k_{F\downarrow}} + \frac{\delta E_{xc}}{\delta k_{F\downarrow}} \left(\frac{\partial k_{F\downarrow}}{\partial n} \right)_{k_{F\uparrow}} \quad (4.30)$$

and

$$\frac{\delta E_{xc}}{\delta |\vec{m}|} = \frac{\delta E_{xc}}{\delta k_{F\uparrow}} \left(\frac{\partial k_{F\uparrow}}{\partial |\vec{m}|} \right)_{k_{F\downarrow}} + \frac{\delta E_{xc}}{\delta k_{F\downarrow}} \left(\frac{\partial k_{F\downarrow}}{\partial |\vec{m}|} \right)_{k_{F\uparrow}} \quad (4.31)$$

so that we may use the expressions for n and $|\vec{m}|$ to find the potentials. Since the magnitude of the magnetization is no longer simply $(k_{F\uparrow}^3 - k_{F\downarrow}^3)/6\pi^2$ as in non-relativistic theory, we must use

$$\frac{\partial k_{F\uparrow,\downarrow}}{\partial n} = \frac{\pi^2 E_{x\uparrow,\downarrow}}{k_{F\uparrow,\downarrow}^2} \frac{(2 + E_{x\uparrow,\downarrow})}{(E_{x\uparrow} + E_{x\downarrow} + E_{x\uparrow} E_{x\downarrow})} \quad (4.32a)$$

$$\frac{\partial k_{F\uparrow,\downarrow}}{\partial |\vec{m}|} = \frac{3\pi^2}{k_{F\uparrow,\downarrow}^2} \frac{E_{x\uparrow} E_{x\downarrow}}{(E_{x\uparrow} + E_{x\downarrow} + E_{x\uparrow} E_{x\downarrow})} \quad (4.32b)$$

In the following we present results based on exchange contributions to E_{xc} which we denote by E_x . Since the Fermi momentum for "up" and "down" spin electrons $k_{F\uparrow}$ and $k_{F\downarrow}$ appear as upper limits in the integrals for E_x and not in the integrands the required differentiations may be done simply and the double integrals reduce to a single one which is then evaluated numerically.

In Fig. 11 we present a plot of V_x as a function of β and ζ . It is seen that the range of β , ζ cancellation is slightly larger than that of the exchange energy. This is displayed as an inset in Fig. 8. Over most of the range of β , ζ investigated the exchange potential is negative. Our numerical calculation reproduces known results in the following cases:

i) For $\zeta = 0$ we obtain the result of Rajagopal (1978)

$$\text{ii) For } \beta \ll 1, V_{x(NR)}^C = -\frac{\beta}{2\pi} [x_{\uparrow} + x_{\downarrow} + O(\beta^2)] \quad (4.33)$$

and

$$\begin{aligned} V_{xNR}^{(tr)} = & \frac{\beta}{4\pi} \beta^2 \left[\frac{2}{3} (x_{\uparrow}^3 + x_{\downarrow}^3) + x_{\uparrow} x_{\downarrow} (x_{\uparrow} + x_{\downarrow}) \right. \\ & \left. + \frac{1}{6x_{\uparrow} x_{\downarrow}} (x_{\uparrow} - x_{\downarrow})^4 (x_{\uparrow} + x_{\downarrow}) \ln \left| \frac{x_{\uparrow} + x_{\downarrow}}{x_{\uparrow} - x_{\downarrow}} \right| \right] \quad (4.34) \end{aligned}$$

where $x_{\uparrow} = k_{F\uparrow}/k_F = (1+\zeta)^{1/3}$ and $x_{\downarrow} = k_{F\downarrow}/k_F = (1-\zeta)^{1/3}$.

In Table VII, the values of V_x for a representative set of (β, ζ) are given. In Fig. 12 we present W_x as a function of β and ζ .

From the plot it is seen that W_x is nowhere positive. Its magnitude remains smaller than V_x for $\beta < 1$ as known from non-relativistic expressions. However, for values of $\beta > 1$ the magnitude of W_x rapidly becomes much larger than V_x . For heavy elements such as actinides this feature of W_x may play an important role in determining their magnetic properties. We again have the following limiting cases.

i) For $\zeta=0$, $W_x=0$ as it must

$$\text{ii) For } \beta \ll 1, W_{x(\text{NR})}^C = -\frac{\beta}{2\pi} [x_{\uparrow} - x_{\downarrow} + O(\beta^2)] \quad (4.35)$$

$$W_{x\text{NR}}^{(\text{tr})} = \frac{\beta}{4\pi} \beta^2 \left[\frac{4}{9} (x_{\uparrow}^3 - x_{\downarrow}^3) + x_{\uparrow} x_{\downarrow} (x_{\uparrow} - x_{\downarrow}) - \frac{1}{6x_{\uparrow} x_{\downarrow}} (x_{\uparrow} - x_{\downarrow}) (x_{\uparrow} + x_{\downarrow})^4 \ln \left| \frac{x_{\uparrow} + x_{\downarrow}}{x_{\uparrow} - x_{\downarrow}} \right| \right] \quad (4.36)$$

In Table VIII, the values of W_x for the same set of (β, ζ) values as those in Table VII are given.

For $\zeta=1$ we have that $|V_x| \neq |W_x|$ but

$$|V_x^{(c)}| = |W_x^{(c)}|, \quad (4.37a)$$

and

$$|V_x^{(tr)}| \neq |W_x^{(tr)}| \quad \text{for all } \beta ; \quad (4.37b)$$

and in particular,

$$|V_x^{(tr)}(\beta \ll 1)| \neq |W_x^{(tr)}(\beta \ll 1)| . \quad (4.37c)$$

This is unlike the non-relativistic case where the potentials felt by the charge and magnetization densities are the same for the fully ferromagnetic case. Here the potentials seen by the two densities are highly asymmetric. We trace this to the fact, as remarked in our earlier paper that in the ultrarelativistic limit fully saturated ferromagnetism is not possible. It should also be noted that if the spin unit vector $\hat{n}$ is parallel or antiparallel to the direction of momentum, i.e., eigenstates of helicity, then the net magnetization of the noninteracting gas is zero from isotropy.

From Figs. 11 and 12, it may be noted that for $\beta > 2$, V_x and W_x display a valley for ζ values close to unity. We believe that this feature is a manifestation of the same relativistic effect on the magnetized electron gas.

The behavior of the potential V_x is quite different from its non-relativistic counterpart as given by Eq.

TABLE CAPTIONS

Table VII. Representative values of the total exchange potential $V_x = V_x^{(c)} + V_x^{(tr)}$.

Table VIII. Representative values of the total exchange potential $W_x = W_x^{(c)} + W_x^{(tr)}$.

$\beta \backslash \zeta$	0.0	0.2	0.4	0.6	0.8	1.0
0.01	-0.0032	-0.0032	-0.0031	-0.0030	-0.0029	-0.0020
0.1	-0.0315	-0.0314	-0.0309	-0.0301	-0.0284	-0.0199
0.5	-0.1259	-0.1258	-0.1252	-0.1236	-0.1198	-0.0873
1.0	-0.1385	-0.1421	-0.1513	-0.1653	-0.1827	-0.1690
1.5	-0.0777	-0.0917	-0.1266	-0.1801	-0.2529	-0.3186
2.0	0.0101	-0.0209	-0.0970	-0.2113	-0.3753	-0.5331
2.5	0.1058	0.0513	-0.0795	-0.2710	-0.5178	-0.7255
3.0	0.2029	0.1186	-0.0794	-0.3603	-0.6966	-0.7538

Table VII.

ζ β	0.2	0.4	0.6	0.8	1.0
0.01	-0.0002	-0.0004	-0.0007	-0.0010	-0.0020
0.1	-0.0022	-0.0044	-0.0069	-0.0101	-0.0200
0.5	-0.0185	-0.03206	-0.0446	-0.0584	-0.1030
1.0	-0.1058	-0.1596	-0.1936	-0.2146	-0.2721
1.5	-0.3599	-0.5132	-0.5840	-0.5944	-0.5993
2.0	-0.8553	-1.1616	-1.2537	-1.1969	-1.0819
2.5	-1.6270	-2.0887	-2.1131	-1.8622	-1.6318
3.0	-2.6736	-3.2029	-2.9569	-2.2852	-2.1048

Table VIII.

(4.33). At low values of ζ , V_x changes sign while $V_x^{(NR)}$ is monotonic and of one sign. For $\zeta \approx 1$, $V_x \sim V_x^{(NR)}$ and they are of the same sign. The departure of W_x is more drastic from its non-relativistic value given by Eq.

(4.35). For $\beta > 1$ and $\zeta > 0$, the magnitude of W_x is much larger than that given by its non-relativistic expression

(4.35). As noted earlier, W_x is much larger than V_x for $\beta > 1$. The application of these potentials in a high Z solid state system should therefore be of considerable interest as we expect these potentials may help explain the magnetic properties of some actinides and some heavy rare earths.

It is of interest to note the following concerning correlation effects in the relativistic context. The correlation contribution does not seem to be as important in the relativistic case as in the non-relativistic case. While no calculation of correlation effects exist for the polarized electron gas one may get some idea of it from its behavior in the case of unpolarized gas (Ramana and Rajagopal (1981)). In the non-relativistic case in range $\beta \sim 0.002$ to 0.014 (corresponding to $r_s \sim 6-1$) the correlation potential drops from 44% of exchange potential to 14% and proceeding up in density at $\beta = 0.5$ where it has dropped to 1.3%. However, for larger β the transverse contribution being positive begins to dominate the exchange potential and the correlation contribution is the

major one to the total potential between $\beta = 1.75$ and 2.0 where the exchange potential goes through zero and drops again to only 8% of the exchange at $\beta = 2.25$. Thus the contribution of correlation to the total exchange-correlation potential is small at relativistic densities except in a narrow region where the Coulomb and transverse parts of the exchange cancel each other. The behavior of the energy is similar. We expect the correlation contribution to be small in the polarized case, too. It is therefore reasonable to use the exchange only scheme in the relativistic case as a reasonable approximation.

In order to derive the effects of spin-orbit interaction properly in a magnetic system such as Fe, Ni, Co, etc. in principle one must begin with a relativistic theory such as the one given here say, Eq. (47), take its non-relativistic limit. This procedure leads to additional contributions to the spin-orbit coupling. We give here this equation, without derivation:

$$\begin{aligned}
 & \frac{p^2}{2m} + v + \vec{\sigma} \cdot \vec{W} - \frac{p^4}{8m^3} - \frac{p^2 V}{8m^2} + \frac{i \vec{\sigma} \cdot [(\vec{p} V) \times \vec{p}]}{4m^2} - \frac{\vec{\sigma} \cdot \hat{n} (p^2 W)}{8m^2} \\
 & + \frac{i (\vec{\sigma} \cdot \hat{n}) (\vec{V} W \cdot \vec{p})}{4m^2} - \frac{i (\vec{\sigma} \cdot \vec{V} W) (\hat{n} \cdot \vec{p})}{4m^2} - \frac{\hat{n} \cdot (\vec{V} W \times \vec{p})}{4m^2} + \frac{(\vec{W} \cdot \vec{p}) (\vec{\sigma} \cdot \vec{p})}{2m^2} \\
 & - \frac{(\vec{\sigma} \cdot \vec{W}) p^2}{2m^2} + \frac{i (\vec{\sigma} \cdot \hat{n}) (\vec{V} W \cdot \vec{p})}{4m^2} + \frac{(\vec{p} \cdot \vec{W}) (\vec{\sigma} \cdot \vec{p})}{4m^2} \quad \psi = E^{(NR)} \psi
 \end{aligned}$$

where $\hat{n}$ is a unit vector in the direction of magnetization, $\vec{\sigma}$ is the usual Pauli matrix and $\vec{W} = \hat{n}W$. The first, second, fourth, fifth and sixth terms are the usual non-relativistic terms with spin orbit coupling. The third term is the analogue of the second, and seventh of the fifth and the ninth to the sixth. The others are additional terms, due to spin-polarization. It appears from this and the observations in Section IV that the additional contribution besides those arising from V_x are not small in comparison to it, even when one employs the non-relativistic expressions for V_{xc} and W_{xc} of the von Barth-Hedin form, for example. In the case of the unpolarized gas we obtain the result of MacDonald (1978).

FIGURE CAPTIONS

- Fig. 11 Plot of the relativistic exchange potential V_x as a function of density ($\beta = k_F/m$) and the spin polarization parameter ζ . The inset is a plot of critical values of β_c vs ζ_c for which transverse exchange potential cancels the Coulomb exchange potential. V_x is negative below and positive above the curve shown.
- Fig. 12 Plot of the relativistic exchange potential W_x as a function of ζ and β . W_x is nowhere positive.

Fig. 11

Fig. 12

CHAPTER V

SUMMARY, CONCLUSIONS, AND REMARKS

The need for relativistic calculations were felt very early and such calculations have been carried out with increasing sophistication since the 1940's. The recent band structure calculations of MacDonald et al. (1981) show that relativistic effects are important even for valence bands in platinum. The most complete and sophisticated such calculations for atoms which include Lamb shift and vacuum polarization corrections of Huang et al. (1976) show good agreement with the experimental results of Deslattes et al. (1980). However there is a systematic disagreement of a few eV. Further the Dirac-Fock scheme is complicated, for more complex systems, to be implemented in present day computers. It is also not easy to take correlation into account in the Dirac-Fock scheme. Since the density functional formalism and especially the spin density functional version has enjoyed great success in nonrelativistic theory its extension to the relativistic case seems appropriate (Rajagopal, 1978 and MacDonald and Vosko, 1979). Their relativistic exchange potential, including the transverse term, when applied to atoms (Das et al. 1980) leads to energies lying above the Dirac-Fock values, as they should, unlike the $\rho^{1/3}$ exchange potential used in the Dirac

equation.

It seems possible the few eV discrepancy between theory and experiment may be due to correlation contributions. To this end we have calculated the correlation contribution in the relativistic electron gas in the spirit of von Barth and Hedin (1972). To our knowledge the calculation of this correlation potential in a local approximation in the relativistic density functional theory is new. The relativistic results differ significantly from the non-relativistic ones at high densities. The approximations of Jancovici (1962) while close to our results at high densities do not go over to the proper non-relativistic values.

Using the program of Liberman (1971) we calculated the correlation contribution in several heavy atomic systems. The relativistic contributions to correlation, though quite marked in the gas, is not significant in the atoms we investigated. However, the contribution of correlation to the K_{α} , X-ray energies serves to explain some of the discrepancy between theory and experiment. It should be of some interest to examine the effects of relativistic correlation on the knight shift of heavy systems.

We have also assessed the role of the Breit interaction vis-a-vis the full transverse interaction. This

was done perturbatively within the Dirac-Fock scheme but not in the local density one. The Breit interaction is no simpler to use, in the local scheme, than the full transverse interaction. Therefore the transverse interaction can be used in SCF calculations though the Breit interaction is the major part of the transverse interaction. When examining the transverse contributions a comparison with the results of Mann and Johnson (1971) showed that non-local effects may indeed be significant.

In the second part of the thesis we have generalized the spin density functional formalism of the non-relativistic theory to the relativistic case. We have not seen such a treatment in the literature. We have calculated the exchange energy and the exchange potentials that appear in an effective one particle Dirac equation. A calculation of the magnetization of the polarized relativistic electron gas shows that in the ultrarelativistic limit full polarization is not possible. We attribute this to the fact that spin alone is not a good quantum number, but only the projection of spin along the direction of motion. A calculation of the total energy reveals that the ground state of the relativistic electron gas is always unpolarized. This is to be expected since the kinetic energy of the relativistic gas is very large. The improvement of the spin density functional over the density functional formalism in non-relativistic theory

encourages us to believe that this would be the case in relativistic theory too. An application of our potentials should reveal if this is the case. Such an application would be of special interest in the case of rare-earths and actinids.

In our method for the polarized electron gas we have allowed a fictitious magnetic field to polarize the electrons in the rest frame provided by the uniform positive background and then boosted the electrons to their final velocities. The magnetic field was no longer kept. This is the simplest procedure that can be followed. Any calculation in the explicit presence of the magnetic field is prohibitively complicated. However we believe that such a procedure would recover our results in the limit of vanishing field. The use of a fixed reference frame should also not pose any difficulties as such a frame is physically present in any atomic or solid state system.

A non-relativistic limit of the effective one particle Dirac equation in the relativistic local density theory yields contributions in addition to the usual spin orbit coupling arising from the Coulomb field. There is an additional contribution to the spin-orbit interaction due to the use of V_{eff} instead of the Coulomb potential $V(r)$ (MacDonald, 1978). Further there are new contributions which are analogues of the spin-orbit term etc.

and of the same order in v/c arising from the effective potential W (Ramana and Rajagopal, 1981b). An application of this in some physical system should be useful to gauge its importance.

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APPENDIX A

EQUIVALENCE OF THE EXPRESSIONS FOR THE DIELECTRIC CONSTANT GIVEN BY VARIOUS AUTHORS

Starting from Eq. (2.48) we derive explicitly the expressions for the polarizabilities Q_{oo} , Q_{ij} , Q_L and Q_T . We then show the equivalence of the expressions for the dielectric constant given by Jancovici (1962) and Tsytovich (1961).

We have for Q_{oo} , from (2.48)

$$\begin{aligned}
 Q_{oo}(q) = & 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{n_F(p)}{E_p E_{p+q}} \\
 & \frac{\left[(E_{p+q} E_p + E_p^2 + \vec{p} \cdot \vec{q}) (\omega + E_{p+q} - E_p) \right.}{\omega^2 - (E_{p+q} - E_p)^2} \\
 & \quad \left. - (E_p E_{p+q} + E_{p+q}^2 - (\vec{p} + \vec{q}) \cdot \vec{q}) (\omega + E_p - E_{p+q}) \right] \\
 & + 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{(1 - n_F(p))}{E_p E_{p+q}} \\
 & \frac{\left[(E_p^2 - E_p E_{p+q} + \vec{p} \cdot \vec{q}) (\omega - E_p - E_{p+q}) \right.}{\omega^2 - (E_{p+q} + E_p)^2} \\
 & \quad \left. - (E_{p+q}^2 - E_p E_{p+q} - (\vec{p} + \vec{q}) \cdot \vec{q}) (\omega + E_p + E_{p+q}) \right]
 \end{aligned} \tag{A.1}$$

In deriving this expression from (2.48) we have used the substitution $-p-q \rightarrow -p$ in terms occurring with $n_F(p+q)$ and then combined them. The numerators in the two integrands may be simplified by using $E_{p+q}^2 - E_p^2 = 2\vec{p} \cdot \vec{q} + q^2$ and some algebra. The result is (2.62a). The term independent of density in the second integral in (A.1) may be dropped after renormalizing the charge and mass.

The longitudinal polarizability may be similarly calculated

$$Q_L(q) = \frac{q_i q_j}{|\vec{q}|^2} Q_{ij}(q) \quad (A.2)$$

This gives,

$$Q_L(q) = \frac{4\pi e^2}{|\vec{q}|^2} \int \frac{d^3 p}{(2\pi)^3} \left\{ \frac{n_F(p) (E_{p+q} - E_p)^3 [-q^2 + (E_{p+q} + E_p)^2]}{E_p E_{p+q} [\omega^2 - (E_{p+q} - E_p)^2]} \right. \\ \left. + \frac{(1 - n_F(p)) (E_{p+q} + E_p)^3 [q^2 - (E_{p+q} - E_p)^2]}{E_p E_{p+q} [\omega^2 - (E_{p+q} + E_p)^2]} \right\} \quad (A.3)$$

By rewriting $(E_{p+q} - E_p)^3$ as $(E_{p+q} - E_p) \{(E_{p+q} - E_p)^2 - \omega^2 + \omega^2\}$ and separating out the terms proportional to ω^2 we have

$$\begin{aligned}
Q_L(q) \equiv & 4\pi e^2 \frac{\omega^2}{q^2} \int \frac{d^3 p}{(2\pi)^3} \left\{ \frac{n_F(p) (E_{p+q} - E_p) [(E_{p+q} + E_p)^2 - q^2]}{E_p E_{p+q} [\omega^2 - (E_{p+q} - E_p)^2]} \right. \\
& + \left. \frac{(1 - n_F(p)) (E_{p+q} + E_p) [q^2 - (E_{p+q} - E_p)^2]}{E_p E_{p+q} [\omega^2 - (E_{p+q} + E_p)^2]} \right\} \\
& + \frac{4\pi e^2}{q^2} \int \frac{d^3 p}{(2\pi)^3} \left\{ n_F(p) \frac{(E_{p+q} - E_p)}{E_p E_{p+q}} [q^2 - (E_{p+q} + E_p)^2] \right. \\
& + \left. (1 - n_F(p)) \frac{(E_{p+q} + E_p)}{E_p E_{p+q}} [(E_{p+q} - E_p)^2 - q^2] \right\}
\end{aligned}
\tag{A.4}$$

The last term in (A.4) can be shown to be zero by using algebra and the final substitution $\vec{p} \rightarrow \vec{p} - \vec{q}$ when the angular integral vanishes. The term independent of density may again be dropped.

Tsyrovitch defines,

$$\epsilon_L(q) = 1 - \frac{1}{\omega^2} Q_L(q) . \tag{A.5}$$

Jancovici has,

$$\begin{aligned}
\varepsilon_L(q) = 1 + \frac{4\pi e^2}{q^2} & \left\{ \int \frac{d^3k}{(2\pi)^3} \frac{n_F(k) (1-n_F(k+q))}{E_k E_{k+q}} \right. \\
& \cdot \frac{[(E_{k+q}+E_k)^2 - q^2] (E_{k+q}-E_k)}{[(E_{k+q}-E_k)^2 - \omega^2]} \\
& + \int \frac{d^3k}{(2\pi)^3} \frac{n_F(k+q) [(E_{k+q}-E_k)^2 - q^2] [E_{k+q}+E_k]}{E_k E_{k+q} [(E_{k+q}+E_k)^2 - \omega^2]} \left. \right\}
\end{aligned}
\tag{A.6}$$

In the first term of (A.6) we change $k \rightarrow -k-q$ and add dividing by two and in the second term we simply let $k \rightarrow -k-q$.

$$\begin{aligned}
\varepsilon_L(q) = 1 + \frac{4\pi e^2}{q^2} & \left\{ \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} [n_F(k) (1-n_F(k+q)) - n_F(k+q) (1-n_F(k))] \cdot \right. \\
& \left[\left(\frac{(E_{k+q}+E_k)^2 - q^2}{(E_{k+q}-E_k)^2 - \omega^2} \right) \frac{(E_{k+q}-E_k)}{E_k E_{k+q}} \right] \\
& + \int \frac{d^3k}{(2\pi)^3} n_F(k) \left(\frac{(E_{k+q}-E_k)^2 - q^2}{(E_{k+q}+E_k)^2 - \omega^2} \right) \frac{E_{k+q}+E_k}{E_k E_{k+q}} \left. \right\}
\end{aligned}
\tag{A.7}$$

$$\begin{aligned}
&= 1 + \frac{4\pi e^2}{q^2} \int \frac{d^3 k}{(2\pi)^3} \left\{ \left(\frac{(E_{k+q} + E_k)^2 - q^2}{(E_{k+q} - E_k)^2 - \omega^2} \right) \frac{E_{k+q} - E_k}{E_k E_{k+q}} n_F(k) \right. \\
&\quad \left. + \left(\frac{(E_{k+q} - E_k)^2 - q^2}{(E_{k+q} + E_k)^2 - \omega^2} \right) \frac{E_{k+q} + E_k}{E_k E_{k+q}} n_F(k) \right\} \quad (A.8)
\end{aligned}$$

which is (A.5).

For the transverse part we have

$$Q_T(q) = \frac{1}{2} \left(\delta_{ij} - \frac{q_i q_j}{q^2} \right) Q_{ij}(q) \quad (A.9)$$

$$Q_T(q) = 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \left(\frac{n_F(p) - n_F(p+q)}{\omega + E_p - E_{p+q}} \right) \frac{1}{E_p E_{p+q}}$$

$$\cdot \left[E_p E_{p+q} - m^2 - \frac{[(\vec{p} + \vec{q}) \cdot \vec{q}](\vec{p} \cdot \vec{q})}{q^2} \right]$$

$$- 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \left(\frac{1 - n_F(p)}{\omega + E_p + E_{p+q}} \right) \frac{1}{E_p E_{p+q}}$$

$$\left[E_p E_{p+q} + m^2 + \frac{[(\vec{p} + \vec{q}) \cdot \vec{q}](\vec{p} \cdot \vec{q})}{q^2} \right]$$

$$+ 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \left(\frac{1-n_F(p+q)}{\omega-E_p-E_{p+q}} \right) \frac{1}{E_p E_{p+q}}$$

$$\left[E_p E_{p+q} + m^2 + \frac{[(\vec{p}+\vec{q}) \cdot \vec{q}](\vec{p} \cdot \vec{q})}{q^2} \right]$$

Manipulating as in the longitudinal case gives

$$Q_T(q) = 8\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{n_F(p)}{E_p E_{p+q}} \left[\frac{E_p E_{p+q} - m^2 - \frac{[(\vec{p}+\vec{q}) \cdot \vec{q}](\vec{p} \cdot \vec{q})}{q^2}}{\omega^2 - (E_{p+q} - E_p)^2} \right]$$

$$\times (E_{p+q} - E_p)$$

$$+ 8\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{(1-n_F(p))}{E_p E_{p+q}} \left[\frac{E_p E_{p+q} + m^2 + \frac{[(\vec{p}+\vec{q}) \cdot \vec{q}](\vec{p} \cdot \vec{q})}{q^2}}{\omega^2 - (E_{p+q} + E_p)^2} \right]$$

$$\times (E_{p+q} + E_p) \quad (A.10)$$

This can be seen to match Tsytovich's result by rewriting the numerators in (A.10)

$$\begin{aligned}
& \frac{1}{E_p E_{p+q}} \left[E_p E_{p+q} - m^2 - \frac{(\vec{p} \cdot \vec{q})^2}{q^2} - \vec{p} \cdot \vec{q} \right] \\
& \quad m^2 + \frac{(\vec{p} \cdot \vec{q})^2}{q^2} + (p \cdot q) \\
& = 1 + \frac{\quad}{E_p E_{p+q}} \equiv \Lambda_t^{(-)} \text{ of Tsytovich}
\end{aligned}$$

and in the longitudinal case

$$\begin{aligned}
& \frac{1}{q^2 E_p E_{p+q}} \left[(E_{p+q}^2 - E_p^2)^2 - q^2 (E_{p+q} - E_p)^2 \right] \\
& = \frac{1}{q^2 E_p E_{p+q}} \left[(2\vec{p} \cdot \vec{q} + q^2)^2 - q^2 (E_{p+q}^2 + E_p^2 - 2E_p E_{p+q}) \right] \\
& = \frac{2}{q^2 E_p E_{p+q}} \left[q^2 (\vec{p} \cdot \vec{q}) + 2(\vec{p} \cdot \vec{q})^2 - q^2 E_p^2 - q^2 E_{p+q}^2 \right] \\
& = 2 \left[1 + \frac{\vec{p} \cdot \vec{q} + \frac{2(p \cdot q)^2}{q^2} - E_p^2}{E_p E_{p+q}} \right] \\
& \equiv \Lambda_\ell^{(-)} \text{ of Tsytovich.}
\end{aligned}$$

We have thus demonstrated the equivalence.

APPENDIX B

In this we indicate how to get to Eq. (3.1) from (2.61). The approximation $q \ll k_F$ and $\omega \ll E_F$ is made. Then the second term in the integrand of (2.62a) is negligible and the remaining integral simplifies and may be done (Jancovici, 1962 Appendix) to give (using $\omega \rightarrow i\omega$)

$$Q_{00}(q, \omega) \approx 4E_F \left\{ 1 - \frac{\omega E_F}{\beta q} \tan^{-1} \frac{\beta q}{\omega E_F} \right\}$$

This may be used in (2.61) in which the q integral is now cut off at k_F . The further substitutions $\omega/q = u$ and subsequently

$$\frac{u E_F}{\beta} = v \quad \text{and} \quad q = k_F x$$

enables us to perform the x integral resulting in (3.1). We have

$$\Delta E_{\text{corr}}^{(c)} \approx \frac{1}{8\pi^3} \frac{k_F^5}{\sqrt{k_F^2 + m^2}} \int_0^1 x^3 dx \int_{-\infty}^{\infty} dv$$

$$\log \left\{ \left(1 + \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F x^2} R \right) - \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F x^2} R \right\}$$

Note that R does not depend on x and is a function of v only. Integrating by parts with respect to x :

$$\begin{aligned}
 & \approx \frac{1}{8\pi^3} \frac{k_F^5}{\sqrt{k_F^2 + m^2}} \int_{-\infty}^{\infty} dv \left\{ \frac{x^4}{4} \left[\log \left(1 + \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F x^2} R \right) \right. \right. \\
 & \quad \left. \left. - \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F x^2} R \right] \right|_0^1 + \int_0^1 \frac{x^4}{4} dx \\
 & \quad \left[\frac{1}{1 + \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F x^2} R} - 1 \right] \frac{8e^2 \sqrt{k_F^2 + m^2}}{\pi k_F x^3} R \left. \right\} \\
 E_{\text{corr.}}^{(c)} & \approx \frac{1}{8\pi^3} \frac{k_F^5}{\sqrt{k_F^2 + m^2}} \int_{-\infty}^{\infty} dv \left\{ \frac{1}{4} \left[\log \left(\frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F} R \right) \right. \right. \\
 & \quad \left. \left. - \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi k_F} R \right] + \int_0^1 2x dx \left[\frac{-1}{x^2 + \frac{4e^2 \sqrt{k_F^2 + m^2}}{\pi f} R} \right] \right. \\
 & \quad \left. 4 \left(\frac{e^2 \sqrt{k_F^2 + m^2}}{\pi k_F} R \right) \right\}
 \end{aligned}$$

which leads to (3.1).

The transverse part may be done along similar lines.

APPENDIX C

The transverse exchange energy is

$$E_x^{tr} = \iint \frac{d^3p d^3p'}{(2\pi)^6} \frac{4\pi e^2}{[-(E_p, -E_{p'})^2 + |\vec{p}' - \vec{p}|^2]} \frac{n_F(p) n_F(p')}{E_p E_{p'}} \left[E_p E_{p'} - m^2 - \frac{[\vec{p} \cdot (\vec{p}' - \vec{p}) \vec{p}' \cdot (\vec{p}' - \vec{p})]}{|\vec{p}' - \vec{p}|^2} \right]. \quad (C.1)$$

The Breit interaction is the approximation obtained by dropping the energy transfer term $(E_p, -E_{p'})^2$ in the denominator (Brown and Ravenhall, 1951). The integral over the third term in the brackets is zero. This may be shown by doing the angular integrals:

$$\begin{aligned} J &\equiv \int_{-1}^{+1} d\mu \frac{1}{(p^2 + p'^2 - 2pp'\mu)^2} (p'\mu - p)(p' - p\mu) \\ &= \int_{-1}^{+1} d\mu \frac{1}{(p^2 + p'^2 - 2pp'\mu)^2} [(p'^2 + p^2)\mu - pp'\mu^2 - pp'] \end{aligned}$$

Each of the integrals over μ may be separately done and their sum leads to $J=0$. Thus we have

$$E_x^{\text{Breit}} \approx \frac{1}{2} \iint \frac{d^3 p d^3 p'}{(2\pi)^6} \frac{4\pi e^2}{|\vec{p}-\vec{p}'|^2} \frac{1}{E_p E_{p'}} (2E_p E_{p'} - 2m^2) \quad (\text{C.2})$$

doing the angular integrals gives

$$E_x^{\text{Br}} \approx \frac{e^2}{2\pi^3} \int_0^{k_F} \frac{p dp}{E_p} \int_0^{k_F} \frac{p' dp'}{E_{p'}} (E_p E_{p'} - m^2) \ln \left| \frac{p+p'}{p-p'} \right| \quad (\text{C.3})$$

scaling $p = k_F x$, $p' = k_F x'$, $E_p = \sqrt{p^2 + m^2} = m\sqrt{1+\beta^2 x^2} = mE_x$ and $E_{p'} = \sqrt{1+\beta^2 x'^2}$ gives

$$E_x^{\text{Br}} = \frac{3e^2 k_F}{2\pi} N \int_0^1 \int_0^1 x dx x' dx' \left(1 - \frac{1}{E_x E_{x'}} \right) \ln \left| \frac{x+x'}{x-x'} \right| \quad (\text{C.4})$$

$$= \frac{3e^2 k_F}{2\pi} N \int_0^1 \int_0^1 \left[x dx x' dx' \ln \left| \frac{x+x'}{x-x'} \right| - \frac{xx' dx dx'}{E_x E_{x'}} \ln \left| \frac{x+x'}{x-x'} \right| \right]$$

The first integral gives 1/2.

The second integral has to be integrated by parts and symmetrized to give

$$\begin{aligned}
\int_0^1 \int_0^1 \frac{xx' dx dx'}{E_x E_{x'}} \ln \left| \frac{x+x'}{x-x'} \right| &= \frac{E_\beta}{\beta^2} \int_0^1 \frac{x dx}{E_x} \ln \left| \frac{1+x}{1-x} \right| \\
&- \frac{1}{\beta^2} \int_0^1 \left(\frac{dx}{E_x} \right)^2
\end{aligned} \tag{C.5}$$

Now

$$\int_0^1 \frac{dx}{E_x} = \frac{\ln(\beta + E_\beta)}{\beta}$$

using $\beta x = \sinh \theta$. This same substitution may be used in the first integral of (C.5) and the integral may be carried out. The limits have to be taken rather carefully. Alternatively the first integral in (C.5) may be done by splitting the log into

$$\log \left| \frac{1+x}{1-x} \right| = 2 \ln(1+x) - \ln(1-x^2)$$

each of the resulting integrals may be separately done.

APPENDIX D

We present here the expressions for the Coulomb and transverse contributions to the exchange energy after the traces in Eq. (16) and (17) have been carried out

$$E_x^{(c)} = -2\pi e^2 \sum_{\hat{n}, \hat{n}'} \iint \frac{d^3 p d^3 p'}{(2\pi)^6} \frac{n_{F\hat{n}}(\mathbf{p}) n_{F\hat{n}'}(\mathbf{p}')}{|\vec{p} - \vec{p}'|^2} \frac{1}{E_p E_{p'}}$$

$$\left\{ (1 + E_p E_{p'} + \vec{p} \cdot \vec{p}') (1 + \delta_o \delta_o' + \vec{\delta} \cdot \vec{\delta}') - \delta_o \delta_o' E_p E_{p'} \right.$$

$$\left. - \delta_o E_{p'} (\vec{\delta}' \cdot \vec{p}) - \delta_o' E_p (\vec{\delta} \cdot \vec{p}') - (\vec{p} \cdot \vec{\delta}') (\vec{\delta} \cdot \vec{p}') \right\} \quad (D.1)$$

and

$$E_x^{(tr)} = -\pi e^2 \sum_{\hat{n}, \hat{n}'} \iint \frac{d^3 p d^3 p'}{(2\pi)^6} \frac{n_{F\hat{n}}(\mathbf{p}) n_{F\hat{n}'}(\mathbf{p}')}{[(E_p - E_{p'})^2 - |\vec{p} - \vec{p}'|^2]} \frac{1}{E_p E_{p'}}$$

$$\left(E_p E_{p'} - m^2 - \frac{(\vec{q} \cdot \vec{p})(\vec{q} \cdot \vec{p}')}{q^2} - \delta_o \delta_o' \left(E_p E_{p'} + m^2 - \frac{(\vec{q} \cdot \vec{p})(\vec{q} \cdot \vec{p}')}{q^2} \right) \right.$$

$$\left. + \frac{(\vec{q} \cdot \vec{\delta})(\vec{q} \cdot \vec{\delta}')}{q^2} E_p E_{p'} - m^2 - 3 \vec{p} \cdot \vec{p}' \right.$$

$$\left. + 3 \vec{\delta} \cdot \vec{\delta}' \left(\vec{p} \cdot \vec{p}' - \frac{(\vec{q} \cdot \vec{p})(\vec{q} \cdot \vec{p}')}{q^2} \right) \right)$$

$$\begin{aligned}
& - E_{p', \delta_0} \frac{(\vec{\delta}' \cdot \vec{q})(\vec{p} \cdot \vec{q})}{q^2} - E_{p, \delta'_0} \frac{(\vec{\delta} \cdot \vec{q})(\vec{p}' \cdot \vec{q})}{q^2} \\
& + 3 \frac{(\vec{p}' \cdot \vec{\delta})(\vec{\delta}' \cdot \vec{q})(\vec{p} \cdot \vec{q})}{q^2} + 3 \frac{(\vec{p} \cdot \vec{\delta}')(\vec{\delta} \cdot \vec{q})(\vec{p}' \cdot \vec{q})}{q^2} \Big\} \\
& + 3(\vec{p} \cdot \vec{\delta})(\vec{p}' \cdot \vec{\delta}') - 3(\vec{p} \cdot \vec{\delta}')(\vec{p}' \cdot \vec{\delta})
\end{aligned} \tag{D.2}$$

The angular integrals may be done and the resulting integrals over p, p' can be done numerically after scaling out the Fermi momentum k_F . The form of the integrals is

$$E_x^{(c)} = - \frac{e^2 k_F^4}{(2\pi)^3} \sum_{\hat{n}, \hat{n}'} \int_0^{\hat{x}_n} \frac{x^2 dx}{E_x} \int_0^{\hat{x}_{n'}} \frac{x'^2 dx'}{E_{x'}} \left\{ I_1 + \hat{n} \cdot \hat{n}' I_2 \right\} \tag{D.3}$$

where I_1, I_2 are functions of $x, x', E_x, E_{x'}$ and β .

$$E_x^{(tr)} = - \frac{e^2 k_F^4}{(2\pi)^3} 2 \sum_{\hat{n}, \hat{n}'} \int_0^{\hat{x}_n} \frac{x^2 dx}{E_x} \int_0^{\hat{x}_{n'}} \frac{x'^2 dx'}{E_{x'}} \left\{ T_1 + \hat{n} \cdot \hat{n}' T_2 \right\} \tag{D.4}$$

where T_1, T_2 are functions of $x, x', E_x, E_{x'}$ and β , and $k_F \hat{x}_n = k_F \hat{x}_{n'}$ is the Fermi energy for up/down spin electrons. In fact, $x_{\uparrow} = (1+\zeta)^{1/3}$ and $x_{\downarrow} = (1-\zeta)^{1/2}$ in terms of the ζ -parameter.

VITA

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