

A local exchange-correlation potential for the spin polarized case: I

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Abstract. The local density theory developed by Hohenberg, Kohn and Sham is extended to the spin polarized case. A spin dependent one-electron potential pertinent to ground state properties is obtained from calculations of the total energy per electron made with a 'bubble' (or random phase) type of dielectric function. The potential is found to be well represented by an analytic expression corresponding to a shifted and rescaled spin dependent Slater potential. To test this potential the momentum dependent spin susceptibility of an electron gas is calculated. The results compare favourably with available information from other calculations and from experiment. The potential obtained in this paper should be useful for split band calculations of magnetic materials.

1. Introduction

The Hohenberg, Kohn and Sham theory was developed only for the spinless case, except for a short discussion (Kohn and Sham 1965) of the spin susceptibility for a uniform electron gas. Recently Stoddart and March (1970) addressed the spin problem by setting up a density-functional theory of magnetic instabilities in metals primarily aimed at making contact with and extending the Hubbard model. This theory also represents some extension of the Hohenberg, Kohn and Sham work towards a full treatment of the spin polarized case.

We give in the present paper† the general theory for the spin polarized case as well as some approximate results for potentials and spin susceptibilities. First we present an extension of the Hohenberg and Kohn (1964) paper. It is found that a straightforward generalization does not work; in the spin case there is no obvious reason to expect a unique relation between the spin dependent potential and the spin density (in the one-particle case we can show that there are many potentials which give the same spin density). We then generalize the Kohn and Sham (1965) discussion of ground state properties. This leads in a fairly straightforward way to spin dependent effective potentials and two coupled equations for the two components of the spinor wavefunction. In the simplest approximation analogous to the one used by Kohn and Sham only 'spin up' and 'spin down' potentials for an electron gas enter. In the Hartree-Fock approximation the potentials become

$$V^{(\alpha)} = -4(3\rho^{(\alpha)}/4\pi)^{1/3} \text{ Ryd} \quad (1.1)$$

† Preliminary reports of the present work were presented at the Menton (Hedin and Lundqvist 1972) and Wildbad (Hedin 1972) conferences.

where $\rho^{(\alpha)}$ is the density (in atomic units) of electrons with spin α (α is given as + for 'spin up' and as - for 'spin down' electrons).

As a comparison the Slater (1968a, b) potential is $\frac{3}{2}$ larger just as in the spinless case. When we include correlation a simple analytical form can no longer be expected for the potentials. We find however that the numerical results obtained by using the 'bubble' approximation, to be discussed later, can be quite accurately represented by the simple expression

$$v^{(\alpha)} = A(\rho) \left(\frac{2\rho^{(\alpha)}}{\rho} \right)^{1/3} + B(\rho) \quad (1.2)$$

where ρ is the total density

$$\rho = \rho^{(+)} + \rho^{(-)} \quad (1.3)$$

and the potentials A and B are given by the same analytical expression as used in the spinless case by Hedin and Lundqvist (1971).

Given the total density, we thus see that $V^{(\alpha)}$ depends on $\rho^{(\alpha)}$ in the same way as in the Hartree-Fock case, we just have a shift (B) and a rescaling. The rescaling is considerable, at the lower metallic densities the Hartree-Fock result is reduced by almost a factor of two, and the larger Slater potential by correspondingly more. This weaker dependence on spin polarization is in accord with general expectations on the rôle of correlation (see eg Wigner 1938, Herring 1966). It is also in accord with results from energy band calculations using a Slater potential with a constant coefficient, which have shown that values of this coefficient much smaller than unity are needed to obtain reasonable agreement with experiment (see eg Wakoh and Yamashita 1966, Connolly 1967 and Slater 1968a).

In the approximation scheme proposed here, as in that of Kohn and Sham (1965) no density gradient terms are included. To judge the seriousness of that omission the q dependent paramagnetic susceptibility was calculated from the proposed potential and the result compared with that from other more refined calculations and from experiment. The results indicate that it may be possible to neglect the gradient terms in many applications.

2. Generalization of the Hohenberg and Kohn theory

Hohenberg and Kohn (1964) developed a local density theory for a nondegenerate ground state based on two fundamental theorems, namely that the ground state wavefunction is a unique functional of the charge density and that there exists a ground state energy functional which is stationary with respect to variations in the charge density. These results can be generalized to the spin dependent case by replacing the scalar external potential $w(\mathbf{r})$ by a spin dependent potential $w_{\alpha\beta}(\mathbf{r})$ and replacing the charge density $\rho(\mathbf{r})$ by the density matrix $\rho_{\alpha\beta}(\mathbf{r})$. However in this case there is no obvious one-to-one correspondence between $w_{\alpha\beta}$ and $\rho_{\alpha\beta}$ (see the Appendix) and we have to slightly modify the proof by Hohenberg and Kohn to show the unique relationship between the ground state $|\Psi\rangle$ and $\rho_{\alpha\beta}(\mathbf{r})$.

Consider a hamiltonian written in second quantization as

$$H = \sum_{\alpha} \int \psi_{\alpha}^{\dagger}(\mathbf{r}) \left(\frac{p^2}{2m} \right) \psi_{\alpha}(\mathbf{r}) d\mathbf{r}$$

$$\begin{aligned}
 & + \frac{1}{2} \sum_{\alpha\beta} \int \psi_{\alpha}^{+}(\mathbf{r}) \psi_{\beta}^{+}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \psi_{\beta}(\mathbf{r}') \psi_{\alpha}(\mathbf{r}) \, d\mathbf{r} \, d\mathbf{r}' \\
 & + \sum_{\alpha\beta} \int \psi_{\alpha}^{+}(\mathbf{r}) w_{\alpha\beta}(\mathbf{r}) \psi_{\beta}(\mathbf{r}) \, d\mathbf{r}
 \end{aligned} \tag{2.1}$$

where $v(\mathbf{r} - \mathbf{r}')$ is the Coulomb potential $e^2/(4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|)$ and $w_{\alpha\beta}$ is a 2×2 hermitian matrix. The expectation value of H in the ground state is

$$E = T + V + \sum_{\alpha\beta} \int w_{\alpha\beta}(\mathbf{r}) \rho_{\beta\alpha}(\mathbf{r}) \, d\mathbf{r} \tag{2.2}$$

where T and V are the expectation values of the kinetic and potential energies and where the density matrix $\rho_{\alpha\beta}$ is defined as

$$\rho_{\alpha\beta}(\mathbf{r}) = \langle \Psi | \psi_{\beta}^{+}(\mathbf{r}) \psi_{\alpha}(\mathbf{r}) | \Psi \rangle \tag{2.3}$$

From its definition we see that $\rho_{\alpha\beta}$ is a hermitian matrix like $w_{\alpha\beta}$.

Let us now assume that there exist two different ground states $|\Psi\rangle$ and $|\Psi'\rangle$ corresponding to the hamiltonians H and H' and the potentials w and w' in equation 2.1, which both give the same density matrix $\rho_{\alpha\beta}$. Owing to the assumed nondegeneracy of the ground state and to the minimal property of the expectation value of the hamiltonian with respect to variations of the wavefunction we have the strict inequality

$$\langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle \tag{2.4}$$

or

$$E < E' + \sum_{\alpha\beta} \int \{w_{\alpha\beta}(\mathbf{r}) - w'_{\alpha\beta}(\mathbf{r})\} \rho_{\beta\alpha}(\mathbf{r}) \, d\mathbf{r} \tag{2.5}$$

Interchanging primed and unprimed quantities (remember that $\rho'_{\alpha\beta} = \rho_{\alpha\beta}$) and adding we have

$$E + E' < E + E' \tag{2.6}$$

However this is impossible and thus the starting assumption that $|\Psi\rangle$ and $|\Psi'\rangle$ are different is false. We have thus shown that the ground state and hence all ground state properties like the total energy and the one-particle Green function are functionals of the density matrix $\rho_{\alpha\beta}$.

The proof that E given in equation 2.2 is stationary with respect to variations in $\rho_{\alpha\beta}$ under the subsidiary condition that the number of electrons is conserved

$$N = \sum_{\alpha} \int \rho_{\alpha\alpha}(\mathbf{r}) \, d\mathbf{r} \tag{2.7}$$

follows precisely as in the Hohenberg and Kohn paper; a change in $\rho_{\alpha\beta}$ from the correct density matrix corresponds to a change in the wavefunction from the correct state function and thus by the variational principle to a higher energy.

The two basic theorems just discussed say nothing about how wide a class of functions $\rho_{\alpha\beta}(\mathbf{r})$ is defined by equation 2.3, that is correspond to N -particle wavefunctions. This N -representability condition puts quite strong limitations on some quantities like the full density matrix $\rho_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ (Löwdin 1955) but is probably less severe for the density $\rho(\mathbf{r})$ and the density matrix $\rho_{\alpha\beta}(\mathbf{r})$. We take as a working hypothesis that reasonably smooth functions $\rho_{\alpha\beta}(\mathbf{r})$ do not give an energy less than the ground state energy when used in the ground state functional.

3. Generalization of the Kohn and Sham theory

Following Kohn and Sham (1965) we use the minimal property of the functional (2.2) with the subsidiary condition (2.7) to determine the density matrix $\rho_{\alpha\beta}(\mathbf{r})$ corresponding to the potential $w_{\alpha\beta}(\mathbf{r})$. This gives the equations

$$w_{\alpha\beta}(\mathbf{r}) + \sum_{\gamma} \int \rho_{\gamma\gamma}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \delta_{\alpha\beta} + \frac{\delta T_0}{\delta \rho_{\alpha\beta}(\mathbf{r})} + \frac{\delta E_{xc}}{\delta \rho_{\alpha\beta}(\mathbf{r})} = \lambda \delta_{\alpha\beta} \quad (3.1)$$

Here T_0 is the kinetic energy functional for a system of noninteracting Fermi particles and E_{xc} is defined from the relation $T + V = T_0 + V_c + E_{xc}$, where V_c is the classical Coulomb energy. The constant λ is the Lagrange parameter associated with particle conservation. Noting the similarity between equation 3.1 and the corresponding equation for the noninteracting case we can get the density matrix by solving the coupled set of one particle Schrödinger equations

$$\sum_{\beta} \left(-\frac{\hbar^2}{2m} \nabla^2 \delta_{\alpha\beta} + \sum_{\gamma} \int \rho_{\gamma\gamma}(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \delta_{\alpha\beta} + w_{\alpha\beta}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho_{\alpha\beta}(\mathbf{r})} \right) \phi_{\beta}^{(i)}(\mathbf{r}) = E^{(i)} \phi_{\alpha}^{(i)}(\mathbf{r}) \quad (3.2)$$

and summing up to the Fermi level,

$$\rho_{\alpha\beta}(\mathbf{r}) = \sum_{E^{(i)} < E_F} \phi_{\alpha}^{(i)}(\mathbf{r}) \phi_{\beta}^{(i)*}(\mathbf{r}) \quad (3.3)$$

We now have a perfectly well defined and exact procedure to calculate the density matrix if only we know the functional $E_{xc}\{\rho_{\alpha\beta}(\mathbf{r})\}$ or the exchange-correlation potential $v_{xc}^{\alpha\beta}(\mathbf{r})$ defined by

$$v_{xc}^{\alpha\beta} = \frac{\delta E_{xc}}{\delta \rho_{\alpha\beta}(\mathbf{r})} \quad (3.4)$$

To obtain a reasonable approximation for E_{xc} we take the external potential as slowly varying and divide the electronic system into small boxes. In each box the electrons can then be considered to form a spin polarized homogeneous electron gas with spin-up and spin-down densities $\rho^{(+)}(\mathbf{r})$ and $\rho^{(-)}(\mathbf{r})$ given by the eigenvalues of the density matrix $\rho_{\alpha\beta}(\mathbf{r})$. If $\epsilon_{xc}(\rho^{(+)}, \rho^{(-)})$ is the exchange-correlation energy per particle of a spin polarized electron gas we have for the electronic system in the limit of slowly varying density

$$E_{xc}\{\rho_{\alpha\beta}(\mathbf{r})\} = \int \{\rho^{(+)}(\mathbf{r}) + \rho^{(-)}(\mathbf{r})\} \epsilon_{xc}(\rho^{(+)}(\mathbf{r}), \rho^{(-)}(\mathbf{r})) d\mathbf{r} \quad (3.5)$$

Choosing a local coordinate system with z axis along the direction of the local spin $\sum_{\alpha\beta} \sigma_{\beta\alpha} \rho_{\alpha\beta}(\mathbf{r})$, we get by using equations 3.4 and 3.5

$$v_{xc}^{(\alpha)} = \frac{\partial}{\partial \rho^{(\alpha)}} \{(\rho^{(+)} + \rho^{(-)}) \epsilon_{xc}(\rho^{(+)}, \rho^{(-)})\} \quad (3.6)$$

4. A 'two-bubble' approximation for the exchange-correlation energy

To obtain numerical results for the exchange-correlation potential we employ a generalized random phase expression for $\epsilon_{xc}(\rho^{(+)}, \rho^{(-)})$. We start from the well known exact expression for ϵ_{xc} in terms of the polarization propagator (Hubbard 1957)

$$\epsilon_{xc} = -\frac{1}{2\rho} \int_0^{e^2} \frac{d\lambda}{\lambda} \sum_{\mathbf{q}} v(\mathbf{q}) \left(\frac{1}{2\pi i} \int P(\mathbf{q}, \omega) d\omega + \rho \right) \quad (4.1)$$

where $v(\mathbf{q})$ is the Fourier transform of the Coulomb potential.

$$v(\mathbf{q}) = \frac{\lambda}{\epsilon_0 q^2} \quad (4.2)$$

λ is an interaction strength parameter, ρ is the total density of electrons (equation 1.3), and unit volume is assumed.

$P(\mathbf{q}, \omega)$ is the reducible polarization propagator of the spin polarized electron gas which can be expressed in the irreducible propagator $\Lambda(\mathbf{q}, \omega)$ through

$$P(\mathbf{q}, \omega) = \Lambda(\mathbf{q}, \omega) \{1 - v(\mathbf{q}) \cdot \Lambda(\mathbf{q}, \omega)\}^{-1} \quad (4.3)$$

We now approximate $\Lambda(\mathbf{q}, \omega)$ by the 'two-bubble' expression

$$i\Lambda(\mathbf{q}, \omega) = \begin{array}{c} \text{spin up} \\ \text{electrons} \end{array} + \begin{array}{c} \text{spin down} \\ \text{electrons} \end{array} \quad (4.4)$$

In order to make equation 4.1 more suitable for numerical calculation we split ϵ_{xc} into two parts

$$\epsilon_{xc} = \epsilon_x + \epsilon_c \quad (4.5)$$

where ϵ_x is the ordinary Hartree-Fock contribution

$$\epsilon_x = -6 \left(\frac{3}{4\pi} \right)^{1/3} \frac{1}{\rho} (\rho^{(+)}^{4/3} + \rho^{(-)}^{4/3}) \quad (\text{Ryd}) \quad (4.6)$$

Since the propagator $P(\mathbf{q}, \omega)$ is analytic in the quarter plane $\text{Re } \omega > 0, \text{Im } \omega > 0$ we can deform the integration contour along the real axis to an integration along the imaginary axis. The integration over the interaction strength parameter can be performed analytically. After some algebra, going over to dimensionless variables according to $q = 2k_F Q, \omega = (2k_F)^2 W/(2m)$, we arrive at the formula

$$\epsilon_c = -\frac{24}{\pi} \frac{1}{\alpha_0^2 r_s^2} \int_0^\infty \int_0^\infty dQ dW Q^2 [\alpha(Q, W) - \ln \{1 + \alpha(Q, W)\}] \quad (\text{Ryd}) \quad (4.7)$$

The quantities appearing in (4.7) are defined as follows

$$\begin{aligned} \alpha(Q, W) &= \frac{\alpha_0 r_s}{4\pi} \{x_1 \beta(x_1 Q, x_1^2 W) + x_2 \beta(x_2 Q, x_2^2 W)\} \\ \beta(Q, W) &= \frac{1}{Q^2} \left\{ 1 + \frac{W^2 + Q^2 - Q^4}{4Q^3} \ln \frac{W^2 + Q^2(1+Q)^2}{W^2 + Q^2(1-Q)^2} \right. \\ &\quad \left. - \frac{W}{Q} \left(\tan^{-1} \frac{Q+Q^2}{W} + \tan^{-1} \frac{Q-Q^2}{W} \right) \right\} \end{aligned} \quad (4.8)$$

$$\frac{4\pi}{3} r_s^3 a_0^3 = \frac{1}{\rho} \quad \alpha_0 = \left(\frac{4}{9\pi} \right)^{1/3} \simeq 0.52106$$

$$x = \frac{\rho^{(+)}}{\rho} \quad x_1 = (2x)^{-1/3} \quad x_2 = (2 - 2x)^{-1/3}$$

Table 1. The correlation energy ϵ_c for different r_s and spin polarizations x

x	$r_s = 1.0$	2.0	3.0	4.0	5.0	6.0
0.5	-0.1573	-0.1234	-0.1053	-0.0935	-0.0848	-0.0781
0.4	-0.1558	-0.1222	-0.1044	-0.0926	-0.0841	-0.0774
0.3	-0.1511	-0.1187	-0.1015	-0.0901	-0.0819	-0.0754
0.2	-0.1425	-0.1124	-0.0963	-0.0857	-0.0780	-0.0720
0.1	-0.1290	-0.1025	-0.0883	-0.0789	-0.0720	-0.0667
0.0	-0.1040	-0.0850	-0.0746	-0.0674	-0.0620	-0.0579

In table 1 we give the correlation energy ϵ_c , calculated from equation 4.7, as a function of r_s , and the fraction of 'spin-up' electrons, x . The numerical accuracy is 1%. The exchange energy ϵ_x is given by the analytical expression (4.6).

5. A parametrized form of the exchange-correlation energy

In order to make our results for the exchange-correlation energy ϵ_c (and hence for the exchange-correlation potential v_{xc}) easy to use in spin polarized bandstructure calculations we parametrize the results in table 1. In what follows we will use the following notation: x as subscript means exchange, c as subscript means correlation, P as superscript means the paramagnetic state, $x = \frac{1}{2}$, and F as superscript means the ferromagnetic state, $x = 0$. We denote by μ_x and μ_c the contributions to the chemical potential from the exchange and correlation energies. μ_x and μ_c are given by the formulae (see eg Hedin and Lundqvist 1969)

$$\mu_x = \epsilon_x - \frac{r_s}{3} \frac{\partial \epsilon_x}{\partial r_s} \quad \mu_c = \epsilon_c - \frac{r_s}{3} \frac{\partial \epsilon_c}{\partial r_s} \quad (5.1)$$

From the equations 4.6 and 5.1 we see that

$$\mu_x^P = \gamma(\epsilon_x^F - \epsilon_x^P) \quad (5.2)$$

where $\gamma = \frac{4}{3}a/(1-a)$ and $a = 2^{-1/3}$. If we define a function $f(x)$ by

$$f(x) = (1-a)^{-1} \{x^{4/3} + (1-x)^{4/3} - a\} \quad (5.3)$$

we can write the exchange energy ϵ_x in equation 4.6 in the form

$$\epsilon_x = \epsilon_x^P + \gamma^{-1} \mu_x^P f(x) \quad (5.4)$$

Now it turns out that also our approximate numerical results in table 1 for the correlation energy can be represented within our numerical accuracy by a similar expression

$$\epsilon_c = \epsilon_c^P + \gamma^{-1} v_c f(x) \quad (5.5)$$

where the quantity v_c is defined by

$$v_c = \gamma(\epsilon_c^F - \epsilon_c^P) \quad (5.6)$$

According to (4.6) and (5.1) the r_s dependence of the quantities ϵ_x^P and μ_x^P is given by

$$\epsilon_x^P(r_s) = -\frac{\epsilon_x^0}{r_s} \quad (5.7)$$

$$\mu_x^P(r_s) = \frac{4}{3} \epsilon_x^P(r_s) \quad (5.8)$$

where

$$\epsilon_x^0 = \frac{3}{2\pi\alpha_0} \simeq 0.9163 \quad (\text{Ryd}) \quad (5.9)$$

The r_s dependence of the quantities ϵ_c^P and ϵ_c^F can be represented, within our numerical accuracy, by the same analytic expressions as used by Hedin and Lundqvist (1971)

$$\begin{aligned} \epsilon_c^P &= -c^P F\left(\frac{r_s}{r^P}\right) \\ \epsilon_c^F &= -c^F F\left(\frac{r_s}{r^F}\right) \end{aligned} \quad (5.10)$$

where

$$F(z) = (1+z^3) \ln\left(1+\frac{1}{z}\right) + \frac{z}{2} - z^2 - \frac{1}{3} \quad (5.11)$$

and

$$\begin{aligned} c^P &= 0.0504 & c^F &= 0.0254 \\ r^P &= 30 & r^F &= 75 \end{aligned} \quad (5.12)$$

We thus find that the numerical results in table 1 can be reproduced with the aid of the two functions F and f and four parameters c^P , c^F , r^P , and r^F .

We remark that, according to equations 5.1 and 5.10

$$\begin{aligned} \mu_c^P(r_s) &= -c^P \ln\left(1+\frac{r^P}{r_s}\right) \\ \mu_c^F(r_s) &= -c^F \ln\left(1+\frac{r^F}{r_s}\right) \end{aligned} \quad (5.13)$$

The parameters c^P , c^F , r^P , and r^F obey, within an accuracy of 1% the scaling relations

$$c^F = \frac{1}{2}c^P \quad r^F = 2^{4/3}r^P \quad (5.14)$$

appropriate to the random phase approximation (Hedin 1965).

At this stage we point out that it is rather easy to apply our results in more sophisticated treatments of the electron gas correlation if we assume that a polarization dependence of the form 5.5 will survive also in these treatments. We then just have to insert the correct values of ϵ_c^P and ϵ_c^F in equation 5.5. Since the x dependence of ϵ_c is rather weak such a procedure should give a reasonable interpolation between the paramagnetic and the ferromagnetic results.

6. A parametrized form of the exchange-correlation potential

From equation 3.6 we see that the quantity relevant to a one-electron description is

$$v_{xc}^{(+)} = \epsilon_{xc}(\rho^{(+)}, \rho^{(-)}) + \rho \frac{\partial \epsilon_{xc}}{\partial \rho^{(+)}} \quad (6.1)$$

Using previous equations we get after some straightforward algebra:

$$v_{xc}^{(+)} = (\mu_x^P + v_c)(2x)^{1/3} + \mu_c^P - v_c + \tau_c f(x) \quad (6.2)$$

where

$$\tau_c = \mu_c^F - \mu_c^P - \frac{4}{3}(\epsilon_c^F - \epsilon_c^P) \quad (6.3)$$

For $v_{xc}^{(-)}$ we get the same kind of equation with x and $1-x$ interchanged. Note that if we

neglect correlation, the quantities v_c , μ_c^P and τ_c vanish and $v_{xc}^{(+)}$ reduces to the Kohn–Sham modification of the Slater approximation $v_x^{(+)} = \mu_x^P(2x)^{1/3} = \frac{2}{3}V_s^{(+)}$ (Slater 1968a,b). From equation 6.2 we also see that in the paramagnetic case, $x = \frac{1}{2}$, we have $v_{xc}^{(+)} = \mu_{xc}^P$ ($f(\frac{1}{2}) = 0$) which of course is the usual Kohn–Sham result. To give a feeling for the density dependence and relative importance of the different terms in $v_{xc}^{(+)}$ we tabulate them in table 2 as functions of r_s .

Table 2. Parameters for the exchange-correlation potential, v_{xc}

r_s	$-\mu_x^P$	$-\mu_c^P$	v_c	$-A = -(\mu_x^P + v_c)v_c$	$-B = -\mu_c^P$	$-\tau_c$	$-v_{xc}^{(+)} (x = 1)$
1.0	1.222	0.173	0.284	0.938	0.457	0.011	1.649
2.0	0.611	0.140	0.204	0.406	0.344	0.006	0.862
3.0	0.407	0.121	0.161	0.246	0.282	0.004	0.596
4.0	0.305	0.108	0.133	0.173	0.241	0.002	0.461
5.0	0.244	0.098	0.112	0.132	0.210	0.001	0.378
6.0	0.204	0.090	0.096	0.108	0.186	0.001	0.323

Remembering that there is an uncertainty in our estimates for μ_{xc}^P of about 0.02 – 0.04 Ryd (Hedin and Lundqvist 1969) we see from table 2 that the quantity τ_c may be neglected. By using better dielectric functions (Singwi *et al* 1970, Geldart and Taylor

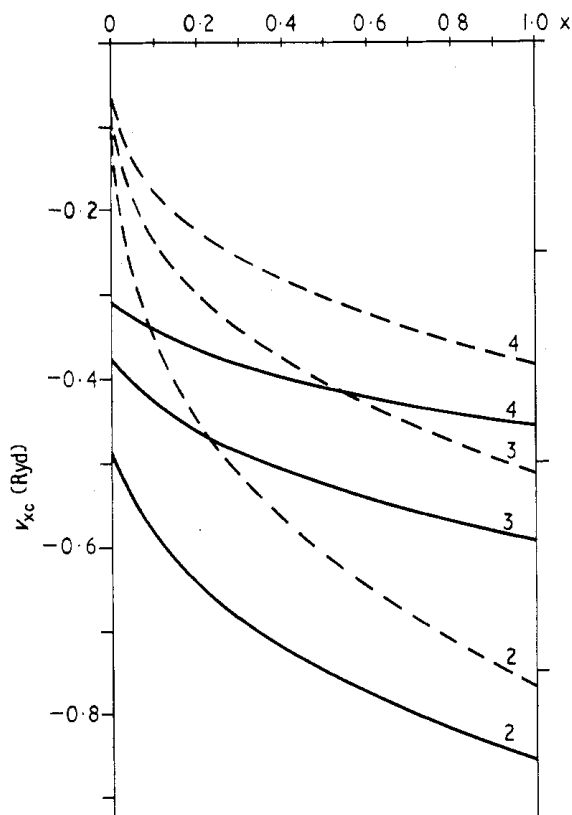


Figure 1. Our result for the exchange-correlation potential for spin-up electrons as a function of the fraction (x) of spin-up electrons. The r_s value for each curve is indicated in the figure. The parametrized expression in equation 6.4 gives accurately the same result except for small x (say $x < 0.1$). The broken curves are with correlation neglected.

1970) in estimating ϵ_{xc} we can bring down the error to about 0.01 Ryd; still, however, τ_c can be neglected.

We can now write our exchange-correlation potential $v_{xc}^{(+)}$ as

$$v_{xc}^{(+)}(r_s, x) = A(r_s)(2x)^{1/3} + B(r_s) \quad (6.4)$$

where

$$\begin{aligned} A(r_s) &= \mu_x^P(r_s) + v_c(r_s) \\ B(r_s) &= \mu_c^P(r_s) - v_c(r_s) \end{aligned} \quad (6.5)$$

According to equation 6.4 the derivative, with respect to x , of $v_{xc}^{(+)}$ goes to infinity as $x^{-2/3}$ when x tends to zero. This is due to our choice of parametrization. Actually the derivative of $v_{xc}^{(+)}$ goes to infinity as $x^{-1/3}$ in the original 'two-bubble' approximation given by equation 4.4.

If accurate representation for small x (say $x < 0.1$) is needed, the parametrization should not be used.†

In figure 1 the potential $v_{xc}^{(+)}$ is shown as a function of x for $r_s = 2, 3, 4$. The corresponding Hartree-Fock potentials are also shown (by broken curves) demonstrating the strong effect of correlation.

In order to make contact with spin polarized band calculations we follow De Cicco and Kitz (1967) or Slater (1968a) and expand v_{xc} in equation 6.4 to first order in the difference between spin-up and spin-down densities, $\rho^{(+)} - \rho^{(-)}$,

$$v_{xc}^{(+)}(r_s, x) = \mu_{xc}^P(r_s) + \frac{1}{3}A(r_s)\frac{1}{\rho}(\rho^{(+)} - \rho^{(-)}) \quad (6.6)$$

We then define factors $\beta(r_s)$ and $\delta(r_s)$ which express the effect of correlation

$$\mu_{xc}^P(r_s) = \beta(r_s)\mu_x^P(r_s) \quad (6.7)$$

$$A(r_s) = \delta(r_s)\mu_x^P(r_s) \quad (6.8)$$

The parameter $\beta(r_s)$ is extensively discussed in the paper by Hedin and Lundqvist (1971). We just mention that it varies between about $\frac{7}{6}$ and $\frac{4}{3}$ for metallic densities. The parameter $\delta(r_s)$ is displayed in figure 2 together with $\beta(r_s)$ calculated in RPA as well as from the dielectric function of Singwi *et al* (1970).

Wakoh and Yamashita (1966) have done spin polarized approximately selfconsistent band structures calculations on iron using $\beta = \delta$. Considering the parameter δ as the most important parameter for determining the exchange splitting and hence for the saturation magnetization they had to use the value $\delta = 0.75$ to get agreement with the experimental value. De Cicco and Kitz (1967) have done similar calculations on iron and indicate that $\beta = 1.05$ and $\delta = 0.75$ might give better agreement with neutron scattering experiments, while the spin density per unit cell came out somewhat too large. Connolly (1967) has done selfconsistent calculations on nickel. Connolly like Wakoh and Yamashita used $\beta = \delta$. He found that the Slater approximation ($\delta = 1.5$) gave qualitative disagreement with experiment while $\delta = 1$ gave more realistic results.

The results just quoted indicate the magnitude of the parameters β and δ . We emphasize however that one should not use constants for the parameters β and δ , but rather

† For $x < 0.1$ the result for v_{xc} is, from a numerical viewpoint, best calculated directly from the self energy (first order dynamically screened exchange diagram, cf Hedin 1965) rather than through the total energy.

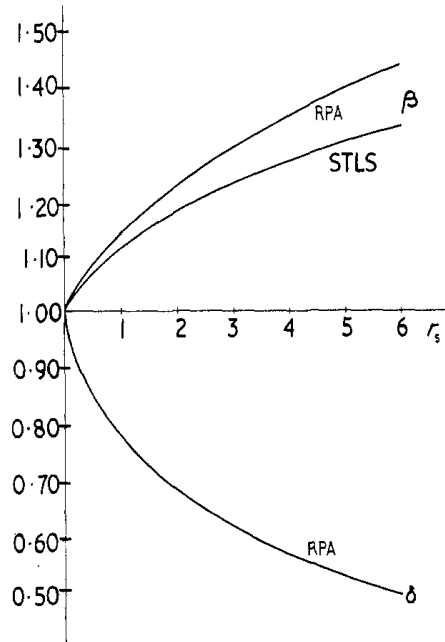


Figure 2. The parameters β and δ defined in equations 6.7 and 6.8 as functions of r_s , calculated in a RPA-type approximation. The curve marked STLS shows the β values obtained from the Singwi *et al* (1970) correlation energies.

density dependent functions. Actually there is no need to use the parameters β and δ at all; they were introduced just to make contact with existing band structure calculations. Instead one should use the potential (6.4). We want to stress once more that a calculation with this potential is computationally no more difficult than the ones already performed.

7. Results for the paramagnetic susceptibility

We consider an electron gas subject to an infinitesimal space dependent magnetic field $B(\mathbf{r})$ along the z direction and study the paramagnetic spin susceptibility. The magnetic field will cause changes in spin-up and spin-down densities $\delta\rho^{(+)}$ and $\delta\rho^{(-)}$. The change in effective potential will be the sum of two terms, one coming from the external field and the other from the changes in the potentials $v_{xc}^{(\alpha)}$ due to the spin density changes. Expanding to first order in the spin density changes we obtain

$$\begin{aligned}\delta V^{(+)}(\mathbf{r}) &= \mu_B B(\mathbf{r}) + \left(\frac{\partial v_{xc}^{(+)}}{\partial \rho^{(+)}}\right)^P \delta\rho^{(+)}(\mathbf{r}) + \left(\frac{\partial v_{xc}^{(+)}}{\partial \rho^{(-)}}\right)^P \delta\rho^{(-)}(\mathbf{r}) \\ \delta V^{(-)}(\mathbf{r}) &= -\mu_B B(\mathbf{r}) + \left(\frac{\partial v_{xc}^{(-)}}{\partial \rho^{(+)}}\right)^P \delta\rho^{(+)}(\mathbf{r}) + \left(\frac{\partial v_{xc}^{(-)}}{\partial \rho^{(-)}}\right)^P \delta\rho^{(-)}(\mathbf{r})\end{aligned}\quad (7.1)$$

where μ_B is the Bohr magneton. From first order perturbation theory we get, going over to Fourier transforms,

$$\delta\rho^{(+)}(\mathbf{q}) = -\frac{mq_F}{2\pi^2} u\left(\frac{q}{q_F}\right) \delta V^{(+)}(\mathbf{q})$$

$$\delta\rho^{(-)}(\mathbf{q}) = -\frac{mq_F}{2\pi^2} u\left(\frac{q}{q_F}\right) \delta V^{(-)}(\mathbf{q}) \tag{7.2}$$

Here q_F is the Fermi momentum and $u(q)$ is the well known function

$$u(q) = \frac{1}{2} + \frac{4 - q^2}{8q} \ln \left| \frac{2 + q}{2 - q} \right| \tag{7.3}$$

By using the symmetry relations

$$\left(\frac{\partial v_{xc}^{(+)}}{\partial \rho^{(+)}}\right)^P = \left(\frac{\partial v_{xc}^{(-)}}{\partial \rho^{(-)}}\right)^P \quad \left(\frac{\partial v_{xc}^{(+)}}{\partial \rho^{(-)}}\right)^P = \left(\frac{\partial v_{xc}^{(-)}}{\partial \rho^{(+)}}\right)^P \tag{7.4}$$

we find from equations 7.1 and 7.2 that

$$\delta\rho^{(+)} + \delta\rho^{(-)} = 0 \tag{7.5}$$

Defining the susceptibility $\chi(\mathbf{q})$ by

$$\chi(\mathbf{q}) = -\frac{\mu_0\mu_B\{\delta\rho^{(+)}(\mathbf{q}) - \delta\rho^{(-)}(\mathbf{q})\}}{B(\mathbf{q})} \tag{7.6}$$

where μ_0 is the permeability of the vacuum we get

$$\chi(\mathbf{q}) = \frac{\chi_0 u(q/q_F)}{1 - Iu(q/q_F)} \tag{7.7}$$

Here

$$I = -\frac{3}{4} \frac{m}{q_F^2} \left(\frac{\partial^2 \epsilon_{xc}}{\partial x^2}\right)_{x=1/2} \tag{7.8}$$

and χ_0 is the Pauli paramagnetic susceptibility. Using our parametrized form (5.4), (5.5) of the exchange-correlation energy ϵ_{xc} , a form which is especially accurate in the paramagnetic region ($x = \frac{1}{2}$), (7.8) can be written

$$I = -\frac{1}{2}\alpha_0^2 r_s^2 A(r_s) \tag{7.9}$$

In table 3 our $q = 0$ susceptibility enhancement $\chi(0)/\chi_0 = (1 - I)^{-1}$, calculated from

Table 3. Spin susceptibility enhancement ($q = 0$)

r_s	HF	Here	Rice	DG	SV	SPW	ST
1.0	1.20	1.15	1.15				
2.0	1.50	1.28	1.27	1.31			
3.0	1.99	1.43	1.39	1.47			
4.0	2.97	1.60	1.48	1.65	1.74	1.50	1.65
					(±0.08)		
5.0	5.85	1.82		1.85			

HF = local density approximation with correlation neglected

Here = local density approximation. Equations 7.7 and 7.9

Rice = Rice (1965). Similar results were obtained by Hedin and Lundqvist (1969).

DG = Dupree and Geldart (1971). Similar results were obtained by Hamann and Overhauser (1966) and by Pizzimenti and Tosi (1971).

SV = Conduction electron spin resonance data from Schumacher and Vehse (1963).

SPW = Spin wave data taken indirectly from Rice (1968).

ST = Data from measurement of total spin susceptibility taken indirectly from Dupree and Geldart (1971).

equation 7.9, is shown as a function of r_s , together with other theoretical estimates and experimental results. From table 3 we see that the result of our calculation of the spin susceptibility enhancement in the long wavelength limit is as close to the best experimental data as the latest and presumably the most careful theoretical estimates by Dupree and Geldart (1971) and by Pizzimenti and Tosi (1971). This is surprising since our numerical results being obtained in a 'two-bubble' approximation, do not account for exchange and short range correlation effects, which have been taken into consideration in the other calculations. The comparison of the q dependence of our susceptibility with that of Singwi *et al* (considered to be the best so far) furnishes a direct test of the validity of the local density approximation. In their article they write the susceptibility in the same form as we do (equation 7.7) only they get a q dependent I ($= I(q)$).

However they find the q dependence of I to be rather weak, especially for $q < k_F$ and for low densities ($r_s > 3$). We take this as an indication of the reliability of the local density approximation at least for disturbances with appreciable Fourier components only up to the Fermi momentum.

8. Concluding remarks

The local density theory developed by Hohenberg, Kohn and Sham in the middle sixties, has in this paper been extended to the spin polarized case. We work with a spin dependent one-electron potential $w_{\alpha\beta}(\mathbf{r})$ as a probe which drives the electronic system into different spin polarized states which we specify with a spin density $\rho_{\alpha\beta}(\mathbf{r})$. The potential $w_{\alpha\beta}$ is equivalent to a spin independent potential $V(\mathbf{r})$ and an interaction between a magnetic field $\mathbf{B}(\mathbf{r})$ and the spin magnetic moment. Our main interest is in systems which are intrinsically spin polarized, like transition metals and non-singlet atoms. The potential $w_{\alpha\beta}$ can then be allowed to approach zero.

We consider in this paper only ground state properties like spin densities and total energies. Numerical estimates are made with a simple extension of the random phase approximation, cf equation 4.4. The resulting potentials are shown in figure 1. The full drawn curves give the correlated potentials $v_{xc}^{(+)}(r_s, x)$ acting on spin-up electrons.

The potential is a function of electron density, r_s , and spin polarization, $x = \rho^{(+)}/\rho$. The broken curves give $v_x^{(+)}(r_s, x)$, the exchange only results. There is clearly a dramatic difference between the two potentials, the v_{xc} curves are much flatter and have an appreciable value also for $x = 0$. This is completely in accord with general expectations (Wigner 1938) on the rôle of correlation.

The slope of the curves at $x = 0.5$ (the paramagnetic case) can be checked against calculated and measured results for the spin susceptibility; the slope is in very good agreement with these other results. There are of course still uncertainties in the values for the potentials v_{xc} , but they seem fairly small compared with the deviations from v_x (exchange-only) results. We also remind here that the potential proposed by Slater (1968a) is $\frac{3}{2}$ times larger than v_x , it thus cuts through and has a vastly larger slope, while its average value comes rather close to that of v_{xc} .

As regards the application of our potentials to band calculations, it is quite clear that they will give much better results than the exchange-only or the Slater potentials. If they will give satisfactory results is very hard to say, they suffer from the same drawback as the paramagnetic potentials discussed recently (Hedin and Lundqvist 1971), namely that no gradient terms are considered. Our results for the susceptibility indicate that the gradient terms may possibly be neglected, but only actual band calculations can

settle this question. Such calculations are facilitated by the parametrized form in which our potentials are given.†

The parametrizations also lend themselves to an easy semiempirical generalization of our results (cf equation 5.5) where the input is the paramagnetic and the ferromagnetic energies; alternatively the paramagnetic spin susceptibility could be used.

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Appendix. The relation between the one-particle potential $w_{\alpha\beta}$ and the spin density $\rho_{\alpha\beta}$

Let $\Psi_{\alpha}^{(0)}(\mathbf{r})$ be the ground state of the hamiltonian

$$H_{\alpha\beta} = -\frac{\hbar^2}{2m} \nabla^2 \delta_{\alpha\beta} + w_{\alpha\beta}(\mathbf{r}) \quad (\text{A.1})$$

and let $\sigma_{\alpha\beta}^{(i)}$ be the cartesian components of the Pauli spin vector operator. We define the unit vector $\hat{u}(\mathbf{r})$ through the equation

$$u^{(i)}(\mathbf{r}) = \frac{\sum_{\alpha\beta} \Psi_{\alpha}^{(0)*}(\mathbf{r}) \sigma_{\alpha\beta}^{(i)} \Psi_{\beta}^{(0)}(\mathbf{r})}{\sum_{\alpha} |\Psi_{\alpha}^{(0)}(\mathbf{r})|^2} \quad (\text{A.2})$$

Using the fact that

$$\sum_i \sigma_{\alpha\beta}^{(i)} \sigma_{\alpha'\beta'}^{(i)} = 2\delta_{\alpha\beta} \delta_{\alpha'\beta'} - \delta_{\alpha\beta'} \delta_{\alpha'\beta} \quad (\text{A.3})$$

it is now easy to show that

$$\sum_{\beta} (\hat{u}\sigma)_{\alpha\beta} \Psi_{\beta}^{(0)}(\mathbf{r}) = \Psi_{\alpha}^{(0)}(\mathbf{r}) \quad (\text{A.4})$$

Defining the potential $V_{\alpha\beta}(\mathbf{r})$ by

$$V_{\alpha\beta}(\mathbf{r}) = V_0(\mathbf{r}) \{(\hat{u}\sigma)_{\alpha\beta} - \delta_{\alpha\beta}\} \quad (\text{A.5})$$

where $V_0(\mathbf{r})$ is some arbitrary spin independent function, and the hamiltonian $H'_{\alpha\beta}$ by

$$H'_{\alpha\beta} = H_{\alpha\beta} + V_{\alpha\beta}(\mathbf{r}) \quad (\text{A.6})$$

we can immediately see that the ground state $\Psi_{\alpha}^{(0)}(\mathbf{r})$ of H is an eigenstate of the hamiltonian H' no matter what scalar potential $V_0(\mathbf{r})$ we put into (A.5). For small enough V_0 , $\Psi^{(0)}$ is also the ground state of H' . We thus have a class of potentials $w_{\alpha\beta}$ which all give the same spin density $\rho_{\alpha\beta}$.

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† Note however that these parametrizations are rather inaccurate for x smaller than 0.1, thus if very large spin polarizations are important, the parametrized forms should not be used.

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