

# Band model for magnetism of transition metals in the spin-density-functional formalism

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**Abstract.** The Hohenberg–Kohn–Sham spin-density-functional (SDF) formalism is applied to calculate magnetic properties of transition metals. A Stoner-like band model is derived in the SDF formalism. The solutions of the SDF equations are assumed to have Bloch character and perturbation theory is used to show that the energy splitting between spin up and spin down states is approximately wavevector independent and proportional to an energy-dependent Stoner parameter. This result makes it possible to obtain magnetic properties from the paramagnetic density of states and the Stoner parameter alone.

Results in the local-spin-density approximation for the Stoner parameters of V, Fe, Co, Ni, Pd, and Pt are presented. The relative stability of the para and ferromagnetic states is found to be correct for all the elements investigated and the total magnetization compares favourably with experiment. Values for the Curie temperature are systematically too high. Experimental estimates of the Stoner parameter are compared with the calculated values and the deviation is at most a few tenths of an eV.

## 1. Introduction

A major difficulty in the description of magnetism in transition metals stems from the d electrons being neither completely localized nor completely itinerant. The band theories of magnetism, e.g., the Stoner model, stress the itinerancy. They can explain the low temperature properties (e.g., Herring 1966, Cracknell 1971, Freeman *et al* 1975) of several transition metals in terms of an adjusted band structure though the construction of a first principle potential required in the calculation is still a major problem (Brinkman 1973).

The Hartree–Fock approximation is frequently used as a basis for band theories (Wohlfarth 1953, 1968). However, the importance of correlation for magnetic properties was pointed out at an early stage by, e.g., Wigner (1934) and Wohlfarth (1953). Band theories can also be obtained in the Kohn–Sham scheme (Kohn and Sham 1965) in its generalization to a spin-density-functional (SDF) formalism. This formalism allows the inclusion of correlation effects, while retaining the conceptual and computational simplicity of the band picture. In principle, an improved description of correlation effects involves ‘simply’ an improved construction of the exchange-correlation function occurring in the theory.

Band theories can include a tendency to formation of localized moments, i.e. the propagating states may have site- and spin-dependent amplitudes, giving magnetic

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moments varying in magnitude and direction from site to site (Friedel *et al* 1961, Lederer and Blandin 1966, Lederer 1966). This possibility is not taken into account in this paper, where the electrons are assumed to have Bloch character. The purpose is (i) to derive a Stoner-like band model in the SDF formalism and (ii) to compare the predictions of this model with experiment, using the local-spin-density (LSD) approximation for exchange and correlation. In the derivation, an expression for the energy splitting of bands with different spins is calculated using perturbation theory. The splitting is approximately wavevector independent and proportional to a generalized, energy-dependent Stoner parameter. Using the LSD approximation, this parameter has been calculated for a number of transition metals (V, Fe, Co, Ni, Pd, Pt) and the results show systematic trends within and between the rows of the periodic system. Neglect of the weak wavevector dependence of the band splitting allows magnetic properties to be expressed simply in terms of the density of states and the Stoner parameter. By using densities of states from published band calculations, the theory is found to give systematically correct predictions for the relative stability of the para- and ferromagnetic phases for all the elements studied. This test is significant, as the same analysis using the  $X\alpha$  approximation (Slater 1974) predicts ferromagnetism for all these metals, except Pt, if recommended (Slater 1974) values of  $\alpha$  are used. The difference is due to inclusion of correlation in the LSD approximation. The results for the total magnetization are reasonable, but the calculated Curie temperatures are systematically too high, as expected for a Stoner model. Comparison with experimental estimates of the Stoner parameter suggests that the error in the calculated values is at most a few tenths of an eV.

The adequacy of the LSD approximation for the description of magnetism in transition metals has independently been investigated by Madsen *et al* (1976). Their self-consistent band calculations using the atomic sphere approximation (Andersen 1973, 1975) with neglect of hybridization were interpreted in terms of Stoner theory and canonical d state density. Their approach is complementary, in that they focus on the volume and structure dependence and hence on band theory.

In § 2 the SDF formalism for  $T \neq 0$  is presented. Following the derivation of a Stoner-like theory and stability criteria, formulae for the magnetic moment and the Curie temperature are obtained. In § 3 results for the Stoner parameter for V, Fe, Co, Ni, Pd, and Pt are presented. The relative stabilities of the para- and ferromagnetic phases are compared and results for the total magnetization and Curie temperature are given. In § 4 it is shown that charge fluctuations are substantially suppressed in the LSD approximation, the trends in the calculated Stoner parameters are explained, the calculated values are compared with experimental estimates of the Stoner parameter and the high results for the Curie temperature are discussed.

## 2. Derivation of a Stoner-like model in the SDF formalism

The main features of the Stoner model (see Stoner 1939 and references therein) are (i) the itinerant description of the electrons, originally assumed to be in a parabolic band, and (ii) the introduction of an exchange energy, which is proportional to the magnetization squared—the constant of proportionality being called the Stoner parameter. This model has been used in discussing many magnetic properties, including the first semiquantitative discussion of a transition metal band structure by Slater (1936) for Ni, which was correctly predicted to be ferromagnetic. The Stoner model

has been derived in the Hartree–Fock approximation by, e.g., Wohlfarth (1953, 1968), who also gave an explicit formula for the Stoner parameter including some correlation.

In the present derivation of a Stoner model the main approximations are the use of a Bloch representation for all states and the LSD approximation, which is introduced to calculate Stoner parameters. This approach neglects effects of localized, fluctuating moments, which may be present in the system. The main problem in the derivation is to determine the energy splitting of bands with different spins. The splitting is due to a lowering (raising) of the exchange-correlation potential, and thus a lowering (raising) of the energy of majority (minority) electrons, when the system is spin polarized. Using first order perturbation theory, the band splitting is obtained as the expectation value of potential splitting, which is related to the spin polarization. It is shown in appendix 1 that the spin polarization is essentially due to spin-flips of d electrons at the Fermi surface. Neglecting other contributions an explicit expression for the spin polarization is obtained (equation 2.9). In appendix 2 the nonspherical part of the spin polarization is found to be of little importance for the properties studied, and neglecting it a formula for the potential splitting is derived. The calculation of the expectation value of this potential is simplified by the small weight in the d band of angular quantum numbers different from two and a simple expression for the band splitting is obtained (equations 2.14 and 2.15) and compared with the results of a spin polarized band calculation.

### 2.1. The SDF formalism

The SDF formalism for  $T = 0$  has been discussed in several papers (Kohn and Sham 1965, Stoddart and March 1971, von Barth and Hedin 1972, Gunnarsson *et al* 1972, Rajagopal and Callaway 1973, Gunnarsson and Lundqvist 1976). In the latter paper the extension to  $T \neq 0$  was treated and we give the basic equations for this case. The equations are in a particularly simple form for a ferromagnetic metal, for which the spin-density everywhere is parallel or antiparallel to some fixed direction, the same all over space. The spin-density at the temperature  $T$  is given by

$$\rho_s(\mathbf{r}) = \sum_i |\psi_{i,s}(\mathbf{r})|^2 f(\epsilon_{i,s}) \quad (2.1)$$

where  $s = +, -$  is a spin index,  $f(\epsilon_{i,s}) = \{1 + \exp[(\epsilon_{i,s} - \mu)/kT]\}^{-1}$  is the usual Fermi-Dirac function and  $\mu$  is the chemical potential. The functions  $\psi_{i,s}(\mathbf{r})$  are the solutions of a Schrödinger-like equation

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_s(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + v_s^{xc}(\mathbf{r}) \right) \psi_{i,s}(\mathbf{r}) = \epsilon_{i,s} \psi_{i,s}(\mathbf{r}) \quad (2.2)$$

where  $v_s(\mathbf{r})$  is some external, spin-dependent potential and  $\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$  is the total density. Equations (2.1 and 2.2) are in principle exact. In practice approximations for the exchange-correlation potentials are necessary, and the local-spin-density (LSD) approximation is used in the numerical calculations. This approximation is exact in the limit of spatially slow and weak density variations and has been found to have a broad range of applicability (Tong and Sham 1966, Lang 1973, Smith *et al* 1973, Lang and Williams 1975, Janak *et al* 1975, Gunnarsson and Johansson 1976). The equation (2.2) is not invariant under rotations in spin space if the LSD approximation is used. However, this is of minor importance for a ferromagnetic system, which has a preferred direction

defined by the magnetic moment. In the LSD approximation the exchange-correlation potentials  $v_s^{xc}$  are related to the exchange-correlation part  $f^{xc}$  of the free energy per electron of a homogeneous electron liquid. For applications in the temperature range considered here, however, data for  $T = 0$  can be used (Gunnarsson and Lundqvist 1976). Then one gets

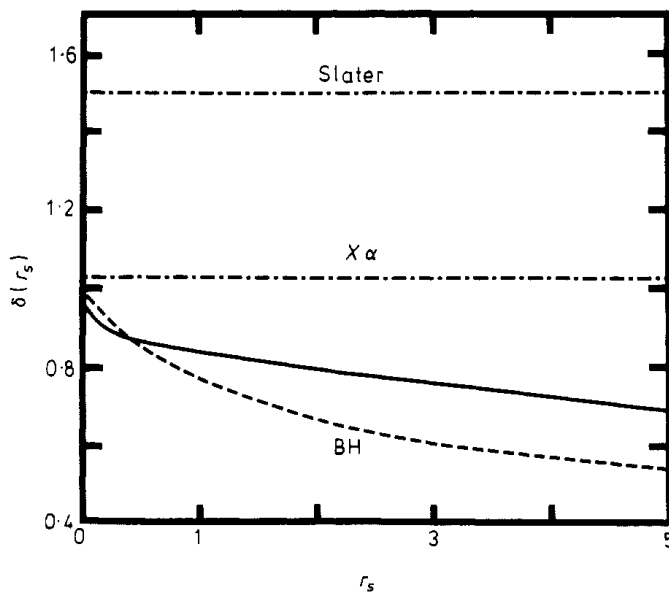
$$v_s^{xc}(\mathbf{r}) \approx \frac{\partial}{\partial \rho_s(\mathbf{r})} \{ \rho(\mathbf{r}) \epsilon^{xc}[\rho_+(\mathbf{r}), \rho_-(\mathbf{r})] \} \quad (2.3)$$

where  $\epsilon^{xc}$  is the exchange-correlation energy per electron of a homogeneous electron liquid. Numerical results for these potentials are given in the literature (von Barth and Hedin 1972, Gunnarsson and Lundqvist 1976). Potentials from the latter paper are used here and are given as an interpolation formula in terms of the density parameter  $r_s$  ( $4\pi r_s^3 a_0^3 / 3 = 1/\rho$ ) and the fractional spin-polarization  $\zeta = m/\rho$  ( $m = \rho_+ - \rho_-$ )

$$v_{\pm}^{xc}(r_s, \zeta) = \mu^x \left( \beta \pm \frac{1}{3} \frac{\delta \zeta}{1 \pm \gamma \zeta} \right). \quad (2.4)$$

Here  $\mu^x = -2/(\pi \alpha r_s)$ ,  $\alpha = (4/9\pi)^{1/3}$ ,  $\beta = 1 + 0.0545 r_s \ln(1 + 11.4/r_s)$ ,  $\delta = 1 - 0.036 r_s - 1.36 r_s / (1 + 10 r_s)$  and  $\gamma = 0.297$ .

For the magnetic properties the most important parameter is  $\delta$ , which for small spin-polarizations determines the splitting of the potentials. The  $\delta$  used here and the result of von Barth and Hedin (1972), both with correlation included, are plotted in figure 1. In the limit of small spin-polarizations the potentials (2.4) can be compared with the  $X\alpha$  potential (Slater 1974) and the Slater potential (Slater 1951a), which would then correspond to  $\delta$  equal to  $\frac{3}{2}\alpha$  and  $\frac{3}{2}$ , respectively. These two values for  $\delta$  are plotted in figure 1 using  $\alpha = 0.70$ , a value typical of those recommended for



**Figure 1.** The function  $\delta(r_s)$  describing the spin splitting of the exchange-correlation potentials (equation (2.4)). The full curve shows the  $\delta(r_s)$  used here and the broken curve the result of von Barth and Hedin (BH) (1972). The chain curves give the  $\delta(r_s)$  derived from the  $X\alpha$  and Slater potentials. Correlation effects are included in the former two curves, which give considerably smaller  $\delta(r_s)$ .

transition metals (Slater 1974). If only exchange is included in the potential (2.3) the so called Kohn–Sham–Gaspar potential is obtained (Kohn and Sham 1965). This potential is represented by  $\alpha = \frac{2}{3}$  and corresponds to  $\delta(r_s) \equiv 1$ . Figure 1 shows that correlation reduces  $\delta$  substantially.

It has been argued that some correlation can be included by using a  $\alpha$  value larger than  $\frac{2}{3}$  as the  $X\alpha$  potential then is closer to the potential (2.4) in the paramagnetic limit. However, figure 1 shows that to simulate the correlation effects on the spin-dependence of the potential (2.4) an  $\alpha$  value smaller than  $\frac{2}{3}$  is required.

The interpolation formula (2.4) was constructed to fit the calculated electron liquid data in the  $r_s$  range 1–5. For the paramagnetic phase the interpolation formula (2.4) gives a somewhat more attractive potential for small  $r_s$  than the result of an  $r_s$  expansion (Carr and Maradudin 1964). This is not important in the present paper, where we are just interested in the spin-dependence. In a full band calculation one might, however, use a more accurate paramagnetic potential (Hedin and Lundqvist 1971) and obtain the spin-dependence from equation (2.4).

### 2.2. Band splitting and spin polarization

First the band splitting is related to the spin polarization. The band energies and wavefunctions of the paramagnetic state are assumed to be known. The effects of introducing a spin polarization are calculated using perturbation theory. As in the original Stoner theory, the net magnetization per atom

$$\Delta m = \int_{\text{WS cell}} [\rho_+(\mathbf{r}) - \rho_-(\mathbf{r})] d^3r \equiv \int_{\text{WS cell}} m(\mathbf{r}) d^3r \quad (2.5)$$

is used as an expansion parameter, and effects of first order in  $\Delta m$  are considered. The exchange–correlation potentials  $v_s^{\text{xc}}$  in equation (2.4) can be expanded as

$$v_+^{\text{xc}}(\mathbf{r}) - v_-^{\text{xc}}(\mathbf{r}) = \Delta m v_{(1)}^{\text{xc}}(\mathbf{r}) + O(\Delta m^2) \quad (2.6)$$

where  $v_{(1)}^{\text{xc}}$  is determined from the spatial distribution of the spin polarization. Equation (2.6) gives the main contribution to the band splitting, which to first order is given by the expectation value of equation (2.6)

$$\Delta \epsilon_{kn} = \epsilon_{kn+} - \epsilon_{kn-} = \langle kn | v_+^{\text{xc}} - v_-^{\text{xc}} | kn \rangle = \Delta m \langle kn | v_{(1)}^{\text{xc}} | kn \rangle \quad (2.7)$$

In addition, the spin polarization causes a shift of the electrostatic potential, which contains a small first order term in  $\Delta m$ . To lowest order in  $\Delta m$ , however, this shift is spin-independent and does not contribute to equation (2.7).

The next step is to find the spin polarization  $m(\mathbf{r})$ , from which  $v_{(1)}^{\text{xc}}$  and  $\Delta \epsilon_{kn}$  can be calculated. In the remaining part of this subsection it will be shown that the spherical average of the spin polarization is

$$\langle m(\mathbf{r}) \rangle = (\Delta m / 4\pi) \phi_2^2(r, \epsilon_F) \quad (2.8)$$

The function  $\phi_l(r, \epsilon)$  is the solution of the radial Schrödinger equation for the energy  $\epsilon$  and the angular quantum number  $l$ , normalized to the Wigner–Seitz sphere.

The spin polarization is caused by two effects: (i) Electrons in states close to the Fermi surface flip their spins due to the changes in the chemical potentials for spin up and spin down electrons when the system is spin polarized. (ii) Spin polarization causes modifications of the potentials, giving changes in the wavefunctions of all states. These changes are different for spin up and spin down states giving a spin polarization. In appendix 1 it is argued that the first effect dominates. According to equation (2.1) it gives the spin polarization

$$m(\mathbf{r}) = \sum_{\mathbf{k}n} |\psi_{\mathbf{k}n}(\mathbf{r})|^2 [f(\epsilon_{\mathbf{k}n+}) - f(\epsilon_{\mathbf{k}n-})] \quad (2.9)$$

to lowest order in  $\Delta m$ .

For the wavefunctions  $\psi_{\mathbf{k}n}$  it is convenient to use a one-centre expansion, (e.g. Seitz 1940)

$$\psi_{\mathbf{k}n}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) \Phi_{\mathbf{k}n}(\mathbf{r} - \mathbf{R}) \quad (2.10)$$

where the vectors  $\mathbf{R}$  give the positions of the lattice sites,  $N$  is the number of sites and

$$\begin{aligned} \Phi_{\mathbf{k}n}(\mathbf{r}) &= \sum_{lm} c_{lm}(\mathbf{k}n) \phi_l(\mathbf{r}, \epsilon_{\mathbf{k}n}) Y_{lm}(\hat{\mathbf{r}}) && \text{inside the Wigner-Seitz sphere} \\ &= 0 && \text{elsewhere.} \end{aligned} \quad (2.11)$$

Here and in the following the Wigner-Seitz cell is approximated by a sphere. The functions  $Y_{lm}(\hat{\mathbf{r}})$  are spherical harmonics and  $c_{lm}(\mathbf{k}n)$  are expansion coefficients. For a muffin-tin potential the wavefunction can always be written as in equation (2.11).

Only states close to the Fermi level contribute to the spin polarization (2.9), and we will now show that these states have essentially d character. In the lowest six unhybridized valence bands the number of electrons per atom with d and sp character are five and one, respectively. Further, the width of the sp band is a factor two to three times larger than the d bandwidth. Assuming that the density of states is proportional to the number of electrons and inversely proportional to the bandwidth, one finds that the d electrons contribute about 90–95 per cent to the density of states within the d band. These simple arguments are supported by band calculations. For instance, for Cu with a band structure similar to the FCC transition metals, it has been reported that within the d band energy range the d character is always more than 90 per cent and for most states more than 95 per cent (Wood 1967). It is therefore a good approximation to assume that only  $l = 2$  terms contribute to the spin polarization. This simplifies the calculations considerably.

In appendix 2 the non-spherical parts of the spin polarization are found to contribute little to the properties considered (in, for instance, the stability criteria (2.16 and 2.17) below it gives a contribution which is less than four per cent of the leading one). Therefore, only the spherical average  $\langle m(\mathbf{r}) \rangle$  of equation (2.9) will be studied

$$\langle m(\mathbf{r}) \rangle = \frac{1}{N} \phi_2^2(\mathbf{r}, \epsilon_F) \sum_{\mathbf{k}n} (f(\epsilon_{\mathbf{k}n+}) - f(\epsilon_{\mathbf{k}n-})) \quad (2.12)$$

where the energy argument  $\epsilon_F$  in  $\phi_2(r, \epsilon)$  is correct to first order in  $\Delta m$ . As  $\phi_2(r, \epsilon_F)$  is normalized to the Wigner-Seitz sphere the sum in equation (2.12) has a simple relation to the net magnetization  $\Delta m$ , and one obtains formula (2.8).

### 2.3. Stoner parameter

From the spin polarization (2.8) the exchange-correlation potentials in equation (2.4,6) can easily be calculated as

$$v_+^{xc}(r) - v_-^{xc}(r) = \Delta m v_{(1)}^{xc}(r) = \frac{1}{6\pi} \mu^x(r_s) \delta(r_s) \frac{\Delta m [\phi_2(r, \epsilon_F)]^2}{\rho(r)}. \quad (2.13)$$

This equation together with equation (2.7) gives the band splitting. The expectation value in equation (2.7) is complicated by the appearance of several  $l$  quantum numbers. However, the magnetic properties are mainly determined by the splitting in the d band region. Following the discussion of §2.2. only the  $l = 2$  components of the wavefunctions are considered in equation (2.7), enabling the band splitting to be expressed as

$$\Delta \epsilon_{kn} = -I(\epsilon_{kn}) \Delta m. \quad (2.14)$$

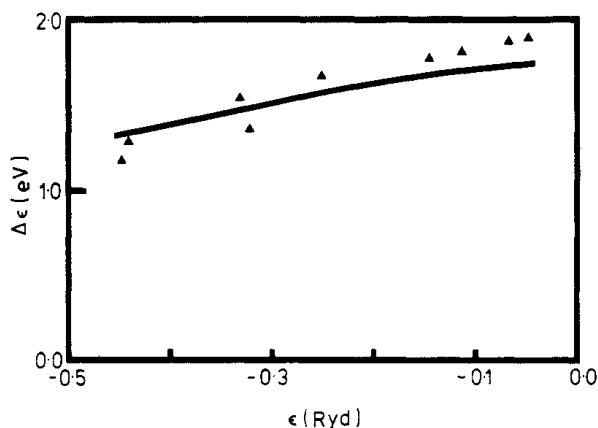
The generalized Stoner parameter  $I(\epsilon)$  is given by equations (2.7, 2.13 and 2.14)

$$I(\epsilon) = - \int_0^{r_{ws}} r^2 dr \left( \frac{\mu^x(r_s)}{6\pi} \right) \delta(r_s) \frac{\phi_2^2(r, \epsilon) \phi_2^2(r, \epsilon_F)}{\rho(r)}. \quad (2.15)$$

This is the final formula for the energy splitting. According to the definition (2.7) this quantity depends *a priori* on both the wavevector  $\mathbf{k}$  and the energy  $\epsilon$ , while our final expression depends on  $\mathbf{k}$  only implicitly through the energy. Besides the explicit formula for  $I(\epsilon)$ , the  $\mathbf{k}$  independence is the main result of the analysis. It follows from the physically well motivated assumptions that (i) the states under consideration are mainly of d character and that (ii) the non-spherical part of the spin polarization gives a small contribution to the band splitting.

The general form as well as the magnitude of the results in equations (2.14 and 2.15) was tested by a comparison with a full spin polarized band calculation for Fe of Wakoh and Yamashita (1966). As this calculation was done using the  $X\alpha$  method with  $\alpha = 0.5$ , we have in this particular case calculated the Stoner parameter with a  $\delta$  value which is consistent with the  $X\alpha$  method, i.e. with  $\delta = \frac{3}{2}\alpha$ . The wavefunctions  $\phi_2(r, \epsilon_F)$  and  $\phi_2(r, \epsilon)$  were obtained by solving the radial Schrödinger equation with the potential being an average of the majority and minority spin potentials calculated by Wakoh and Yamashita. The results for the band splitting as a function of the energy is shown in figure 2. The results calculated from equations (2.14 and 2.15) are compared with the values obtained by Wakoh and Yamashita for states with predominantly d character at various symmetry points. The figure shows that the predicted  $\mathbf{k}$  independence is essentially fulfilled and that the present results also agree well in magnitude with the band calculation, the deviation being typically 5–10 per cent. The agreement is a test of all the approximations except the use of a spherical exchange-correlation potential, as Wakoh and Yamashita, too, neglected non-spherical components of the potential.

The energy dependence is a consequence of the shape of the wavefunctions (see equation (2.15)). The spin polarization is caused by spin flips of electrons at the



**Figure 2.** The spin splitting of the energy bands as a function of the energy. The triangles show the splittings for various symmetry points in the Brillouin zone obtained in a full band calculation (Wakoh and Yamashita 1966). Our results calculated from equations (2.14 and 2.15) are given by the curve. The figure shows that the band splitting is energy-dependent but has only a weak  $k$  dependence.

Fermi energy, which is near the top of the d band for the metals to the right of the 3d series, e.g., iron, and the corresponding wavefunctions are rather contracted towards the nuclei (Wood 1960). Thus the spin polarization is concentrated to the inner parts of the atoms and the difference between the potentials for spin up and spin down electrons is consequently largest there. This difference is effectively picked up by the contracted wavefunctions at the top of the band, while states at the bottom with more extended wavefunctions are less influenced.

The discussion so far has essentially been within the LSD approximation, but the arguments are believed to be of more general validity. Assumption (i) about the d character is essentially independent of the approximation for the exchange-correlation potential, while this approximation of course has to be specified to discuss assumption (ii) about a spherical potential. For potentials with a smooth non local dependence on the density there should however be a tendency to average out the non-spherical part of the density. For such potentials assumption (ii) might therefore be even better than in the LSD approximation. The only change in the derivation above would then be a replacement of the exchange-correlation potential (2.13), which would give a new expression for the Stoner parameter.

#### 2.4. Magnetic properties

The magnetic ground-state properties can be derived from equations (2.1, 2.2, 2.14 and 2.15). The essential  $k$  independence of the band splitting enables these properties to be related to the density of states, which contains the necessary information about the band structure, and the Stoner parameter, which gives the required information about the wavefunctions. Below we give some results, which are needed for the calculations. The Curie temperature is the temperature at which (Stoner 1936)

$$I(\epsilon_F) \int_{-x}^x \frac{\partial f}{\partial \epsilon}(\epsilon) N(\epsilon) d\epsilon + 1 = 0, \quad (2.16)$$

where  $N(\epsilon)$  is the density of states per atom and spin. At  $T = 0$  this equation gives the



Stoner criteria for ferromagnetism (Stoner 1936)

$$I(\epsilon_F) N(\epsilon_F) > 1. \tag{2.17}$$

The susceptibility is given by:

$$\chi = \frac{\chi_0}{1 - I(\epsilon_F)N(\epsilon_F)} \tag{2.18}$$

where  $\chi_0$  is the susceptibility for non-interacting electrons. To calculate the magnetization at  $T = 0$ , we introduce  $\epsilon(n)$ , the energy to which the band has to be filled to accumulate  $n$  electrons per atom and spin.

$$\epsilon(n) = \int_0^n \frac{dn'}{N[\epsilon(n')]} \tag{2.19}$$

If the spin up and spin down bands are filled with  $n_+ = (n + \Delta m)/2$  and  $n_- = (n - \Delta m)/2$ , respectively, the chemical potentials become

$$\mu_{\pm} = \epsilon(n_{\pm}) \mp \frac{1}{2} \Delta m I(\epsilon_F) \tag{2.20}$$

to lowest order in  $\Delta m$ . Equilibrium requires

$$\frac{\partial E}{\partial(\Delta m)} = \frac{1}{2} \left( \frac{\partial E}{\partial n_+} - \frac{\partial E}{\partial n_-} \right) = \frac{1}{2} (\mu_+ - \mu_-) = 0 \tag{2.21}$$

where  $E$  is the total energy of the system. Using equations (2.19 and 2.20) the condition (2.21) is rewritten as (Lomer 1967)

$$I(\epsilon_F) = \frac{1}{\Delta m} \int_n^{n_+} \frac{dn'}{N[\epsilon(n')]} \equiv F(\Delta m) \tag{2.22}$$

This gives the magnetization as a function of the Stoner parameter. If there are more than one solution, the condition  $\partial^2 E / \partial(\Delta m)^2 > 0$  can be used to show that at least one solution is metastable.

$$\frac{\partial^2 E}{\partial(\Delta m)^2} = \frac{1}{2} \frac{\partial}{\partial(\Delta m)} \{ \Delta m [F(\Delta m) - I(\epsilon_F)] \} = \frac{1}{2} [F(\Delta m) - I(\epsilon_F)] + \Delta m \frac{\partial F(\Delta m)}{\partial(\Delta m)} \tag{2.23}$$

At equilibrium the first term is zero according to equation (2.22). This new result shows that the state is metastable if  $F(\Delta m)$  has a negative derivative.

### 3. Results

Calculations are made on V, Fe, Co, Ni, Pd, and Pt, i.e. the transition metals which are ferromagnetic or almost ferromagnetic under normal conditions. The relative stability of the para- and ferromagnetic phases is calculated. For the ferromagnetic metals the Curie temperature and the total magnetization are given.

The key quantity in the calculation of the magnetic properties are the density of states for the paramagnetic phase and the Stoner parameter. In a consistent treatment these quantities should be computed from a band calculation using the exchange-correlation potential (2.4). As such band calculations are not available, band structures obtained with other potentials are used. This introduces uncertainties in the

**Table 1.** The Stoner parameter  $I(\epsilon_F)$  (equation (2.15)) in the LSD approximation, the  $X\alpha$  method and with the Slater potential. We have used the recommended values for  $\alpha$  (Slater 1974) for V–Ni and extrapolated to the values 0.70 and 0.69 for Pd and Pt, respectively. The Slater potential corresponds to  $\alpha = 1.0$ . We give a range of values for the quantity  $I(\epsilon_F)N(\epsilon_F)$  obtained by using values of  $N(\epsilon_F)$  from various band calculations. The theory predicts ferromagnetism if  $I(\epsilon_F)N(\epsilon_F) > 1$  and P(F) shows that the metal is paramagnetic (ferromagnetic) in nature at  $T = 0$ .

Metal	LSD		$X\alpha$		Slater potential	
	$I(\epsilon_F)$	$I(\epsilon_F)N(\epsilon_F)$	$I(\epsilon_F)$	$I(\epsilon_F)N(\epsilon_F)$	$I(\epsilon_F)$	$I(\epsilon_F)N(\epsilon_F)$
V (P)	0.80	0.8–0.9 <sup>a</sup>	1.01	1.0–1.2 <sup>a</sup>	1.41	1.4–1.7 <sup>a</sup>
Fe <sub>BCC</sub> (F)	0.92	1.5–1.7 <sup>b</sup>	1.14	1.8–2.2 <sup>b</sup>	1.60	2.6–3.0 <sup>b</sup>
Co (F)	0.99	1.6–1.8 <sup>c</sup>	1.21	1.9–2.2 <sup>c</sup>	1.71	2.7–3.1 <sup>c</sup>
Ni (F)	1.01	2.1 <sup>d</sup>	1.23	2.6 <sup>d</sup>	1.74	3.6 <sup>d</sup>
Pd (P)	0.70	0.8 <sup>e</sup>	0.86	1.0 <sup>e</sup>	1.23	1.5 <sup>e</sup>
Pt (P)	0.63	0.5 <sup>e</sup>	0.78	0.7 <sup>e</sup>	1.13	1.0 <sup>e</sup>

(a) Yasui *et al* (1970) and Papaconstantopoulos *et al* (1972)

(b) Mattheiss (1965), Snow and Waber (1969) and Connolly (1970)

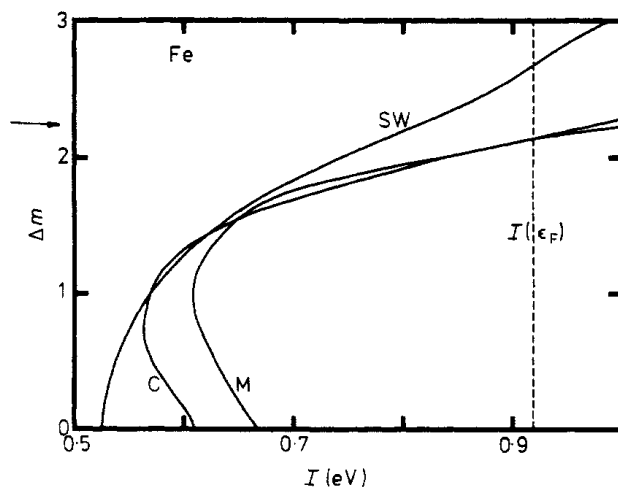
(c) Wakoh and Yamashita (1970) and Ishida (1972)

(d) Hodges *et al* (1966)

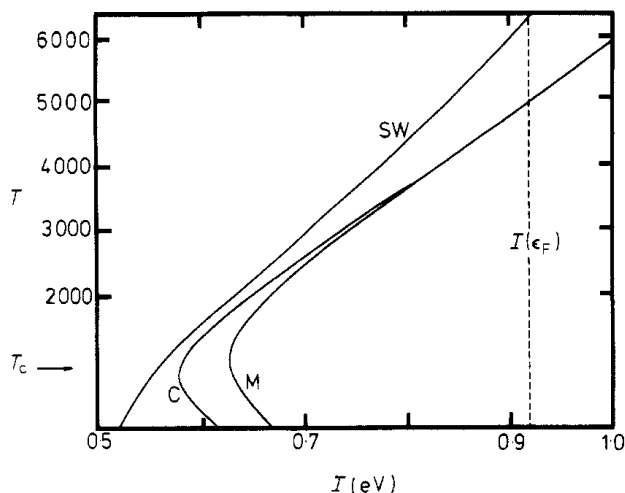
(e) Andersen (1970)

results, since the densities of states differ appreciably between different band calculations due to different potentials, methods of calculation and numerical accuracy. The main conclusions obtained in the following seem, however, to be independent of the band calculations chosen.

To calculate the Stoner parameter one needs to know the electron density and the radial d wavefunction. The choice for these quantities is described in appendix 3. The results for the Stoner parameter obtained with the LSD approximation, the  $X\alpha$  method and the Slater potential are compared in table 1. It shows that the  $X\alpha$  and Slater potentials give larger Stoner parameters than the LSD approximation. This is due to the improper treatment of correlation in the former two approximations.



**Figure 3.** The magnetic moment of iron in Bohr magnetons as a function of the Stoner parameter  $I$  (equation (2.22)). The curves are obtained for different densities of states (Snow and Waber (SW) 1969, Mattheiss (M) 1965, Connolly (C) 1970). The arrow shows the experimental moment and the broken line our calculated value for the Stoner parameter.



**Figure 4.** The Curie temperature of iron as a function of the Stoner parameter (equation (2.16)) for the same densities of states as in figure 3. The arrow marks the experimental Curie temperature.

Some paramagnetic band calculations have been collected to check the stability criterion (2.17). Table 1 shows the range of values for the quantity  $I(\epsilon_F)N(\epsilon_F)$  with  $N(\epsilon_F)$  obtained from different band calculations. We notice that for all the metals studied the LSD approximation gives the correct result for the relative stability of the para- and ferromagnetic states.

The  $X\alpha$  and Slater potentials give a stronger tendency to ferromagnetism than the LSD approximation, the Slater potential predicting all the metals studied, except possibly Pt, to be ferromagnets. The same seems to be true in the  $X\alpha$  method, too. In the  $X\alpha$  approximation, however, V and Pd are close to the phase transition and the uncertainty in the band calculations makes it difficult to definitely assess the states of these two metals in the  $X\alpha$  scheme. Thus Cronklin *et al* (1972) have reported V to be paramagnetic in the  $X\alpha$  approximation.

To calculate the magnetic moment at  $T = 0$  equation (2.22) has been used. The quantity  $F(\Delta m)$  for iron is plotted in figure 3 for various calculations of the density of states. The calculated magnetic moments fall in the range 2.1–2.7 Bohr magnetons compared with the experimental result 2.2. For both Co and Ni the majority spin d band is found to be full. This is correct for Ni, as is well known, and probably also for Co (Wohlfarth 1970). The actual values of the magnetic moment for the latter two metals are of less interest in this context as they essentially just reflect the number of unfilled d states in the paramagnetic phase.

The Curie temperature is calculated from equation (2.16). The value of

$$\left( - \int_{-\gamma}^{\alpha} \frac{\partial f(\epsilon)}{\partial \epsilon} N(\epsilon) d\epsilon \right)^{-1}$$

for iron as a function of the temperature is shown in figure 4. The Curie temperatures obtained for the ferromagnetic metals considered are shown in table 2. The results are systematically much larger than the correct ones.

#### 4. Discussion

The description of charge fluctuations in transition metals has attracted considerable interest and Hartree-Fock band theories have been criticized for allowing large

**Table 2.** The Curie temperature (K) in the LSD approximation compared with experiments.

Metal	LSD	Experiment
Fe	4400–6200	1040
Co	3300–4800	1400
Ni	2900	631

fluctuations in the number of d electrons on a particular atom. For this reason the Hubbard model (Hubbard 1963) was proposed, which due to its relative simplicity allows a treatment beyond the Hartree-Fock approximation. In this model the importance of the fluctuations is determined by the Coulomb repulsion  $U$ , and for an infinite  $U$  there would be no fluctuations at all. Estimates of  $U$  (Herring 1966, Watson 1973, Cox *et al* 1974) indicate that  $U$  is not very large for transition metals and that the fluctuations are reduced but not negligible. A measure of the fluctuations is

$$\Delta = \frac{1}{n} \int d^3r \int_{r' \neq r} d^3r' \langle \hat{\rho}(r) \hat{\rho}(r') \rangle \theta(r_{\text{WS}} - r) \theta(r_{\text{WS}} - r') - (n - 1) \quad (4.1)$$

where  $\langle \hat{\rho}(r) \hat{\rho}(r') \rangle$  is the density-density correlation function,  $n$  is the number of electrons per atom,  $\theta(x)$  is the Heaviside step function and the origin is at one of the nuclei. If the electrons are treated as independent, i.e.  $\langle \hat{\rho}(r) \hat{\rho}(r') \rangle = \langle \hat{\rho}(r) \rangle \langle \hat{\rho}(r') \rangle$ , one gets  $\Delta = 1$ . In the opposite limit of extreme correlation, where the number of electrons on each atom is always exactly  $n$ , one gets  $\Delta = 0$ . For the LSD approximation we use (Gunnarsson and Lundqvist 1976)

$$\langle \hat{\rho}(r) \hat{\rho}(r') \rangle = \langle \hat{\rho}(r) \rangle [\langle \hat{\rho}(r') \rangle + \langle \hat{\rho}(r) \rangle \{g[|r - r'|, \rho(r)] - 1\}]. \quad (4.2)$$

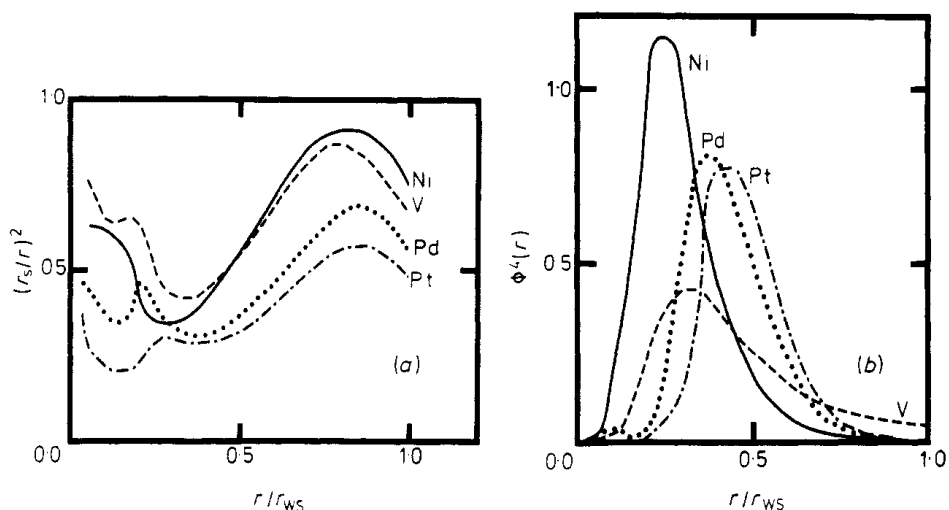
Using equations (4.1) and (4.2) and the random phase approximation for  $g[|r - r'|, \rho(r)]$  (Hedin 1965)  $\Delta = 0.1$  is obtained for iron. Thus the fluctuations are substantially suppressed in the LSD approximation.

Table 1 exhibits certain trends for the Stoner parameter, and to understand them it is useful to rewrite equation (2.15) as

$$I(\epsilon_F) = \frac{4}{9\pi\alpha} r_{\text{WS}} \int_0^1 \left(\frac{r_s}{r}\right)^2 \delta(r_s) \Phi^4(r, \epsilon_F) d\left(\frac{r}{r_{\text{WS}}}\right) \quad (4.3)$$

where  $\Phi(r, \epsilon_F) = r\phi_2(r, \epsilon_F)$ . As  $\delta$  has roughly the same spatial dependence for all the metals, varying between 0.8–0.9 over the region of interest (cf figure 1), the other two factors are the important ones for the trends. Plots of  $(r_s/r)^2$  and  $\Phi^4(r, \epsilon_F)$  against the scaled radius  $r/r_{\text{WS}}$  for some typical metals are given in figure 5.

Figure 5a illustrates the decreasing trend of  $(r_s/r)^2$  along the 3rd row series V–Ni and along the VIII group series Ni, Pd, and Pt, which reflects the increasing density along these series. A high electron density means that a certain spin polarization gives a smaller fractional spin polarization  $\zeta$  and thus a smaller difference between the majority and minority spin potentials (see equation (2.4)). This is the main source of the  $r_s$  dependence in equation (4.3) and gives a factor  $r_s^3$ . In addition the quantity  $\mu^x$  in the exchange-correlation potential contributes a factor  $r_s^{-1}$ . The wavefunctions gradually contract along the series V–Ni, as is indicated by the results for V and Ni in figure 5b. The contraction is partially due to a more binding potential at the end of the series, connected with the incomplete screening of the increased nuclear

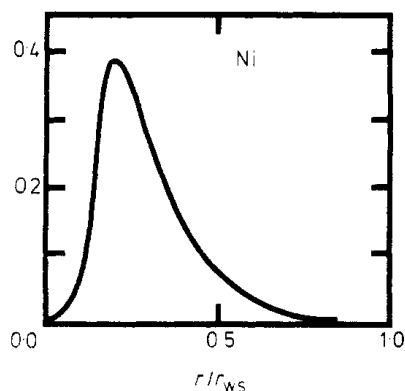


**Figure 5.** (a) The quantity  $(r_s/r)^2$  (appearing in equation (4.3)) as a function of  $r/r_{ws}$ , where  $r$  and  $r_{ws}$  are the distance from the nucleus and the Wigner-Seitz radius, respectively. The bulk densities are obtained by superposing the atomic densities. (b) The wavefunction  $\Phi(r, \epsilon_F) = r\phi_2(r, \epsilon_F)$  to the fourth power. The figure shows the trends for the 3rd row and the VIII group series.

charge (cf. Slater's rules (Slater 1951b and Coulson 1961)). A second reason is the energy-dependence of the wavefunctions. These gradually contract as their energies are increased (Wood 1960). Therefore the successive filling of the d band along the 3rd row series gives a further contraction of  $\Phi(r, \epsilon_F)$ . In the series Ni, Pd, and Pt, on the other hand, the increasing number of nodes makes the wavefunction expand. The integral (4.3) can be considered as a weighted average of  $(r_s/r)^2 \delta(r_s) \Phi^2(r, \epsilon_F)$  with the normalized weighting factor  $\Phi^2(r, \epsilon_F)$ . If the wavefunction  $\Phi(r, \epsilon_F)$  is concentrated within some region of space, the main contribution to this average comes from a region where  $\Phi(r, \epsilon_F)$  tends to make the average quantity large. This tends to give a large Stoner parameter and reflects the importance of exchange if the wavefunctions are essentially confined to a small region of space.

The two factors  $(r_s/r)^2$  and  $\Phi^4(r, \epsilon_F)$  work in the opposite direction in the series V, Fe, Co, and Ni. The numerical results and the figure show, however, that the change in the wavefunction is the more important one. In the series Ni, Pd, and Pt both factors tend to decrease the Stoner parameter in accordance with table 1.

Finally, figure 6 shows the integrand of equation (4.3) for Ni. Due to the factor  $\Phi^4(r, \epsilon_F)$  most of the contribution to the Stoner parameter comes from the high



**Figure 6.** The integrand of equation (4.3) as a function of  $r/r_{ws}$  for Ni. The figure illustrates the importance of the high-density region in the inner parts of the d shell.

density region, with  $r_s$  typically in the range 0.3–1.0. The  $r_s$  values corresponding to the average density are considerably larger, being about 1.2–1.6.

In § 3 magnetic properties calculated in the LSD approximation were compared with experiments. The opposite route will now be followed and estimates of the Stoner parameter extracted from experiments will be compared with calculated values.

For Fe Gold *et al* (1971) have calculated de Haas-van Alphen data assuming a constant band splitting. They obtained fairly good agreement with experiments if they used 0.99 eV (compared to 0.92 eV calculated in the LSD approximation) for the Stoner parameter, the value for which they found the correct net magnetization.

Wakoh and Yamashita (1970) found in a calculation on Co that a spin splitting of 1.2 eV between the spin up and spin down densities of states gave good agreement with photoemission data for the ferromagnetic phase. This number corresponds to the value 0.76 eV (LSD 0.99 eV) for the Stoner parameter.

For Ni, Zornberg (1970) has adjusted a parametrized band structure to fit a large amount of experimental data, including Fermi surface data, optical data and the total magnetization. He obtained a Stoner parameter in the range 0.75–1.0 eV (LSD 1.01 eV). Mook *et al* (1969) have used a band calculation to describe the intensity variation in neutron scattering against spin waves, obtaining a Stoner parameter of 1.0 eV.

For Pd and Pt estimated values for the susceptibility enhancement (Andersen 1970) and formula (2.18) have been used to estimate the Stoner parameters. The values 0.74 (LSD 0.70) and 0.86 (LSD 0.63) eV were obtained for Pd and Pt, respectively.

Finally, Asano and Yamashita (1973) have made self-consistent  $X\alpha$  calculations for the ferro- and antiferromagnetic 3rd row metals. For each metal they adjusted the band splitting until they obtained the correct magnetic moment. With  $\alpha = 0.8$  a Stoner parameter in the range 0.7–0.8 eV was required. They also remarked that this value would increase by about 0.05 eV if they used  $\alpha = \frac{2}{3}$ , a value which gives paramagnetic bands closer to those used here. These estimates indicate that the calculated values for the Stoner parameter are fairly accurate.

The  $X\alpha$  approximation gives Stoner parameters which are substantially larger (20–60 per cent) than the estimates above (except for Pt). The enhanced tendency to ferromagnetism has also been observed in band calculations by, e.g., Wakoh and Yamashita (1966) and DeCicco and Kitz (1967).

The calculated Curie temperatures  $T_c$  are much too high (table 2) as is expected for a Stoner-like model (e.g., Friedel *et al* 1961, Mott 1964). Figure 4 shows that too high a result for  $T_c$  is obtained for all the band structures considered, and that a moderate change in  $I(\epsilon_F)$  is not sufficient to give the correct value for  $T_c$ . The inadequacy of the Stoner model at high temperatures is also indicated by experiments (Fadley and Wohlfarth 1972) and in particular, there is evidence that for the paramagnetic phase there exist localized moments with lifetimes long enough to be observed. Effects of the fluctuations of these moments, for instance an increased entropy, have not been included in the present treatment. Band theories can, however, describe the formation of localized moments (Friedel *et al* 1961, Lederer and Blandin 1966, Lederer 1966). The Curie temperature should then be mainly determined by the interaction between the localized spins and not by the Stoner parameter (Friedel *et al* 1961, Slater 1974). In a straightforward application of the SDF formalism this has to be described through the exchange-correlation functional. An alternative approach of obtaining the Curie temperature, which demands less from the functional, would be to calculate the excitation energies of the system, using the same formalism as

for the ground state. The free energy, for instance, is then obtained by summing over all excited states according to the formula  $F = -kT \ln[\sum_n \exp(-E_n/kT)]$ . This sum includes states which differ by not having the same orientation of the localized moments. The free energy would then contain effects of the spin fluctuations, e.g., it would give a high entropy.

In summary, it has been found that the LSD approximation gives a reasonable description of the zero-temperature magnetic properties. Comparison with estimates for the Stoner parameter extracted from experiments indicates that the errors in the calculated values should be at most a few tenths of an eV. The results obtained suggest that the LSD approximation should be useful for the calculations on transition metal systems at  $T = 0$ .

### Acknowledgments

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### Appendix 1

In a spin-polarized system the potentials for spin up and spin down electrons are different, and the wavefunctions are therefore spin-dependent. This effect (called (ii) in §2.2) gives rise to a spin polarization. In the following this spin polarization will be shown to be small compared with that caused by spin-flips (effect (i)).

Perturbation theory is used and the spin polarization is calculated to lowest order in the net magnetization  $\Delta m$ . For the wavefunctions of the paramagnetic state the representation in equations (2.10 and 2.11) is used. Orthonormality requires

$$\sum_{lm} c_{lm}^*(kn) c_{lm}(kn') \langle kn|kn' \rangle_l = \delta_{nn'} \quad (\text{A1.1})$$

where

$$\langle kn|kn' \rangle_l \equiv \int_0^{r_{ws}} r^2 dr \phi_l(r, \epsilon_{kn}) \phi_l(r, \epsilon_{kn'}).$$

To lowest order in  $\Delta m$  the spin polarization due to distortions of the wavefunctions is

$$m(r) \equiv \rho_+(r) - \rho_-(r) = \Delta m \sum_{kn}^{\text{occ}} \sum_{n' \neq n} \left( \frac{\langle kn'|v_{(1)}^{xc}|kn \rangle}{\epsilon_{kn} - \epsilon_{kn'}} \psi_{kn'}(r) \psi_{kn}^*(r) + \text{C.C.} \right) \quad (\text{A1.2})$$

All terms in equation (A1.2) with  $n'$  occupied cancel. Appendix 2 shows that it is a reasonable approximation to assume  $v_{(1)}^{xc}(r)$  to be spherically symmetrical and utilizing this approximation one gets

$$m(r) = \Delta m \sum_{kn}^{\text{occ}} \sum_{n'}^{\text{unocc}} \sum_{lm} \left( c_{lm}^*(kn') c_{lm}(kn) \frac{\langle kn'|v_{(1)}^{xc}|kn \rangle_l}{\epsilon_{kn} - \epsilon_{kn'}} \psi_{kn'}(r) \psi_{kn}^*(r) + \text{C.C.} \right) \quad (\text{A1.3})$$

where

$$\langle kn'|v_{(1)}^{xc}|kn \rangle_l = \int_0^{r_{ws}} r^2 dr \phi_l(r, \epsilon_{kn'}) v_{(1)}^{xc}(r) \phi_l(r, \epsilon_{kn}).$$

The orthonormality condition (A1.1) provides a relation between the coefficients  $c_{lm}(kn)$ . It can be used to replace all the coefficients with a certain  $l$  value in equation (A1.3). As the bands considered are predominantly of d character, it is convenient to remove all the terms with  $l = 2$ .

$$m(r) = \Delta m \sum_{kn}^{\text{occ}} \sum_{n'}^{\text{unocc}} \sum_{\substack{l \neq 2 \\ m}} \left( c_{lm}^*(kn') c_{lm}(kn) \frac{\langle kn' | v_{(1)}^{xc} | kn \rangle_l}{\epsilon_{kn} - \epsilon_{kn'}} \psi_{kn}(r) \psi_{kn'}^*(r) + \text{C.C.} \right) \quad (\text{A1.4})$$

where

$$\overline{\langle kn' | v_{(1)}^{xc} | kn \rangle_l} = \langle kn' | v_{(1)}^{xc} | kn \rangle_l - \langle kn' | v_{(1)}^{xc} | kn \rangle_{l=2} \langle kn' | kn \rangle_l / \langle kn' / kn \rangle_{l=2}$$

For the spherical average  $\langle m(r) \rangle$  of  $m(r)$  we obtain

$$\begin{aligned} \langle m(r) \rangle = & \frac{\Delta m}{4\pi N} \sum_{kn}^{\text{occ}} \sum_{n'}^{\text{unocc}} \sum_{\substack{l \neq 2 \\ m}} \left( c_{lm}^*(kn') c_{lm}(kn) \sum_{\substack{l' \neq 2 \\ m'}} c_{l'm'}(kn') c_{l'm'}^*(kn) \right. \\ & \left. \times \frac{\overline{\langle kn' | v_{(1)}^{xc} | kn \rangle_l}}{\epsilon_{kn} - \epsilon_{kn'}} \overline{\phi_{l'} \phi_l} + \text{C.C.} \right) \end{aligned} \quad (\text{A1.5})$$

where  $\overline{\phi_l \phi_l} = \phi_l \phi_l - (\langle kn' | kn \rangle_l / \langle kn' | kn \rangle_{l=2}) \phi_2 \phi_2$ . For brevity the arguments of the two functions  $\phi_l$ ,  $r$ ,  $\epsilon_{kn'}$  and  $r$ ,  $\epsilon_{kn}$ , respectively are omitted. The sum over  $\mathbf{R}$  and  $\mathbf{R}'$  (cf. equation (2.10)) disappears because the density in one single cell is considered and because functions centred in different cells do not overlap.

The potential  $v_{(1)}^{xc}(\mathbf{r})$  is large in the regions of space where the d wavefunctions are large. Therefore the integral  $\langle kn' | v_{(1)}^{xc} | kn \rangle_l$  is largest for  $l = 2$  and for  $l \neq 2$  the first term in  $\overline{\langle kn' | v_{(1)}^{xc} | kn \rangle_l}$  is neglected. Using  $\epsilon_F$  for the energy arguments it is assumed that

$$\overline{\langle kn' | v_{(1)}^{xc} | kn \rangle_l} \approx -\langle \epsilon_F | v_{(1)}^{xc} | \epsilon_F \rangle_{l=2} \quad (\text{A1.6})$$

where  $\langle \epsilon_F | v_{(1)}^{xc} | \epsilon_F \rangle_{l=2} = -I(\epsilon_F)$  is the expectation value of  $v_{(1)}^{xc}$  for the wavefunction  $\phi_2(r, \epsilon_F)$ . Numerical calculation shows that there are appreciable cancellations between the two terms in  $\langle kn' | v_{(1)}^{xc} | kn \rangle_l$ . For  $\epsilon_{kn}$  and  $\epsilon_{kn'}$  in the energy range of the lowest six valence bands and for  $l \leq 2$  we find the absolute value of the left hand side of equation (A1.6) to be overestimated by about 50–100 per cent. As the expectation value of the spin polarization will be calculated, the spin polarization in the d wavefunction region is particularly important. Therefore the last term in  $\overline{\phi_l \phi_l}$  is assumed to dominate and the approximation

$$\overline{\phi_l(r, \epsilon_{kn'}) \phi_l(r, \epsilon_{kn})} \approx -\phi_2^2(r, \epsilon_F) \quad (\text{A1.7})$$

is made. Numerical estimate shows that this approximation, too, means that the contribution of the wavefunction distortion to the Stoner parameter is overestimated by about 50–100 per cent. The energy denominator in equation (A1.5) is the difference in energy between an unoccupied and an occupied state and is always nonzero. It is approximated by the d bandwidth  $W$ . This might be an underestimate of equation (A1.5). To get an upper limit for the sums over the coefficients  $c_{lm}(kn)$  the results of a band calculation (Wood 1967) is used. For the d-like bands of Cu it has been found that

$$\sum_m |c_{2m}(kn)|^2 \geq 0.9 \quad (\text{A1.8})$$



Using Schwartz inequality one obtains

$$|\sum_{l \neq 2}^m c_{lm}^*(kn')c_{lm}(kn)|^2 \leq \sum_{l \neq 2}^m |c_{lm}(kn')|^2 \sum_{l \neq 2}^m |c_{lm}(kn)|^2 \leq \begin{cases} 0.01 \text{ if both } n \text{ and } n' \text{ are d-like} \\ \text{bands} \\ 0.1 \text{ if either } n \text{ or } n' \text{ is a d-like} \\ \text{band} \end{cases} \quad (\text{A1.9})$$

First the contribution to equation (A1.5) from the six lowest valence bands is considered. It is assumed that the number of nonzero terms in the  $k$  sum equal  $Nn_n^{\text{occ}}n_n^{\text{unocc}}$ , where  $n_n^{\text{occ}}$  and  $n_n^{\text{unocc}}$  are the numbers of occupied and unoccupied states per atom and spin in the bands  $n$  and  $n'$ , respectively. This overestimate gives

$$\langle m(r) \rangle \leq \frac{2\Delta m}{4\pi W} I(\epsilon_F) \phi_2^2(r, \epsilon_F) (0.1 n_d^{\text{occ}} n_{sp}^{\text{unocc}} + 0.1 n_{sp}^{\text{occ}} n_d^{\text{unocc}} + 0.01 n_d^{\text{occ}} n_d^{\text{unocc}}) \quad (\text{A1.10})$$

Using the calculated values for  $I(\epsilon_F)$  and typical numbers for  $n_d^{\text{occ}}$ ,  $n_{sp}^{\text{occ}}$  and  $W$  for various transition metals equation (A1.10) is found to contribute about 5–10 per cent of the total spin polarization.

In the estimate of (A1.5) only the six lowest valence bands were included. In this way effects of different hybridization for majority and minority spin electrons were taken into account. In addition, the functions  $\phi_2(r, \epsilon)$  tend to contract (expand) for the majority (minority) spin electrons. To include this effect fully one would also have to include higher bands in equation (A1.5). Instead, an explicit calculation on the function  $\phi_2(r, \epsilon)$  for both spin states in iron has been performed. It is found that the distortion of the radial wavefunction contributes only a few (1–3) per cent to the band splitting.

In, e.g., iron there is in the interstitial region probably a very weak spin polarization which has opposite sign to the net magnetization (Shull 1967). This negative magnetization is supposed to be due to the above mentioned contraction of the majority spin states towards the nuclei (DeCicco and Kitz 1967). It is, however, not important for the splitting of the d bands as the d electrons are mostly in the region of the very much larger, positive spin polarization.

It is concluded that the spin polarization due to the deformation of the wavefunctions  $\psi_{kn}$  is small and could be neglected in this calculation.

## Appendix 2

In the derivation in § 2, the non-spherical part of the spin polarization was neglected. This approximation is discussed here, assuming cubic symmetry of the metal.

Quite generally the spin-density can be written as

$$m(\mathbf{r}) = \langle m(r) \rangle \left( 1 + \sum_{l \neq 0}^m A_{lm}(r) Y_{lm}(\hat{\mathbf{r}}) \right) \quad (\text{A2.1})$$

where  $\langle m(r) \rangle$  is the spherical part of the spin-density. Due to the cubic symmetry all  $A_{lm}(r) \equiv 0$  for  $l < 4$  (von der Lage and Bethe 1947). Terms with  $l \geq 5$  are very small as the s, p and d parts of the wavefunctions do not contribute to such terms. In addition, when we eventually take the expectation value of the spin polarization in equations (2.7,13), the s, p, and d parts of the wavefunctions will not couple to terms with  $l \geq 5$  in equation (A2.1). Thus only the  $l = 4$  terms are important and

$$m(\mathbf{r}) = \langle m(r) \rangle [1 + f(r) K_{4,1}(\hat{\mathbf{r}})] \quad (\text{A2.2})$$

where

$$K_{4,1}(\hat{r}) = \sqrt{\frac{7}{3\pi}} \{Y_{4,0}(\hat{r}) + \sqrt{\frac{5}{14}} [Y_{4,4}(\hat{r}) + Y_{4,-4}(\hat{r})]\} \quad (\text{A2.3})$$

is a cubic harmonic introduced by von der Lage and Bethe (1947). In appendix 1 we showed that the spin-density is essentially due to spin-flips of d electrons at the Fermi surface. The spherical and non-spherical parts of the spin polarization therefore have the same  $r$  dependence, described by  $\phi_2^2(r, \epsilon_F)$ . We can thus assume  $f(r)$  to be just a number  $f$ . This number can be determined experimentally from, e.g., neutron diffraction experiments.

Using the result (A2.2) for the spin polarization in equation (2.13 and 2.7) we get the ratio between the spherical and non-spherical contribution to the band splitting of a state ( $kn$ )

$$r_{kn} = f \sum_{mm'} c_{2m}^*(kn) c_{2m}(kn) \int d\Omega Y_{2m}^*(\hat{r}) Y_{2m}(\hat{r}) K_{4,1}(\hat{r}). \quad (\text{A2.4})$$

Using the explicit form for  $K_{4,1}(r)$  in (A2.3) we obtain

$$r_{kn} = (f/\sqrt{21}) \left( 3 \sum_m |c_{2m}(kn)|^2 a_m + 5 \operatorname{Re} c_{2,2}(kn) c_{2,-2}^*(kn) \right) \quad (\text{A2.5})$$

where  $a_m = 1$  if  $m = 0$ ,  $-\frac{2}{3}$  if  $|m| = 1$  and  $\frac{1}{6}$  if  $|m| = 2$ . If a state contains fractions  $0.4 + x_{kn}$  and  $0.6 - x_{kn}$  of functions with  $E_g$  symmetry ( $3z^2 - r^2$ ,  $x^2 - y^2$ ) and  $T_{2g}$  symmetry ( $xy$ ,  $yz$ ,  $zx$ ), respectively

$$r_{kn} = (5f/\sqrt{21}) x_{kn} \quad (\text{A2.6})$$

Estimates from neutron scattering data (Shull 1967) gives that  $f \lesssim 0.2$  for Fe, Co, and Ni. For pure  $E_g$  and  $T_{2g}$  states this gives  $r \lesssim 0.13$  ( $E_g$ ) and  $r \lesssim -0.09$  ( $T_{2g}$ ). The effects of the nonspherical spin polarization may therefore be of importance when calculating for instance the Fermi surface. In this paper, however, only integral properties of the band splitting are considered and for these there are large cancellations between states with positive and negative  $r$ . For instance, to derive the stability criteria in § 2.4 the magnetization  $\Delta m$  due to an external magnetic field is considered. From equation (2.1) one gets

$$\Delta m \equiv n_+ - n_- = \frac{1}{N} \sum_{kn} [f(\epsilon_{kn+} - \mu_B H) - f(\epsilon_{kn-} + \mu_B H)] \quad (\text{A2.7})$$

If  $H$  is a weak field the Fermi-Dirac function can be expanded

$$\Delta m = \sum_{kn} [-\Delta m I(\epsilon_F) (1 + (5/\sqrt{21}) f x_{kn}) - 2\mu_B H] \frac{\partial f(\epsilon_{kn})}{\partial \epsilon}$$

However, the average of  $x_{kn}$  over the Fermi surface is  $\sqrt{21} f/5$  and

$$\Delta m = (-\Delta m I(\epsilon_F) (1 + f^2) - 2\mu_B H) \int_{-x}^x \frac{\partial f(\epsilon)}{\partial \epsilon} N(\epsilon) d\epsilon \quad (\text{A2.9})$$

A non-zero magnetization can be obtained in the limit  $H = 0$  if the Stoner parameter satisfy

$$I(\epsilon_F) (1 + f^2) \int_{-x}^x \frac{\partial f(\epsilon)}{\partial \epsilon} N(\epsilon) d\epsilon + 1 = 0. \quad (\text{A2.10})$$

This is the criteria (2.16) except for the factor  $(1 + f^2)$ . Thus in this case the non-spherical part of the spin-polarization effectively increases the Stoner parameter with at most four per cent.

### Appendix 3

In our calculation of  $I(\epsilon_F)$  in equation (2.15) we have to know the electron density  $\rho(r)$  and the radial d wavefunction  $\phi_2(r, \epsilon_F)$ . For the electron density we have used the spherical average of superposed atomic densities. The atomic densities calculated by Herman and Skillman (1963) have been used. An electron density obtained from a full selfconsistent band calculation would give only a small change in the result for  $I(\epsilon_F)$ . For most elements results for the wavefunction are not available and we have therefore estimated it in various ways. For V and Fe we have solved the radial Schrödinger equation with potentials from band calculations by Yasui *et al* (1970, 1973), respectively. For Co we have used the renormalized atom result of Hodges *et al* (1972). Finally, for Ni, Pd, and Pt we have utilized the proximity of the Fermi level to the top of the d band and the fairly strong binding of the electrons, which implies that the wavefunctions resemble the atomic ones. As the wavefunction at the top of the d band is approximately zero at the Wigner-Seitz radius, we have smoothly changed the atomic wavefunctions to satisfy this condition. This modification of the wavefunction changes  $I(\epsilon_F)$  by at most ten per cent, which could be considered as an upper limit for the uncertainty in  $I(\epsilon_F)$  due to errors in the wavefunction.

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