united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR 1216 - 4

Joint INFM - the Abdus Salam ICTP School on
"Magnetic Properties of Condensed Matter Investigated by Neutron Scattering and Synchrotron Radiation Techniques"

1 - 11 February 2000

MAGNETIC MOMENT FORMATION

M. WEINERT
Department of Physics
Brookhaven National Laboratory
Upton, NY 11973
U.S.A.

School on Magnetic Properties of Condensed Matter... Trieste, Italy, February 2000

Magnetic Moment Formation

M. Weinert

Department of Physics
Brookhaven National Laboratory
Upton, NY 11973 U.S.A.

1. Introduction

Magnetism is a subject that has both important technological and basic questions that must be answered. Magnetism is not, however, a question that can be addressed without also considering other questions. The modern theory of magnetism is based on quantum mechanics and thus is intimately interwoven with the electronic structure of the systems. Likewise, the electronic structure is dependent on the structural properties of the materials. To give a complete description of all aspects of the problem for any arbitrary system is at present unattainable. Instead, a combination of different models to describe various aspects of the problem are used. These models range from well-known statistical mechanics models to empirical tight-binding to first-principles electronic structure calculations. Each of these different types of approaches have strengths and weakness; rather than any single one providing "the answer," the insight gained from all these approaches is complementary. For example, while spin models such as the Heisenberg model are quite useful for obtaining critical behavior, for many problems the question is not what happens given a spin S, but why is the spin S? To understand the microscopic basis of the parameters used in simple models, one must turn to quantum mechanics and electronic structure calculations.

In these lecture notes, I will focus on an itinerant, or band, theory approach to magnetism. The basis of so-called "first-principles" calculations that are often reported in the literature will be discussed, both to point out the physical problems that can be treated and the limitations (which are often glossed over). By first-principles is meant that the parameters of the theory are fixed by the basic assumptions and equations of quantum mechanics and, for our discussion, density functional theory. In principle, the only input needed for the theory are the atomic numbers of the constituent atoms of a system; all other properties follow as a direct consequence of the density functional equations. In practice, the definition has to be modified since one is always limited to some set of model systems. These limitations might include system size, crystal structure, perfect ordering, low or zero temperature, or any number of other restrictions on the "phase space" to probe. While some of these restrictions and limitations are burdensome, the goal of calculations is not merely to obtain numbers, but rather insight. By focusing on well-defined—but restricted—models, one may hopefully learn which aspects of the problem are important. On the other hand, if one were only interested in the final number or result, one would not need to do any calculations at all since nature has already provided the answer via an analog computation that we cannot duplicate.

The starting point for these lectures is atomic physics. After that, a simple Stoner-like model of magnetism will be presented. This model demonstrates the underlying physical assumptions and results one would expect from simplified electronic structure calculations. In particular, the various conditions necessary for magnetic ordering, either ferromagnetic or antiferromagnetic, are discussed. Understanding these concepts makes the results of the first-principles calculations less surprising. After describing the basics of the spin-density functional theory approach to electronic structure calculations, a number of examples and other properties will be discussed.

2. Simple Atomic Physics and Band Theory

Atoms provide a good starting point for discussing magnetic systems and electronic structure in general. The shell structure of atoms is well-known from introductory courses. The atomic states can be described by the quantum numbers $\vec{L}$, L_z (orbital angular momentum), $\vec{S}$, S_z (spin), and $\vec{J} = \vec{L} + g\vec{S}$ and the eigenvalue spectrum breaks up into multiplets labeled by these numbers. The interactions of the electrons in a given configuration can be described in terms of direct and exchange terms. Exchange is a consequence of the antisymmetrization requirement, hence quantum mechanical in origin. To ensure the antisymmetrization, the wave functions are generally written as Slater determinants of single-particle orbitals. Although some levels can be single determinants, often the wave functions are linear combinations of several determinants. Exchange can be thought of a providing an effective attraction among electrons of the same spin and is the underlying cause of magnetism. Although generally not appreciated, there is *not* a unique separation into direct and exchange terms; different members of a multiplet may have different exchange and direct terms.

When atoms are brought together, the electrons on different atoms interact. Slater determinants can still be written down, but now the single-particle orbitals are modified from the atomic orbitals. Determining the form of these orbitals and their properties is the goal of band theory. In its simplest form, band theory is a one-electron mean-field theory. Ideally, the single-particle states correspond to the quasi-particle states of the system. The standard introduction to band theory generally starts with a single-particle Schrödinger equation and a periodic potential. From this simple description, the relationship to the atomic physics amy not be clear. The assumption, often not stated, is that in band theory the antisymmetization condition of the wave functions is satisfied if the band states are considered as the orbitals of a large single determinantal wave function. The approximation of only considering single determinantal wave functions means that correlations arising from interactions among determinants are neglected. This statement, while generally correct, ignores the fact that a determinant can be written in terms of its cofactors, which in turn are determinants; hence a large single determinantal wave function can be considered as a sum of smaller determinants. Thus, in this formulation of band theory, the many-body effects are hidden in the potential. In addition, band theory obeys the symmetries of the system, e.g., because of translation symmetry, the states can be put into the Bloch form and labeled by momentum k, i.e., $\psi_k(\vec{r}) = e^{ik\cdot r}u_k(\vec{r})$, where u_k is periodic. Partly for this reason, the band states provide a reasonable starting point even for "highly correlated" systems, Often both the atomic (localized) and band theory approaches are applied to the same problem, but sometimes with quite different results, neither of which may agree with experiment. In the localized limit, the multiplet structure of atoms is in principle well understood. The calculation of the exact energy positions of the different multiplet levels, however, is difficult because of the interaction among different configurations with the same symmetry, so-called configuration interaction. Straightforward configuration interaction calculations are generally not feasible since the number of configurations that must be considered increases exponentially with the number of electrons, even if the number of different (excited) configurations are limited. Hence, such calculations are restricted to rather small number of atoms. Band theory, on the other hand, attempts to optimize the orbitals and potential in a single determinantal wave function in such a way as to accurately treat the (mean field) Coulomb interactions for the many atom system, while including some aspects of the correlations. This difference in the underlying assumptions regarding the form of the wave functions between the localized/atomic picture and band theory is why neither approach is correct in all cases: band theory is missing (multiconfiguration) correlations, while the localized picture is missing the long-range interactions among atoms.

3. Simple Model of Magnetism

In this section, a simple itinerant model of magnetic systems will be described. This model has a long history and, although it may not be quantitatively correct, does capture the essential physics. Such models are important in that they provide a framework within which to interpret the results of full-scale calculations, as well as providing a means to build ones physical intuition.

Consider a (non-magnetic) band Hamiltonian of the form

$$H_0 = \sum_{k\sigma} \epsilon_k a^\dagger_{k\sigma} a_{k\sigma}. \tag{1}$$

The Bloch annihilation operator $a_{k\sigma}$ for an electron with momentum k and spin σ is related to the Wannier annihilation operator $c_{i\sigma}$ for an electron with spin σ at site i by

$$a_{k\sigma} = \frac{1}{\sqrt{N}} \sum_i e^{ikR_i} c_{i\sigma}, \tag{2}$$

where N is the total number of unit cells in the crystal. Assuming that the interactions between (quasi)particles on different sites are screened, then the self-consistent (mean) field interaction Hamiltonian is described by

$$H_I = U \sum_{i\sigma} \left[\langle c^\dagger_{i\bar{\sigma}} c_{i\bar{\sigma}} \rangle c^\dagger_{i\sigma} c_{i\sigma} - \langle c^\dagger_{i\sigma} c_{i\bar{\sigma}} \rangle c^\dagger_{i\bar{\sigma}} c_{i\sigma} \right], \tag{3}$$

where U is the strength of the interaction between quasiparticles and $\bar{\sigma}$ represents a spin antiparallel to σ.

In what follows, we restrict ourselves to the case where the change in symmetry due to the interaction term is commensurate with the zeroth-order system. In particular, this case includes both ferromagnetic ($Q = 0$) and antiferromagnetic ($Q = G/2$, where G is a reciprocal lattice vector) ordering. Using Eq. 2 in Eq. 3 gives

$$\begin{aligned} H_I = U \sum_{k\sigma} \Big[& n^0_{\bar\sigma} \left(a^\dagger_{k\sigma} a_{k\sigma} + a^\dagger_{k+Q\sigma} a_{k+Q\sigma} \right) + n^Q_{\bar\sigma} \left(a^\dagger_{k\sigma} a_{k+Q\sigma} + a^\dagger_{k+Q\sigma} a_{k\sigma} \right) \\ & + C_0 \left(a^\dagger_{k\bar\sigma} a_{k\sigma} + a^\dagger_{k+Q\bar\sigma} a_{k+Q\sigma} \right) + C_Q \left(a^\dagger_{k\bar\sigma} a_{k+Q\sigma} + a^\dagger_{k+Q\bar\sigma} a_{k\sigma} \right) \Big], \end{aligned} \tag{4}$$

where we have defined the following averages:

$$n^0_\sigma = \sum_k \langle a^\dagger_{k\sigma} a_{k\sigma} \rangle, \tag{5a}$$

$$n^Q_\sigma = \sum_k \langle a^\dagger_{k+Q\sigma} a_{k\sigma} \rangle, \tag{5b}$$

$$C_0 = - \sum_k \langle a^\dagger_{k\sigma} a_{k\bar\sigma} \rangle, \tag{5c}$$

$$C_Q = - \sum_k \langle a^\dagger_{k+Q\sigma} a_{k\bar\sigma} \rangle. \tag{5d}$$

Note that these averages depend on the eigenfunctions of Eq. 1, thus defining a self-consistency condition for the matrix elements. Using these definitions, other quantities can be written in terms of these (mean field) averages. For example, the total energy corresponding to the Hamiltonian $H = H_0 + H_I$

$$E_T = \sum_{k\sigma} \epsilon_k \langle a^\dagger_{k\sigma} a_{k\sigma} \rangle + \frac{1}{2} U \sum_{i\sigma} [\langle c^\dagger_{i\bar\sigma} c_{i\bar\sigma} \rangle \langle c^\dagger_{i\sigma} c_{i\sigma} \rangle - \langle c^\dagger_{i\sigma} c_{i\bar\sigma} \rangle \langle c^\dagger_{i\bar\sigma} c_{i\sigma} \rangle] \tag{6}$$

can be expressed in terms of the self-consistent eigenvalues E_k with occupation f_k and the matrix elements as

$$E_T = \sum_{k\sigma} f_{k\sigma} E_{k\sigma} - U \left[n^0_\uparrow n^0_\downarrow + n^Q_\uparrow n^Q_\downarrow - {C_0}^2 - {C_Q}^2 \right]. \tag{7}$$

The ferromagnetic ($q = 0$) and antiferromagnetic ($q \neq 0$) components of the magnetization, $M(q)$, and particle number, $n(q)$, are

$$M(0) = \mu_B \left[-2C_0 \hat{x} + \left(n^0_\uparrow - n^0_\downarrow \right) \hat{z} \right], \tag{8a}$$

$$M(Q) = \mu_B \left[-2C_Q \hat{x} + \left(n^Q_\uparrow - n^Q_\downarrow \right) \hat{z} \right], \tag{8b}$$

$$n(0) = n^0_\uparrow + n^0_\downarrow = n, \tag{9a}$$

$$n(Q) = n^Q_\uparrow + n^Q_\downarrow. \tag{9b}$$

Choosing the $\hat{z}$ axis as the spin quantization axis, then $C_0 = C_Q = 0$, and a number of the equations simplify; e.g., the last term in the interaction Hamiltonian of Eq. 3 vanishes.

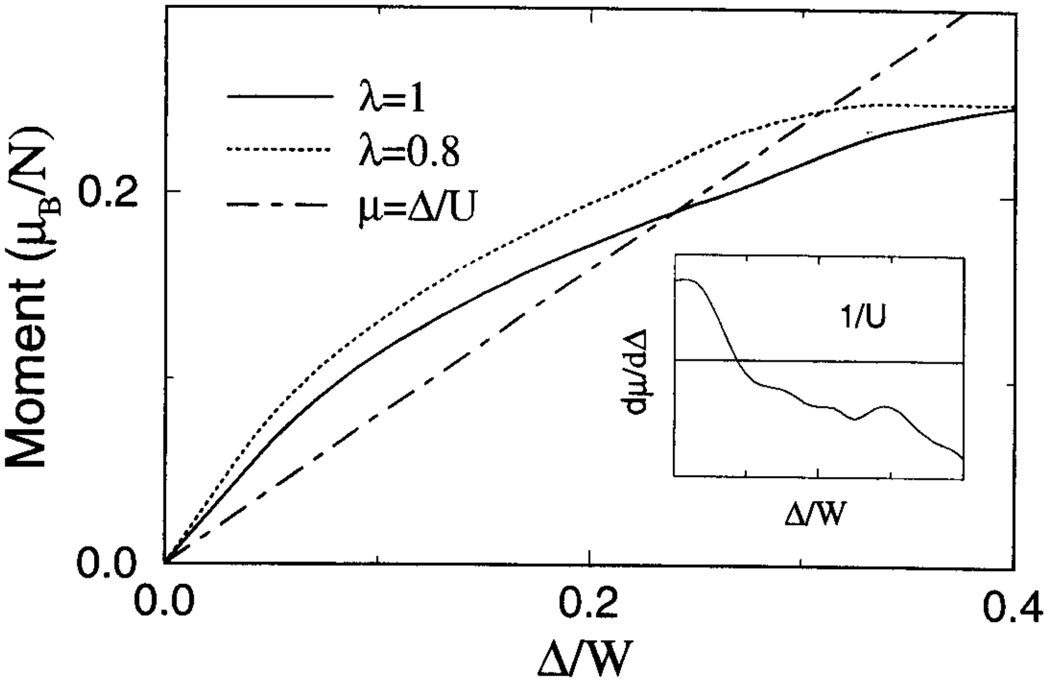

Figure 1. Graphical solution to Eq. 11 for a model density of states of bandwidth λW, where W is the nominal bandwidth. The moment μ is in units of μ_B per number of states in the whole band ($N = 10$), the exchange splitting Δ is in units of the bandwidth W. Also given is Δ/U, where U is the interaction strength. The insert gives the derivative $d\mu/d\Delta$ for $\lambda = 1$; at $\Delta = 0$, this corresponds to the susceptibility.

At this point, it is useful to point out that it is simple to include these effects in a tight-binding model. The interaction Hamiltonian of Eq. 3 is clearly given in terms of local quantities such as the local moment, thus defining a simple self-consistent problem for these quantities. Note that in such a tight-binding formulation, the ferromagnetic and antiferromagnetic systems are treated the same. In particular, the interaction strength U for each atom is fixed and physically is related to the (screened) Coulomb integral of the one-particle state. (Typical values for the transition metals are on the order of 0.5–1 eV.) Although it might appear that this model is describing localized, rather than itinerant (band) magnetism, in fact, this is the Stoner itinerant model of magnetism, once the identification of U to the Stoner parameter I is made. This correspondence between localized and itinerant magnetism as different limits of the same physics is important to keep in mind when considering magnetic behavior of complicated systems.

We now turn to a discussion of the ferromagnetic case, which corresponds to choosing $n_\uparrow^Q = 0 = n_\downarrow^Q$ (no lowering of the translational symmetry) and $n_\uparrow^0 \neq n_\downarrow^0$. The resulting Hamiltonian is easily solved to yield

$$E_{k\sigma} = \epsilon_k + U n_{\bar{\sigma}}. \tag{10}$$

The self-consistency condition can be rewritten in terms of the spin splitting $\Delta = E_{k\downarrow} - E_{k\uparrow}$ as

$$\Delta = U(n_\uparrow - n_\downarrow) = U\mu(\Delta), \tag{11}$$

where $\mu(\Delta)$ is the on-site magnetic moment, given as a function of the exchange splitting.

The self-consistency requirement embodied in Eq. 11 can be solved for a given density of states and a value of U. From the density of states, and the requirement of charge neutrality, it is straightforward to generate the value of the magnetic moment as a function of the exchange splitting. In Fig. 1, we show $\mu(\Delta)$ as a function of the exchange splitting (in units of the bandwidth) obtained for a model density of states corresponding to a bcc metal such as Fe at a fractional filling of 0.75. (This density of states is in fact the majority local density of states obtained from a first-principles local density calculation for Fe, but which has been modified to artificially remove all states above and below the "d" bands and then scaled to have the correct number of states. Thus, this model density of states will have approximately the correct features and at the same time is in the spirit of the simple model with its single set of bands.) In general, $\mu(\Delta)$ is a monotonically increasing function that saturates. The exact shape will depend on the density of states of the particular system. To graphically solve the self-consistency condition given by Eq. 11, the line $\mu = \Delta/U$, which depends only on the interaction strength U, is also given in Fig. 1. Where these two lines intersect gives both the exchange splitting and the magnetic moment. It is obvious from the figure that a ferromagnetic solution is guaranteed only if the initial slope of $\mu(\Delta)$ is greater than $1/U$ (cf. the insert in Fig. 1). (There exist forms of $\mu(\Delta)$ such that the above condition does not hold, but which will still intersect the line Δ/U; in these cases, at least two self-consistent ferromagnetic solutions must exist.) The slope, $d\mu/d\Delta$ at Δ=0 is simply one half the total density of states at the Fermi level, $n(E_F)$, for the non-magnetic system. Thus, the condition for a magnetic solution is then simply

$$\frac{1}{2}Un(E_F) > 1, \tag{12}$$

i.e., the standard Stoner criterion for ferromagnetism. (The factor of 1/2 is due to our definition of U; the Stoner parameter I as normally given is $I = U/2$, or else $n(E_F)$ is per spin direction.) Hence, as mentioned above, we recover the itinerant magnetism results from this simple model. The description of ferromagnetic ordering given here highlights different aspects than the conventional Stoner approach based on the susceptibility, but the two approaches are equivalent.

From this analysis, we can draw some conclusions regarding magnetism at interfaces and surfaces. At a surface, the density of states is generally narrower due to the reduction of nearest neighbors. At an interface, the bandwidth of the density of states will depend on the structure and elements. Assume that at an interface or surface that the bandwidth is changed by a factor λ, but that the shape remains the same. Then the curve $\mu(\Delta)$ will shift, as for example shown in Fig. 1 for λ=0.8. (The bandwidth W which is used to scale all the energies corresponds to λ=1.) Since U is assumed unchanged, the model would predict an increased moment at the surface since $\lambda < 1$, in qualitative agreement with first-principles calculations for magnetic surfaces. In addition, it is possible that bulk non-magnetic system could have a ferromagnetic surface, although this has not been found to be the case for either V or Pd surfaces, the two most likely candidates. (Free-standing monolayers have, however, been predicted to be magnetic.) For interfaces, the bandwidth should be larger than for the surface, thus the increase in magnetic moment should be less. Although, as will be discussed later, these trends are normally seen in first-principles calculations, it is important to realize that in cases where the interface bonding is strongly modified at the surface, the simple picture given in Fig. 1 may not be valid. A tight-binding model that actually calculates $\mu(\Delta)$ and takes changes in hybridization in to account might well reproduce most of the correct behavior.

At this point, we turn to the more complicated case of antiferromagnetic order. For this case, we have $n_\uparrow^0 = n_\downarrow^0$ and $n_\uparrow^Q = -n_\downarrow^Q$. Using these relationships, the single particle equations can be solved, but clearly the eigenvalues will depend on the details of the electronic band structure of the non-magnetic systems. Thus, a simple graphical solution of the self-consistency equations, similar to that show in Fig. 1 for the ferromagnetic case, cannot be obtained. However, within a linear response treatment similar to that shown in the inset to Fig. 1 and Eq. 12, an approximate Stoner criterion for antiferromagnetism can be obtained.

To proceed, first consider the unperturbed Green's function $G^0(E)$ for the nonmagnetic system. In the Wannier basis used above, the Green's function connecting sites i and j is given in terms of the non-magnetic eigenvalues by

$$G_{ij}^0(E) = \sum_k \frac{e^{ik\cdot(r_i - r_j)}}{E - \epsilon_k + i\delta}\,. \tag{13}$$

The properties of the system in the presence of a magnetic field described by a potential V can be determined from the Green's function of the perturbed system. In linear response, this Green's function is given by

$$G(E) = G^0(E) + G^0(E)\,V\,G^0(E)\,. \tag{14}$$

Let the potential V be represented by site-diagonal terms $\Delta\,\widehat{m}_i$ that all have the same magnitude Δ, but possibly different directions, $\widehat{m}_i$. This local approximation for V is consistent with our original choice of the Hamiltonian, Eq. 3, and corresponds to a "staggered" magnetization. The induced local moments, m_i, again within linear response, are given by

$$m_i = \sum_j \chi_{ij}(E_F)\,\Delta\,\widehat{m}_j, \tag{15a}$$

$$\equiv \Delta\,\chi_i(E_F). \tag{15b}$$

Thus, the local moment is related to the magnitude of the exchange splitting by the total susceptibility $\chi_i(E_F)$.

By using the relationship between the density of states and the Green's function,

$$n(E) = -\frac{1}{\pi}\,\mathrm{Im}\,G(E), \tag{16}$$

it is straightforward to show that the nonlocal susceptibilities χ_{ij} are given by

$$\chi_{ij}(E_F) = \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE\,G_{ij}^0(E)\,G_{ji}^0(E)\,. \tag{17}$$

A simple sum rule for the non-local susceptibilities can be obtained by making use of the identity $G^2 = -\partial G(E)/\partial E$:

$$\begin{aligned}\sum_i \chi_{0i} =& \ \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE \sum_i \left(G^0_{0i}(E)\right)^2 \\ =& -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE\,\frac{\partial G^0(E)}{\partial E} \\ =& -\frac{1}{\pi}\,\mathrm{Im}\,G^0(E_F) \\ =& \ \ n(E_F)\,. \end{aligned} \tag{18}$$

This result, of course is simply the ferromagnetic susceptibility that already appeared in Eq. 12. The antiferromagnetic susceptibility, χ_{AFM}, that is appropriate for the Stoner criterion is

$$\chi_{AFM} = \sum_i \chi_{0i}\,\widehat{m}_0 \cdot \widehat{m}_i\,. \tag{19}$$

Using these results, it is possible to obtain an approximate criterion for antiferromagnetism using only density of states information. If we assume that χ_{0i} vanishes for sites beyond nearest neighbors, then χ_{AFM} is given approximately by

$$\chi_{AFM}(E_F) \approx 2\,\chi_{00}(E_F) - n(E_F), \tag{20}$$

where $\chi_{00}(E_F)$ is the local susceptibility:

$$\chi_{00}(E_F) = \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dE\,\left(G^0_{00}(E)\right)^2\,. \tag{21}$$

The Green's function $G^0_{00}(E)$ can be written in the form

$$G^0_{00}(E) = I(E) - i\,\pi\,n(E)\,. \tag{22}$$

where the real part $I(E)$ is related to the density of states via a Hilbert transform:

$$I(E) = P\int_{-\infty}^{\infty} dz\,\frac{n(z)}{E-z}\,, \tag{23}$$

where P denotes the Cauchy principal part. The local susceptibility is thus given by

$$\chi_{00}(E_F) = -2\int_{-\infty}^{E_F} dE\,n(E)\,I(E)\,. \tag{23}$$

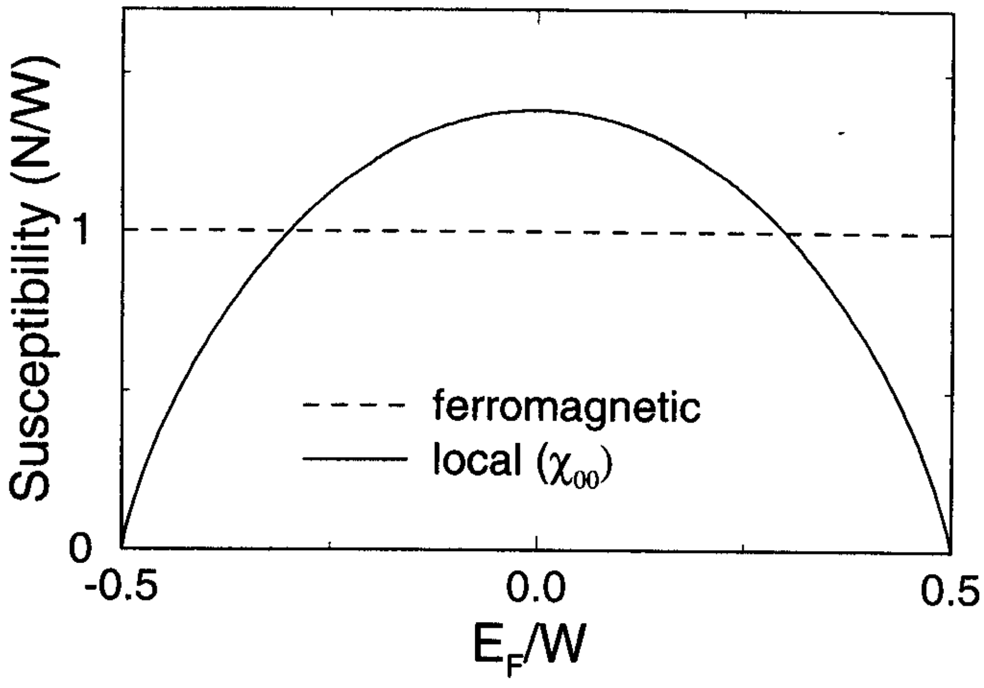

Figure 2. Local and ferromagnetic susceptibilities for a rectangular density of states with bandwidth W and integral N, as a function of Fermi energy E_F.

The local and ferromagnetic ($n(E_F)$) susceptibilities have different structure as a function of energy, resulting in different magnetic ordering with band filling. In Fig. 2, χ_{00} and $\chi_{FM} = n(E_F)$ are shown for the simple case of a rectangular density of states. From this figure, the tendency for antiferromagnetism near the middle of the transition metal rows is obvious; whether a stable magnetic solution exists will also depend on the value of U.

From Eq. 20, we can obtain an approximate form for χ_{AFM} using only density of states information; the reason that it is not exact within our model is because of the approximations made concerning the decay of χ_{0i} and the nearest neighbor approximations. Actual densities of states are more complicated than the simple rectangular density of states used in Fig. 2. In Fig. 3 the antiferromagnetic and ferromagnetic susceptibilities for the same model density of states used in Fig. 1 are given as a function of band filling (rather than Fermi level position), along with $1/U$, the line above which a magnetic solution is favored. For the ferromagnetic case, χ_{FM} is simply the density of states, but plotted against fractional filling, not energy. Several features are evident in Fig. 3. First, χ_{AFM} is slightly negative near the ends, which is an artifact of our assumptions of neglecting all contributions beyond nearest neighbors. As already seen in Fig. 2, χ_{FM} and χ_{AFM} have different structure as a function of band filling; in particular, χ_{AFM} is larger than χ_{FM} near half-filling, i.e. the local susceptibility χ_{00} is increased relative to the density of states. These results demonstrate the well-known tendency towards antiferromagnetism at the center of the transition metal row. The fact that $\chi_{00} > \chi_{FM}$ near half-filling has its physical origin in atomic Hund's rule-type arguments: The maximum spin M occurs for half-filling, hence the atomic (local) susceptibility $\chi = \partial M/\partial H$ will also be largest. Other points to note include that for a given strength of U, there is a larger tendency towards

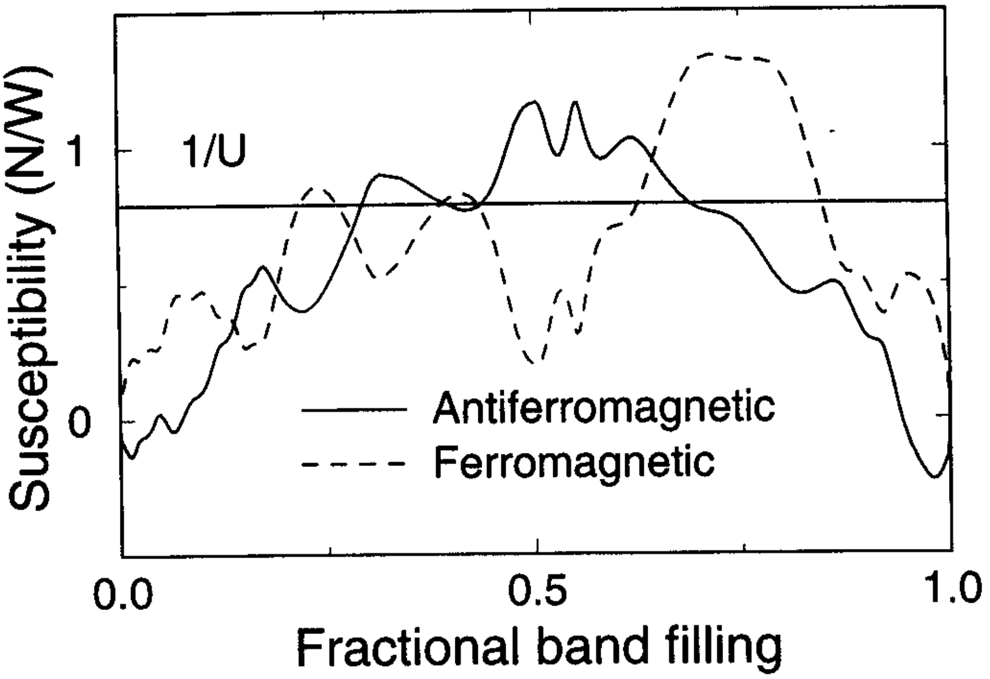

Figure 3. Antiferromagnetic and ferromagnetic susceptibilities for the same model density of states used in Fig. 1 as a function of fractional band filling calculated using Eqs. 18, 20–23.

magnetism at the right end of the row. (U also will increase near the end of the transition metal row because of the increasing localization of the d orbitals.) For the density of states used here, χ_{FM} and χ_{AFM} are such that the two susceptibilities cross each other several times. Other authors have discussed this behavior previously; in particular, Heine, et al. have shown that in general there must be a least two crossing.

Similar arguments as given above for increased ferromagnetism at surfaces can be made for increased antiferromagnetic susceptibility at surfaces and interfaces. One major difference between the Stoner criteria for ferromagnetism and antiferromagnetism is that while χ_{FM} depends only on the density of states at the Fermi energy, χ_{AFM} has contributions from all parts of the band, as can be seen from the form of the local susceptibility given in Eq. 23.

The model discussed above leaves out many important effects. For example, the hybridization between the compact d electrons and the more diffuse sp electrons is ignored, and thus the RKKY interaction is not included. Likewise, correlation effects are not explicitly included, although these effects are known to be important. Although these are serious shortcomings, the model has demonstrated the relationship between magnetic ordering and the one-particle properties of the electronic structure. Moreover, as discussed above, features such as the observed enhanced magnetism at surfaces are natural consequences of this model. Clearly this model is not first-principles since the various parameters are not determined by the model itself. The quantitative predictions of this model using parameters determined elsewhere are often not particularly accurate. However, as a *framework* for understanding the basic physical mechanisms of magnetism, this model is has great utility.

4. Spin Density Functional Theory

Density functional theory (DFT) in its local spin density approximation (LSDA) or (more recently) generalized gradient approximation (GGA) has been the main underlying basis for first-principles electronic structure calculations of magnetic systems. The theory is based on the Hohenberg-Kohn theorem—and its generalization to magnetic systems—that the ground state energy of a many-body system is a unique functional of the charge and spin densities and is a minimum for the true ground state densities. Kohn and Sham showed that this functional could be written as

$$E[n] = T_s[n] + U[n] + E_{xc}[n, m]. \tag{24}$$

The classical Hartree (Coulomb) energy, U, for electrons and nuclei of charge Z_ν is given by

$$U[n] = \frac{1}{2}\int d\vec{r}\,d\vec{r}\,'\,\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} - \sum_\nu Z_\nu \int d\vec{r}\,\frac{n(\vec{r})}{|\vec{r}-\vec{R}_\nu|} + \frac{1}{2}\sum_{\nu,\nu'}\frac{Z_\nu Z_{\nu'}}{|\vec{R}_\nu - \vec{R}_{\nu'}|}. \tag{25}$$

External fields other that the nuclear charges that couple to the charge and/or spin densities can be included by adding in terms of the form $\int d\vec{r}\, n(\vec{r}) v_{ext}(\vec{r})$. The "kinetic" energy term T_s corresponds to the kinetic energy of a set of non-interacting particles with the same density n:

$$T_s[n] = \sum_{i\sigma}\int d\vec{r}\;\psi^*_{i\sigma}(\vec{r})\left(-\frac{1}{2}\nabla^2\right)\psi_{i\sigma}(\vec{r}), \tag{26}$$

where the density for spin σ is given in terms of the single-particle wave functions $\psi_{i\sigma}$ by

$$n_\sigma(\vec{r}) = \sum_{i\sigma}\psi^*_{i\sigma}(\vec{r})\psi_{i\sigma}(\vec{r}). \tag{27}$$

The spin density $m(\vec{r})$ is simply the difference between the spin-up and -down densities, $m(\vec{r}) = n_\uparrow(\vec{r}) - n_\downarrow(\vec{r})$, and the total density is given by $n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})$. The exchange-correlation energy, E_{xc}, is a functional of both the charge and spin density. In the LSDA for example, the unknown form is approximated locally by the exchange-correlation energy appropriate to a homogeneous electron gas of the same density:

$$E^{LDA}_{xc}[n, m] \approx \int d\vec{r}\; n(\vec{r})\epsilon_{xc}[n(\vec{r}), m(\vec{r})]\,. \tag{28}$$

(The local density form of the exchange energy is $\epsilon_x \propto (n_\uparrow^{4/3}+n_\downarrow^{4/3})/n$.) From this functional form, and the relationship between the densities and the single-particle wave functions, a set of self-consistent equations can be derived. These Schrödinger-like single-particle equations,

$$\left\{-\frac{1}{2}\nabla^2 + V_C(\vec{r}) + \mu^\sigma_{xc}(\vec{r})\right\}\psi_{i\sigma}(\vec{r}) = \epsilon_i\,\psi_{i\sigma}(\vec{r}), \tag{29}$$

have a spin-dependent effective exchange-correlation potential given by

$$\mu_{xc}^{\pm}(\vec{r}) = \frac{\delta E_{xc}[n,m]}{\delta n(\vec{r})} \pm \frac{\delta E_{xc}[n,m]}{\delta m(\vec{r})}. \tag{30}$$

This set of single-particle Kohn-Sham equations would, in principle, give the exact solution to the many-body problem if the exact functional form of the exchange-correlation potential were know. Unfortunately, the exact form is not known (otherwise the complete solution to the underlying many-body problem would also be known). Thus, approximations such as the LSDA or GGA must be made. The types of properties that can be determined from DFT calculations include moments and spin densities, and properties derived from investigating the variation of the total energy with respect to some parameter, e.g. structural properties. Formally, the eigenvalues and eigenfunctions obtained from the single-particle equations do not have any physical meeting, but are simply a device to solve the underlying self-consistent problem. However, from a heuristic point of view (and with some formal justification), the eigenvalues and eigenfunctions can be used as approximations to the quasi-particle band structures of the real materials.

There are a number of deficiencies in the LSDA and GGA. As shown above and as mostly implemented, the coupling of the spin and lattice is neglected. Thus, while the relative spin ordering (ferro- versus anti-ferromagnetic) can be obtained, the spin direction relative to the lattice is indeterminate. By including spin-orbit effects, the direction of the magnetic moment and magnetic anisotropies can be calculated. While spin-orbit will also induce an orbital moment, Hund's second rule (orbital angular momentum) effects are not correctly handled within the LSDA or GGA. In fact, it can be shown that *any* approximation that depends only on the charge and spin density must fail to reproduce multiplet structure correctly, while a current-density functional theory could in principle. Although various attempts to include orbital effects in solids have been made, at present none has been theoretically justified with anything resembling rigor. Even with a number of well documented shortcomings, calculations using these approximations have been surprisingly successful in describing the properties of magnetic systems.

To solve the DFT equations, there are many possible methods; which one is used is generally a matter of personal preference. However, certain features are common. For instance, the methods must be able to treat the transition metal elements. The d electrons are rather compact, while the s and p electrons are more diffuse. In augmented methods (e.g., FLAPW), the wave functions around the atom are expanded in partial waves, with the radial functions calculated in the *actual* (spherical) potential. Thus, the shape of the d, as well as the sp, wave functions are described correctly. Moreover, these methods generally explicitly include all electrons, including the core electrons. (In all LSDA/GGA methods, including pseudopotential methods, the core density is necessary for the calculation of accurate spin-dependent exchange-correlation potentials and energies. Since these functionals are non-linear, neglect of the core density can result in gross errors.)

Most of the magnetic systems are close-packed metals. For many properties, the electronic structure is dominated by the behavior of the electrons near the atoms, where the density and potential are rather spherical in shape. This observation lead to the so-called "muffin-tin" and "atomic sphere" approximations that ignores the non-spherical

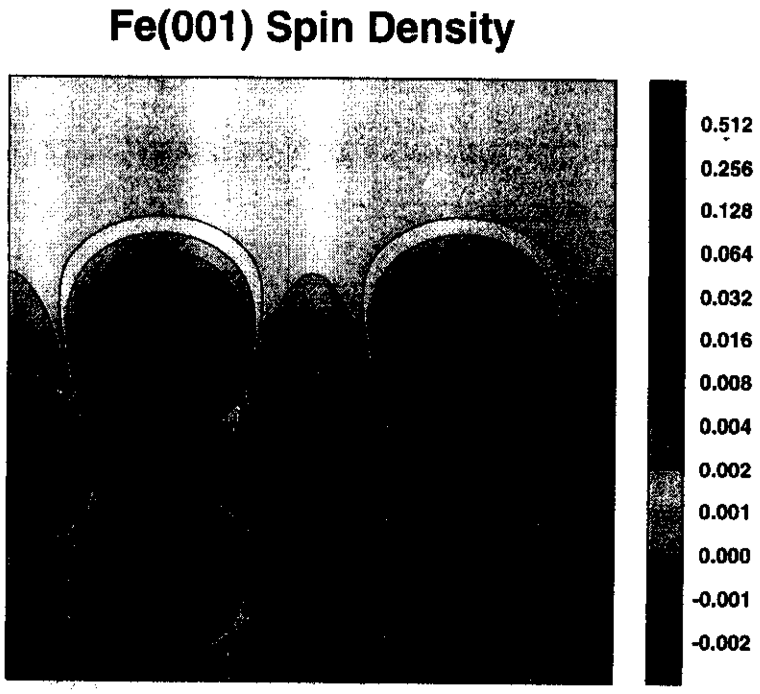
Fe(001) Spin Density

Figure 4. Spin-density for Fe(001) surface. Notice the negative density in the interstitial region.

contributions to the density and potential. While these approximations can be quite adequate for many problems, experience has shown that there are cases were the full anisotropic shape of the density and potential can have important consequences. Many calculations for magnetic systems now routinely calculated the full shape dependence of the potential and densities. While these types of details are important in assessing the quality of the calculations, important physical results can still be obtained from calculations with varying degrees of sophistication.

5. Examples and Other Topics

At this point a few examples are will be given. First-principles calculations for the $3d$ transition-metals give quite reasonable results for the magnetic moments, e.g., $\sim$2.2 μ_B for Fe and 0.56μ_B for Ni. Note that these are non-integral values, providing evidence for the itinerant, rather than localized, nature of the magnetism in these systems. Besides magnetic moments, the calculations provide the spin density itself, as is shown in Fig. 4. A point to notice is that the spin density in the interstitial is negative, as was observed in a set of classical neutrons scattering experiments. The negative densities in the interstitial and at the nucleus (which can be measured using hyperfine techniques) have a common origin in that the majority orbitals are attracted to the region of space where the majority d electrons are, leaving behind minority states. Another effect of magnetism on structure is the expansion of the lattice. The rationale for this behavior is simply that in order to have a moment, electrons must have been transferred from the minority to the majority levels; since states higher in the band are more antibonding, the transfer of electrons results in an expansion.

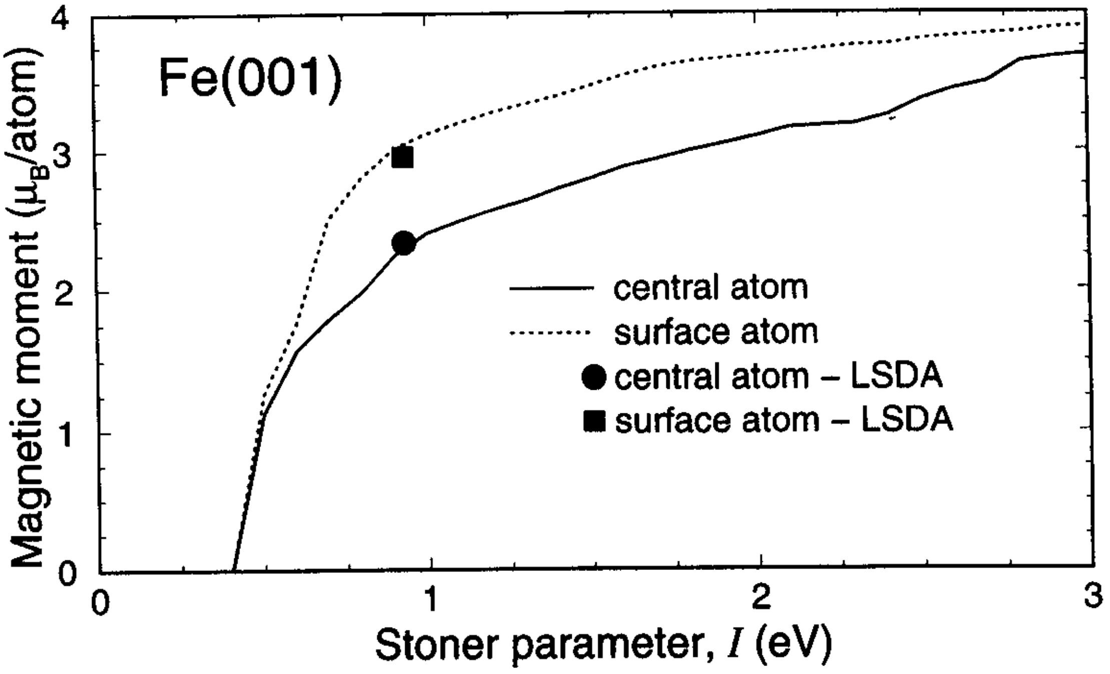

Figure 5. The bulk and surface magnetic moments for Fe(001) calculated using the generalized Stoner model as a function of Stoner parameter I. The LSDA values are given for comparison.

Stoner model: In Section 3, the simple Stoner-like model was introduced. This model goes beyond the standard linear response arguments and allows for re-hybridization effects. The advantage of such a model is in the systematics that can be considered. As an example, consider an Fe(001) surface. Theory predicted the large moments at the surface at a time that experiments were still claiming magnetic "dead" layers. Starting from the paramagnetic wave functions, which include much of the Coulomb effects already, the model is solved self-consistently for different values of the Stoner parameter I. For an I corresponding to LSDA, almost perfect agreement is obtained with the full calculation; had one started from a crude set of bands, the results would not have been as good. As can be seen quite clearly, the formation of moments requires a minimum I, as expected from the previous discussion.

Orbital moments: From atomic physics, one would expect large orbital moments, but these are not seen in solids. The quenching of orbital magnetism can be obtained as a consequence of crystal field splitting: In the atom, there is full rotational symmetry, whereas in a crystal, the potential has lower symmetry. This non-spherical potential results in coupling of different states. Then since $[L_z, V] \neq 0$, one obtains $\langle L_z \rangle$=0. This result can be verified by direct computation. A related symmetry argument follows from time reversal. If ψ_k is an eigenfunction of a real Hamiltonian H, then so is ψ_k^*, and furthermore is degenerate with ψ_K. However, ψ_k^* is a Bloch function corresponding to momentum $-k$, i.e., the time-reversed state. Since these two states must enter equally and $L_z^* = -L_z$, $\langle L_z \rangle$=0.

Magnetocrystalline anisotropy: In a magnetic system, the magnetic moment will have a tendency to align itself along the "easy" direction; the energy due to this so-called magnetocrystalline anisotropy (MCA) is referred to as the magnetic anisotropy energy (MAE). Van Vleck proposed that the magnetocrystalline anisotropy originates from the spin-orbit coupling: The different orbital character of the electron states will generate an anisotropic electrostatic interaction between the orbital angular momenta of different atoms, which in turn are coupled to the spin momenta on-site by the spin-orbit interaction. This interaction gives rise to an apparent dipole-dipole coupling between the spins of different atoms, with a coupling constant larger than that due to pure magnetic forces between the spins. Building on Van Vleck's work, Brooks and Fletcher used the itinerant model in an attempt to explain the MAE for cubic crystals. In cubic crystals, the first contributions to the MAE come in fourth order perturbation theory due to the symmetry of the energy surfaces, analogously to the fact that the first nonzero lattice harmonic is $\ell = 4$. If the symmetry of the system is reduced, lower orders in perturbation theory can contribute to the MAE. That an anisotropy enhanced by orders of magnitude might occur at a surface due to the reduced symmetry was originally pointed out by Néel.

In standard LSDA calculations, the direction of the spin moment is indeterminant, i.e., the total energy is independent of the relative orientation of the spin direction and the lattice. The spin-orbit interaction, by coupling the spin and space coordinates provides a mechanism for fixing the direction of the spin moment. In the single-particle Hamiltonian, the spin-orbit interaction is represented by a term of the form $H_{so} = \xi \vec{\sigma} \cdot \vec{L}$, where the spin-orbit coupling constant ξ depends on the gradient of the potential. The approach often taken is to first self-consistently calculate the spin-polarized electronic structure, neglecting the spin-orbit interaction. The spin-orbit interaction is then included in a final perturbation in which the direction of the spin moment is specified. Such a treatment is justified since the spin-orbit interactions for the valence levels of the $3d$ transition metals is small. Rather than calculating the total energy differences directly, they are approximated by the differences in one-electron energies, with and without the spin-orbit interaction included. This procedure can be justified under certain conditions regarding changes in the charge and spin densities. Because the energy shifts are quite small, of these types of calculations have extremely slowly convergent Brillouin zone sums, often requiring on the order of 10,000 k-points.

Much of the effort on magnetic anisotropy has focused on surfaces, in particular, on monolayers as a model of ferromagnetic films on non-magnetic surfaces. While monolayers are easiest to calculate, the interactions with a substrate can lead to considerable modification of the easy axis, and cannot be neglected in realistic comparisons with experiment. Since the magnetic dipole energy—which favors in-plane magnetization—of a uniformly polarized film is proportional to the volume (the MAE is proportional to the surface area), the dipole energy will quickly dominate the anisotropy energy when the film becomes larger than a few monolayers.

This work was supported the Division of Materials Sciences, U.S. Department of Energy (contract No. DE–AC02–98CH10886).