How Can Metallic Ferromagnetism Be Explained?

Itinerant Ferromagnetism of the Transition Metals: Our Present Understanding

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In a recent review, Landrum and Dronskowski (LD)[1] gave an introduction to the itinerant ferromagnetism (that is the ferromagnetism arising from the delocalized electrons) of the transition metals covering ab initio as well as model calculations. They presented a new chemical picture by reinterpreting standard density functional (DF) results. However already in their introduction they deviate from the basic understanding of the itinerant ferromagnetism of transition metals within the frame of DF theory. Also the subsequent discussion by LD of results from the Hubbard model is inadequate. Important contributions to this field were not cited, and the comparison of density functional and model results for the transition metals was absent. No wonder that the chemical picture of itinerant ferromagnetism proposed by the authors is inadequate and irrelevant. To be able to judge the proposal of the authors, a basic view of our present understanding of the itinerant ferromagnetism is needed as gained from DF as well as model calculations.

Itinerant ferromagnetism is a consequence of electronic interactions. Without the specific influence of the interactions, the electrons would very much prefer to occupy the lowest-lying single-particle states, and be maximally delocalized. Such a delocalization causes maximal charge fluctuations on a local or atomic level. These fluctuations cost Coulomb interaction energy. Usually such charge fluctuations are reduced by correlations that correct them independently on individual atoms, but sometimes a state with a coherent long-range order that also reduces such fluctuations is energetically more favorable. Itinerant ferromagnetism is such a case. It is particularly interesting since the ferromagnetically ordered electrons are still partly delocalized.

Thus, itinerant ferromagnetism is characterized by a competition between delocalization (and band or kinetic energy) and localization (and interaction energy). A single property like the newly claimed antibonding nature of particular electrons can therefore not be the sole explanation of ferromagnetism. To demonstrate the competition underlying ferromagnetism, it is worthwhile to separate the total energy of the electronic ground state as a function of its magnetic moment M_0 into two parts, one part describing the loss in delocalization or kinetic energy of the underlying single particle ground state, integrating over incremental contributions Δ, and the other, the gain in interaction energy, integrating over I. The ground state energy E_G is thus described by Equation (1). The function I as a parameter independent of M, has been introduced by Stoner[2] M was later generalized by Wohlfarth.[3] Magnetism occurs when $I(0) \geq \Delta(0)$, and the ground state moment is given by the condition $I(M_0) = \Delta(M_0)$.

$$E_G(M_0) \ = \ E_G(0) + \frac{1}{4}\int_0^{M_0} \Delta(M) dM^2 - \frac{1}{4}\int_0^{M_0} I(M) dM^2 \tag{1}$$

Equation (1) is exact. All unknown effects are simply transferred into the unknown function $I(M)$. Such a separation is justified if the detailed differences between the individual transition metals are covered by the first term, and if $I(M)$ is largely independent of individual details. This is the case for the local density approximation (LDA) of the DF theory. The ground state energy of a magnetic state obtained in LDA can be easily split in analogy to Equation (1).[4] Here, $I(M)$ reduces to a quantity I_{LDA} that is almost independent of M and of the lattice parameters, and also shows a smooth dependency on the atomic number.[4] In LDA, the differences in ferromagnetism for different solids originate mostly from the first term $\Delta(M)$. This term is dominated by the details of the density of state per spin $n(E)$ of the nonmagnetic ground state which may be obtained from a LDA calculation. When all secondary changes to the band structure besides a refilling of the bands (a good zero-order approximation) are ignored then Equation (2) holds for $\Delta(0)$, and $\Delta(M)$ averages over the inverse densities of state at the Fermi energy of the shifted bands. This result is plausible because the higher the density of state, the less band energy is lost for the redistribution.

$$\Delta(0) \ = \ \frac{1}{n(E_F)} \tag{2}$$

These findings indicate that in the frame of LDA, details of the density of states around the Fermi energy play the

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dominant role, and that ferromagnetism can only be expected if the density of state at the Fermi energy is high enough for the nonmagnetic state. It plays no role whatsoever whether this density of state is connected to bonding or antibonding parts of the bands, or to corresponding parts of partial distributions.

The LDA results explain the ferromagnetism of the transition metals and of their alloys astonishingly well.[4, 5] They are deficient only for partial properties, a few of which will be mentioned below. On the other hand, LDA fails for itinerant antiferromagnetism, and for the (partially itinerant) magnetism of the transition metal compounds. By definition, success and failure are connected to the quantity I_{LDA} which is an approximation to the true $I(M)$. I_{LDA} is a DF construct solely based on the properties of the homogeneous electron gas, while the true $I(M)$ is expected to be related to effective atomic interactions. Atomic orbitals are well pronounced in the transition metals, and the fluctuations causing ferromagnetism are consequently fluctuations on the atomic scale. The homogeneous electron gas on which the LDA is based contains no information whatsoever about atomic orbitals.

A detailed understanding of the function $I(M)$ can be gained from calculations where atomic interactions appear explicitly. For the ferromagnetic transition metals, such calculations were not yet performed on an ab initio level. However, on a model level, such an investigation was made. Here the energy bands obtained, for example, from LDA calculations are used for a single-particle model Hamiltonian to which effective atomic interactions are added. The resulting generalized Hubbard Hamiltonian is then fully treated.

Such a model approach to ferromagnetism was first performed by Stoner for a single band system with the density of state per spin, $n(E)$. He treated the interaction in a mean field approximation (MFA). If one assumes an atomic interaction U then in MFA it leads to Equation (3) for the

$$I_{\mathrm{MFA}}(1) \; = \; \mathrm{U} \tag{3}$$

MFA-Stoner parameter $I_{\mathrm{MFA}}(1)$ of the single band and the so called Stoner criterion for the onset of ferromagnetism reads $Un(E_{\mathrm{F}}) > 1$. In the MFA, no correlations are included in the computation. The only way to avoid the repulsive interactions is through magnetic ordering. In reality, however, electrons can correlate in the nonmagnetic case. This reduces the interaction costs, even without order, and strongly diminishes the Stoner parameter which is then smaller than U. When assuming a structureless density of state (i.e. $n(E) = W^{-1}$; $W =$ band width), then from the above Stoner criterion it follows that ferromagnetism can occur in MFA only for $U/W > 1$. However, MFA is a poor approximation for such a ratio of U/W, and correlations are important in this range and are expected to shift the ferromagnetic transition to very much larger ratios if they do not eliminate it all together. This turns the single-band ferromagnetism into a strong-correlation problem, and makes the original separation of the total energy of Equation (1) questionable. Ferromagnetism in not strongly correlated single-band systems can only be expected with the Fermi energy in the vicinity of a density of state maximum. This would imply small magnetic moments. As far as the theoretical coverage of single-band itinerant ferromagnetism is concerned, I am aware of a single unequivocal derivation of a ferromagnetic ground state for a (one-dimensional) single-band Hamiltonian.[6]

Happily, all this changes for systems with sufficient degenerate bands N, like the transition metals ($N = 5$). In such a case, the atomic interactions are best described by Slater parameters. The two most relevant ones are U and J. They lead to interactions of $U + 2J$, $U - J$, and U for electrons in the same orbital, and in different orbitals with same or different spins, respectively, and to an exchange interaction J.[7, 8] The U of the single-band Hamiltonian operator used above is here replaced by $U + 2J$. In terms of these interaction parameters, the MFA Stoner parameter for the N band system reads as Equation (4). The prefactor $1/N$ compensates a

$$I_{\mathrm{MF}}(N) \; = \; \frac{1}{N}(U + (N+1)J) \tag{4}$$

similar prefactor in the inverse density of state (for a constant density of state, $n(E) = N/W$). Thus the exchange interaction J between degenerate orbitals strongly favors itinerant ferromagnetism. When assuming a ratio U/J of about five, then even with correlation corrections added, ferromagnetism can be expected for ratios $U/W < 1$, that is, in a domain where a weak correlation expansion is sufficient, and where the Stoner separation of the energy in Equation (1) is still meaningful.

For all existing compounds in the solid state, effective atomic interactions U are expected to be limited to $U < 10$ eV. The above simple model consequently indicates that itinerant ferromagnetism with large moments can only be expected for densely packed solids with narrow-band contributions, like those built by d or f orbitals, or for molecular crystals with narrow bands. But ferromagnetism with small moments might occur in the vicinity of every sufficiently strong density of state maximum.

In the correlation context, the N-fold degeneracy has another advantage. While in a single band the charge fluctuation per atom is covered by a single correlation operator on that atom, in an N-fold degenerate band, the N fluctuations arising in MFA are covered by $N(N+1)/2$ density correlation operators on that atom. The latter describe the correlations either on the individual atomic orbitals or between pairs of them on the same atom. These correlation channels mutually screen each other thus less burden is put on the individual operators and the validity range of a weak correlation expansion is significantly extended.[7] Because of this screening, we could perform correlation calculations that satisfactorily converge for five-band Hubbard–Hamiltonian operators. In the relevant interaction-parameter range, the validity of the used weak correlation expansion was verified.[7] For the correlation calculations, a model variant of the local ansatz (LA) was used. The LA is a method for the ab initio correlation treatment of large molecules and solids (for the most recent publication, see [9]). The LA is related to quantum chemistry methods but differs by the efficient use of local (not orthogonal) correlation operators. In contrast to the LDA, it does not suffer from any homogeneous electron gas approximation.

The required interaction parameters of the model were chosen so that the correct ground state moment was obtained. The required values were reasonable,[8] and their variation with the atomic number could be understood.[10] Roughly, the following relationships hold: $W \approx 5$ eV, $U \approx 3.5$ eV, $J \approx 0.7$ eV.[8] It turned out that the same interaction parameters were needed, among other things, for a successful description of the X-ray core spectroscopy,[11] anisotropic exchange splitting for Ni,[12, 8] satellite structures[12, 13] and photoemission line broadening.[14] Also many-body features in the Compton profiles could be explained.[15] The Compton experiments represent a definite proof for the validity of such a weak correlation scenario.

The LA treatment of the model was fully satisfactory. This method can be regarded as the canonical approach to the treatment of the ground state of the five-band model for transition metals. The LA calculations were significantly easier to perform than the much more recent attempts to handle single-band or two-band models.[16, 17] The experience gained from the latter calculations is, because of the discrepancies in the degeneracies, of no value for understanding the transition metals themselves.

Very recently, we managed to derive model interaction parameters from the full Hamiltonian with the help of the LA (for the method, see ref. [10]). Relevant results have so far been obtained for Cu in high-temperature superconductors,[9] and for V.[18] These are in the range of the values obtained from our model calculations described above. This indicates that not only the single-particle features of the model Hamiltonian but also its interaction parameters can be closely tied to the full Hamiltonian operator. While J roughly corresponds to the atomic exchange interaction, the values of U differ greatly from the unscreened interactions U_0 for single atoms, which are in the range of 20 eV. This is because of a necessary convolution of the long-range Coulomb interaction into a local term (in zero-order, $U \approx U_0 - V$, where V is the largest neighboring interaction). In the past it had been argued that the dominant reduction is because of the screening by the 4s,4p electrons.[19] Such a screening is also present but its effect on the interaction strength is relatively small.[9, 18] Again, we found that the interaction parameters U for delocalized electrons are basically disconnected from interactions in the atomic limit.[10]

Since the weak correlation approximation applies, and consequently the Stoner approach of Equation (1) is still meaningful, it makes sense to condense the interaction contributions into the Stoner parameter (now called I_{LA}), and to compare the it to I_{LDA}. The true model Stoner parameter I_{LA} is typically half as large as I_{MFA} (given in Equation (4)) for the same Hamiltonian operator.[20] Half of the contributions to I_{LA} originate from the exchange contributions (J), and these are also roughly half as large as those obtained in the MFA.[20] In contrast to I_{LDA} and I_{MFA}, I_{LA} is not independent of bandfilling; it is strongly reduced by correlations near half filling. This is plausible since near half filling, antiferromagnetism is expected, and ferromagnetic ordering would not lead to any energy gain as compared with incoherent correlations on the individual atoms. The preference of antiferromagnetism around half filling had also been found from short-range correlation studies for these models.[21] I_{LA} is also largely M dependent. This is because of magnetic or Hund's rule correlations that are very efficient even without magnetic order.[22] They reduce I_{LA} considerably more for $M = 0$ than for the maximal moment. This M dependence is very important in the computation of the Stoner transition temperature. A constant (not M dependent) Stoner parameter leads to a Stoner magnetic transition temperature that is much too high. This was always interpreted as a need for dominant fluctuation corrections, either resulting from order parameter fluctuations, or from disordered local moments. In reality this deviation is caused mainly by the M dependence of the Stoner parameter. With the M dependence properly included, the Stoner transition temperature reduces, and the difference of this (order parameter) mean field temperature from the true transition temperature seems to be more reasonable.[20]

All this demonstrates that I_{LA} displays deviations from I_{LDA} that make sense. We even found an interpretation that explains many LDA deficiencies for the transition metals, and matches I_{LDA} to a particular approximate treatment of the atomic interactions. We had found many properties significantly influenced by U, regardless of whether they originated from exchange anisotropies or from correlation corrections. Whenever such effects showed up, LDA calculations had shortcomings for the same properties.[7, 8, 20] These findings can be condensed into the conclusion that LDA seems to overscreen the Coulomb interaction and is best related to our results by setting $U = 0$. This leaves only J as a possible origin of I_{LDA}. A connection between both is actually gained from single atom calculations. When applied to an atom with a partially filled shell, the LDA without symmetry breaking seems to reproduce an energy that equally averages over all possible electronic states while only the symmetry broken result represents the Hund's rule ground state. This indicates that LDA is able to recognize the atomic exchange interaction J_{atom} but treats it in MFA, that is it accommodates it only when the symmetry is explicitly broken. Essentially the same happens when a solid is calculated. Consequently, the LDA can be interpreted as handling the two atomic interactions U and J very differently. The first quantity seems to be completely neglected while the second is accommodated in MFA. For I_{LDA}, we propose the Equation (5).[20, 23] Support for

$$I_{\mathrm{LDA}} = \frac{N+1}{N} J_{\mathrm{atom}} \tag{5}$$

this interpretation comes from another LDA deficiency. In LDA, not only ground states with a globally broken symmetry but also with a locally broken symmetry are obtained. The latter states are often used as a basis for disputed disordered local moment theories. Such a local symmetry breaking is a MFA artifact and would never occur in a correct correlation calculation.[21]

In our interpretation, the success of LDA for the ferromagnetism of the transition metals arises from the chance compensation of two errors. The first is the complete omission of U from the Stoner parameter, and the second is the MFA for J. From our experience it seems as if for $N = 5$, that is, in the case of the transition metals, both errors almost exactly compensate each other. This interpretation is supported by the failure of LDA when antiferromagnetism is concerned. There, U apparently plays a relatively larger role. Degeneracies greater than five do not occur in nature, however, our interpretation predicts difficulties of the LDA with ferromagnetism for degeneracies smaller than five.

With the help of this unified interpretation of the itinerant ferromagnetism, we may now investigate the interpretation by LD. LD have based their picture on LDA calculations, but never introduced or explained I_{LDA}. Therefore, their interpretation is not consistent. The second relevant feature is the density of state around the Fermi energy. The authors did not use this density of state but elaborated on more general antibonding properties of electrons close to the Fermi energy, properties that naturally include the density of state. It will now be demonstrated for the specific ferromagnetic metals that besides I only the density of state itself plays a role, and that the new antibonding features from LD are not needed. The following discussion represents standard knowledge that has been available for few decades, except from a small correction resulting from our connection of I_{LDA} and J_{atom}. The discussion is qualitative, but still contains the essential features of the full quantitative treatment. For a qualitative treatment I refer to the citations given below, and to a large number of LDA publications.

Let us begin with the difference between fcc and bcc-Fe. The fcc Fe is not magnetic. In this case, I or I_{LDA} are apparently a little bit smaller than the inverse 3d density of state. Except for a few spikes, the fcc 3d-density of state is essentially a constant (see Figure 22 in ref. [1]). However, the same is not true for bcc-Fe. The bcc density of state has a pronounced minimum with two peaks around it (see Figure 17 in ref. [1]), and the Fermi energy of the nonmagnetic state lies in the middle of one of the maximums. Because of the higher density of state, the Stoner criterion is fulfilled for the bcc case which has the same I_{LDA} as the fcc case, and the system is ferromagnetic. However, bcc-Fe is not completely ferromagnetic. Even this can be understood in the Stoner picture. With increasing moment M, the Fermi energies for the new majority band and for the minority band move out of the maximum of the density of state. Beyond the ground state moment M_0, the Stoner criterion is no longer fulfilled, and a complete magnetization is not allowed.

The next topic concerns the transition from fcc-Fe to -Co and -Ni. All cases show the same (rather constant) density of state so that the different positions of the Fermi energies are not expected to be responsible for the onset of magnetism. However, because of the stronger localization of the 3d orbitals for the heavier elements, the band width W shrinks and the density of state increases when going to Ni, while the exchange interaction J and also the interaction U rise, therefore the Stoner parameter increases. Consequently, the Stoner criterion can be fulfilled, and Co and Ni are ferromagnetic.

The same arguments apply when going to the 4d and 5d elements Pd and Pt. Again the density of state is similar to that of Ni, but the band width W is larger, and correspondingly the interactions J and U, and thus I are smaller. Therefore, the Stoner criterion can no longer be fulfilled. The origin of the decrease of J is, by the way, not a result of stronger screening but because the 4d and 5d atomic orbitals are more diffuse (a consequence of the enlarged core and the Fermi exclusion). J is basically a bare, unscreened matrix element. The decrease of U with rising principle atomic quantum numbers has been discussed in detail for the series of elements C to Sn.[24]

For all the explanations given above only the detailed densities of state and a little knowledge of I were used. There is no need for seemingly new information like the crystal-orbital Hamilton population (COHP) of LD in the context of itinerant ferromagnetism. Further conclusions drawn from the COHP picture are wrong. The negative energies of the local 3d COHPs have nothing to do with magnetism itself. In my opinion, they might be connected to the charge transfer from the 4s,4p orbitals to 3d. There is even an indirect relation between this charge transfer and magnetism (causing the inverse magneto volume effect for Ni[9]), but this is out of the range of the LDA that was used by LD.[9] Additionally, the narrowing of the majority band and the widening of the minority band do not cause ferromagnetism but instead represent an attempt to reduce a little the band-energy losses originating from the ferromagnetic redistribution.

To conclude, itinerant ferromagnetism is caused by atomic interactions, and is strongly supported by the same exchange interactions J between degenerate atomic orbitals explain the Hund's rule order in atoms. Ferromagnetism may occur only if the band width of the electrons involved is sufficiently small, as was predicted by Stoner half a century ago. The LDA is successful for the transition metals because the Stoner theory applies and because apparently two errors in the Stoner parameter I_{LDA} almost compensate one another. Our LA model computations have demonstrated that the Stoner theory can be applied because the 3d electrons of the transition metals are weakly correlated, a result of mutual screening.

A long time ago Van Vleck proposed a theory for the itinerant ferromagnetism of the transition metals[25] that is complementary to the Stoner theory. His theory is based on the existence of localized magnetic moments, based on the strong correlation limit. This theory was shown to be false by experiments, by LDA calculations, and also by our work. Nevertheless, proposals similar in spirit to the theory of van Vleck have reappeared in very recent work on Hubbard models, always because of a false choice of degeneracy for the used models. LD have proposed to submit the old work of van Vleck to Occams razor (see citation 13 in ref. [1]). I feel that the speculation of van Vleck was not unreasonable in his time. I would rather propose to apply this tool to the most recent contributions of LD in the field of itinerant ferromagnetism. Landrum and Dronskowski should have known better.

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Reply

Gregory A. Landrum and Richard Dronskowski*

In the preceding paper,[1] many-body theorist Gernot Stollhoff criticizes our recent review of a chemistry-oriented approach to understanding metallic ferromagnetism.[2] Although we heartily welcome a lively debate between chemists and physicists on the subject, Stollhoff's critique, in our view, misses the deciding point.

Within the largest part of his text, Stollhoff goes to great lengths to speak in favor of the Hubbard ansatz and related theories based on $W/J/U$ parameters. He also presents his own mini review explaining ferromagnetism in metallic species. For an, admittedly quite concise, treatment of Hubbard models, the reader is referred to Sections 2.3, 3.1, and especially 5.1 of our review.[2] As we have already said, Stollhoff's theoretical approach is far from being the only theory in existence. Stollhoff questions both density functional theory (DFT) as well as the local density approximation (LDA), and promotes his own computational approach. Stollhoff obviously has severe problems with accepting DFT in general, but that is another matter. With respect to our own theory, we do not demand that the method we are using to construct chemical explanations be 100 percent "accurate" (whatever that means) although the LDA is, as he admits, totally precise in its predictions with respect to ferromagnetism and the transition metals.

It is true that our results are based on density functional (mostly LDA) calculations; while the LDA performs astonishingly well in most cases, there are deficiencies that we summarized in Sections 5.2 and A.1. Two years ago an independent review on the successes and failures of DFT was presented from the perspective of the physics community.[3] However, the presence of antibonding states at the Fermi level is observed, which we view as the ferromagnetic "fingerprint", in *both* LDA and gradient corrected calculations (see Section A.1)! This much at least is not an artifact of the LDA. It was not in fact our intention to "sell" DFT or LDA or any other numerical theory as the optimum solution. On the contrary, as we demonstrated in Appendix B, a much more primitive theory, the extended Hückel (!) is able to reproduce the ferromagnetic fingerprint, provided that the method is asked the right questions. Thus, we have demonstrated that the characteristic effect is theoretically "good-natured" and does not need an excessively sophisticated treatment. Also, our approach is orbital oriented and may thus be easily subjected to a chemical interpretation. It is hard for us to say whether equations (1)–(6) of Stollhoff's article[1] contain chemically valuable information, and we leave this decision to the experimentalists.

Towards the end Stollhoff touches our contribution directly. When talking about fcc- and bcc-Fe, Stollhoff actually uses our results but does not present new information. With respect to his discussion of Co and Ni, he does not consider the changing position of the Fermi energy within the fcc density of states since our explanation allows more immediate insight than his $W/J/U$ reasoning. In fact, the crystal-orbital Hamilton population (COHP) result in Figure 21 of ref. [2] qualitatively demonstrates the different strengths of ferromagnetism in Fe, Co, and Ni! Concerning Stollhoff's remarks on the heavier transition metals, he does not realize the analogy between main group and transition metal chemistry as far as differential shielding is concerned. He writes about the situation with Pd and Pt: "The origin of the decrease of the J is, by the way, not a result of stronger screening but because the 4d and 5d atomic orbitals are more diffuse (a consequence of the enlarged core)." Exactly, the 4d and 5d atomic orbitals are more diffuse, and the core is enlarged. This was the basis of our argument. We did not attempt to explain the decrease of J, we wanted to avoid any mention whatsoever of J in our treatment of the heavier transition metals.

On the other hand, Stollhoff does not seem to understand the origin of the negative COHP at the Fermi energy although

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