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LETTER TO THE EDITOR

Electron correlation effects and ferromagnetism in iron

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Abstract

Electron correlation effects in Fe are analysed using a first-principles linear combination of atomic orbitals scheme. In our approach, we first use a local orbital density functional solution to introduce a Hubbard Hamiltonian without fitting parameters. In a second step, we introduce a many-body solution to this Hamiltonian using a dynamical mean-field approximation. Our analysis shows that magnetism in Fe is an effect associated with the first atomic Hund's rule. Moreover, we also find important correlation effects in the Fe spin-polarized density of states. The photoemission spectra can be explained using a value of U^{eff} as large as 4 eV, provided that the satellite peaks appearing around 3–5 eV below the Fermi energy are interpreted appropriately.

The electronic properties of ferromagnetic metals are still a subject of controversy [1–3]. Although density functional theory-local density approximation (DFT-LDA) calculations yield the correct magnetization for the itinerant-electron ferromagnets Fe, Co and Ni, the origin of ferromagnetism in these metals and the role of electron correlations are not completely understood (e.g. see [4, 5]); in particular, the relative importance of the local Coulomb interaction for d orbitals, U^{eff} , versus intra-atomic exchange (first Hund's rule) is not completely established. Even from an experimental point of view, there is a lack of agreement on whether or not a satellite peak exists in the photoemission spectrum of iron around 5 eV below the Fermi energy [2].

In the conventional view of itinerant ferromagnetism [6], spin polarization is determined by the Stoner parameter, I , that defines the energy of the atomic d orbitals as $(E_d - In_d)$, n_d being the occupation number of the orbital under consideration. In the case of Fe, DFT-LDA calculations yield a value $I = 3.9$ eV [7], and a *surprisingly large* value of $U^{\text{eff}} \sim 4\text{--}6$ eV [8, 9] for the effective Coulomb interaction between the d electrons. Since the atomic-like properties of the d states are of crucial importance for the magnetic properties of these materials, linear

combination of atomic orbitals (LCAO) methods provide the appropriate conceptual framework for understanding those properties and for analysing the role of electron correlations. In LCAO theories of ferromagnetism, including Hubbard Hamiltonians, I is written as $(\tilde{U}^{\text{eff}} + 4J^x)$ [10], where J^x defines the screened intrasite exchange interaction between the atomic d electrons having the same spin; it is commonly accepted that J^x practically coincides with its atomic value [8]. In the case of Fe, $J^x = 0.83$ eV and, therefore, we should take $\tilde{U}^{\text{eff}} \sim 0.6$ eV to recover the value $I = 3.9$ eV that corresponds to the correct magnetization. This result suggests the presence of dramatic electron correlation effects in Fe, which would be responsible for the renormalization of U^{eff} from ~ 5 eV to $\tilde{U}^{\text{eff}} \sim 0.6$ eV. On the other hand, the value of U^{eff} inferred from the photoemission spectra [11–13] by identifying photoemission peaks with quasi-particle peaks yields $U^{\text{eff}} \approx 2$ eV [1, 9]. This result seems to indicate that electron correlation effects for Fe are not strong, in contradiction to the previous analysis.

The purpose of this letter is to show that these apparent contradictions disappear once electron correlation effects [14] are properly analysed using a first-principles LCAO scheme. In our approach, reminiscent of the LDA+ U scheme [15], we first formulate a local density (LD) solution for a generalized Hubbard Hamiltonian. This LD solution provides the link between the generalized Hubbard Hamiltonian and local orbital DFT-LDA methods, allowing us to obtain that Hamiltonian from first principles, without having to introduce fitting parameters. In a second step, we introduce a many-body solution for the Hubbard Hamiltonian using a dynamical mean-field (DMF) approximation [16]: in this way we analyse the spin-polarized electron density of states (DOS) for Fe and compare it with the experimental evidence [11–13]. From our analysis, we obtain two different results. First, using our LD solution for the Hubbard Hamiltonian, we show that electron correlation effects screen strongly the effective Coulomb interaction contributing to the Stoner parameter: in this scenario, \tilde{U}^{eff} is not larger than 0.6–0.7 eV. We find, however, that the effective interaction appearing in the Hubbard Hamiltonian is around 4 eV, in reasonable agreement with other first-principles calculations [8, 9]; using this value and the many-body techniques mentioned above, we also find that the spin-polarized DOS for Fe is in good agreement with the photoemission data, provided that we interpret appropriately the satellite peaks appearing in the spectrum around 3–5 eV below the Fermi energy [9].

Our starting point is the generalized Hubbard Hamiltonian:

$$\hat{H} = \hat{H}^{OE} + \frac{1}{2} \sum_{i,\alpha\sigma \neq \beta\sigma'} U_i \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma'} - \frac{1}{2} \sum_{i,\alpha\sigma \neq \beta\sigma} J_i^x \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma} + \frac{1}{2} \sum_{i \neq j}^{\alpha\sigma, \beta\sigma'} J_{i\alpha, j\beta} \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma'}, \quad (1)$$

where \hat{H}^{OE} defines a one-electron contribution and U_i and $J_{i\alpha, j\beta}$ are the intrasite and intersite Coulomb interactions between different orbitals $\phi_{i\alpha}$ and $\phi_{j\beta}$ (for the sake of simplicity, U_i is an average of the different interactions inside the i -site); we also introduce the intrasite exchange Coulomb interaction, J_i^x , associated with the first atomic Hund's rule. Equation (1) has been written in an orthogonal local basis, $\phi_{i\alpha}$, defined by Lowdin's transformation $\phi_{i\alpha} = \sum_{j\beta} (S^{-1/2})_{i\alpha, j\beta} \psi_{j\beta}$, $\psi_{j\beta}$ being the local basis used in the DFT-LDA calculation from which we obtain Hamiltonian (1), as explained below ($S_{i\alpha, j\beta}$ is the overlap between orbitals $\psi_{i\alpha}$ and $\psi_{j\beta}$).

The LD solution of Hamiltonian (1) is obtained by introducing the kinetic and many-body energies of the system as a function of the orbital occupancies, $n_{i\alpha\sigma}$ [17]. This implies that the total energy is a function of those numbers, $n_{i\alpha\sigma}$, that play the role of the electron density, $\rho(\vec{r})$, in the conventional DFT approach. Then, we can write the following equation:

$$E[\{n_{i\alpha\sigma}\}] = T[\{n_{i\alpha\sigma}\}] + E^H[\{n_{i\alpha\sigma}\}] + E^{XC}[\{n_{i\alpha\sigma}\}], \quad (2)$$

where $T = \langle \Psi_0 | \hat{H}^{OE} | \Psi_0 \rangle$, Ψ_0 being the ground state of the total LD Hamiltonian; E^H is the

Hartree energy and E^{XC} is the exchange–correlation energy associated with Hamiltonian (1). On the other hand [17],

$$E^X[\{n_{i\alpha\sigma}\}] = -\frac{1}{2} \sum_{i,\alpha\sigma \neq \beta\sigma} J_i^x n_{i\alpha\sigma} n_{i\beta\sigma} - \frac{1}{2} \sum_{i\alpha\sigma} J_i n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}), \quad (3)$$

an equation that yields the exchange energy as the sum of an intrasite contribution and of the intersite interaction between the electron charge, $n_{i\alpha\sigma}$, and its hole, $(1 - n_{i\alpha\sigma})$. In this equation, J_i is practically the Coulomb interaction between charges located in nearest-neighbour atoms. Because of the crystal symmetry, we assume that no exchange hole appears in the atom where the electron is located. On the other hand, we have also shown [17] that the correlation energy is given by

$$E^C[\{n_{i\alpha\sigma}\}] = -\frac{1}{2} \sum_{i\alpha\sigma} f_i (U_i - J_i) n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) \quad (4)$$

where $(U_i - J_i)$ is an effective intrasite Coulomb interaction between i -site orbitals. In equation (4), f_i ($0 < f_i < 1$) measures the fraction of the exchange–correlation hole that is transferred to the atom i due to intrasite correlation effects. Equations (2)–(4) allow us to substitute Hamiltonian (1) for an effective Hamiltonian where, instead of the many-body terms, we introduce the local potentials ($V_{i\alpha\sigma}^H$ and $V_{i\alpha\sigma}^{XC}$) given by

$$V_{i\alpha\sigma}^H = \frac{\partial E^H[\{n_{i\alpha\sigma}\}]}{\partial n_{i\alpha\sigma}} = \sum_{\beta\sigma' \neq \alpha\sigma} U_i n_{i\beta\sigma'} + \sum_{j\beta\sigma' (j \neq i)} J_{i\alpha,j\beta} n_{j\beta\sigma'} \quad (5)$$

$$V_{i\alpha\sigma}^{XC} = \frac{\partial E^{XC}[\{n_{i\alpha\sigma}\}]}{\partial n_{i\alpha\sigma}} = - \sum_{\beta \neq \alpha} J_i^x n_{i\beta\sigma} - J_i (\frac{1}{2} - n_{i\alpha\sigma}) - f_i (U_i - J_i) (\frac{1}{2} - n_{i\alpha\sigma}), \quad (6)$$

where f_i has been assumed to be constant.

This is the main result of our LD analysis and shows how to reduce the generalized Hubbard Hamiltonian, equation (1), to an effective one-electron Hamiltonian, taking into account all the many-body contributions. Conversely, we can use this equivalence to go from a LD solution to a generalized Hubbard Hamiltonian: assume that we solve the conventional DFT-LDA equations for a given crystal (say, paramagnetic Fe) using a local orbital basis (as is done in the Fireball [18] and Siesta [19] codes); then, we can subtract from the one-electron levels associated with the orthogonalized orbitals, $\phi_{i\alpha}$, the potentials given by equations (5) and (6). This difference defines Hamiltonian H^{OE} in equation (1), and allows us to introduce the Hubbard Hamiltonian by means of the interactions U , J and J^x . Notice that in this approach we have to calculate these interactions using the orthogonalized orbitals, $\phi_{i\alpha}$. In our actual calculations, we have employed the Fireball code for paramagnetic Fe and used the corresponding local orbital basis.

Ferromagnetic Fe has been analysed in our LD approach by looking for a magnetic solution where some charge is transferred between spins up and down. This implies that self-consistent potentials, $V_{i\alpha\uparrow}$ and $V_{i\alpha\downarrow}$, should appear for different spins, in such a way that

$$V_{i\alpha\uparrow} = U_i (N_i - n_{i\alpha\uparrow}) + \sum_{j\beta\sigma' (j \neq i)} J_{i\alpha,j\beta} n_{j\beta\sigma'} - J_i^x (N_{i\uparrow} - n_{i\alpha\uparrow}) - J_i (\frac{1}{2} - n_{i\alpha\uparrow}) - f_i (U_i - J_i) (\frac{1}{2} - n_{i\alpha\uparrow}) \quad (7)$$

where N_i is the total charge in the d orbitals for the i -site, while $N_{i\uparrow}$ represents the total spin-up charge. Notice how the terms contributing to $V_{i\alpha\uparrow}$ correspond to the Hartree, the intra-atomic exchange, the extra-atomic exchange and the correlation contributions, respectively. Due to

the magnetic polarization, we find changes in the many-body potential w.r.t. the paramagnetic solution. This yields

$$\delta V_{i\alpha\uparrow} = -(1 - f_i)(U_i - J_i)\delta n_{i\alpha\uparrow} - J_i^x(\delta N_{i\uparrow} - \delta n_{i\alpha\uparrow}) \quad (8)$$

where the total charge, N_i , has been assumed to be constant and independent of the atomic magnetization. Equation (8) defines how the $i\alpha \uparrow$ -level depends on the atomic polarization, $\delta n_{i\alpha\uparrow}$. This quantity should be obtained self-consistently by means of a band-structure calculation whereby the atomic charges, $\delta n_{i\alpha\uparrow}$, are a function of $\delta V_{i\alpha\uparrow}$. These two conditions yield $\delta n_{i\alpha\uparrow}$ and the crystal magnetization. Equation (8) allows us, however, to calculate directly the Stoner parameter, I , which we define as $|\delta V_{i\alpha\uparrow}/\delta n_{i\alpha\uparrow}|$. Equation (8) yields the following result:

$$I = (1 - f_i)(U_i - J_i) + 4J_i^x \quad (9)$$

assuming $\delta N_{i\uparrow} = 5\delta n_{i\alpha\uparrow}$, as corresponds to d orbitals. In our calculations for Fe, we find $U_i = 14.7$ eV (taking into account atomic relaxation), $J_i = 6$ eV and $J_i^x = 0.83$ eV.

A word of caution should be introduced here, because in our discussion we have neglected an effect that leads to a further reduction in the effective interaction between orbitals. This is associated with the sp-band screening that has been shown by other authors [8] to reduce $(U_i - J_i) = U_i^{\text{eff}}$ to values close to 5 eV. In our calculations, performed introducing a Lindhard dielectric function, we have found that U_i^{eff} is reduced to 4.0 eV. If we introduce this value in equation (9) and take $f_i = 0.83$ (the value that corresponds to this reduced interaction), we find $I = 4.0$ eV, in good agreement with DFT-LDA calculations. We have also analysed how I depends on U_i^{eff} by calculating f_i for different intrasite Coulomb interactions. Our results show that, in the 2–5 eV range, $(1 - f_i)U_i^{\text{eff}}$ is almost insensitive to the values of U_i^{eff} . These results show that the Stoner parameter is mainly controlled by J_i^x ; in other words, ferromagnetism in Fe is an effect mainly associated with the intra-atomic first Hund's rule.

Next, we calculate many-body effects introducing a local self-energy, $\Sigma_{i\alpha\sigma}(\omega)$, within the DMF approximation. This is a reasonable approximation, considering that correlation effects in Fe are associated with the intrasite Coulomb interaction between d orbitals. As discussed in [17], $\Sigma_{i\alpha\sigma}(\omega)$ is calculated by means of an appropriate interpolation between two limits:

- (1) first, we calculate the atomic limit, assuming U_i^{eff} much larger than the metal bandwidth;
- (2) second, we obtain the second-order self-energy, $\Sigma_{i\alpha\sigma}^{(2)}(\omega)$, using as the expansion parameter U_i^{eff} ;
- (3) finally, we calculate the self-energy by interpolating between these two limits.

We should stress that, in this solution, $\Sigma_{i\alpha\sigma}^{(2)}$ is calculated using the local DOS defined by the LD solution discussed above. Finally, we replace $V_{i\alpha\sigma}^c$, in our effective LD Hamiltonian, by that self-energy; then, we use a conventional Green-function formalism to calculate the LD of states. At this point, we should comment that consistency between the LD and the self-energy formulations imposes the following Luttinger sum rule: $V_{i\alpha\sigma}^c = \Sigma_{i\alpha\sigma}(E_F)$. The factor f_i in equation (4) has been determined from this equation, this procedure satisfying the Luttinger condition automatically. The price that we have to pay is the introduction of a self-consistent loop in the calculation.

Figure 1 shows our calculated LD and many-body DOS for ferromagnetic Fe. The comparison between these two densities of states shows that correlation effects are important for Fe: first, we notice that the energy difference between the two maxima appearing in the spin-up and spin-down DOS for the LD solution is reduced by almost a factor of two in the many-body case (for comparison, see [5] where $U = 2.3$ eV is used). This is a typical band-narrowing effect appearing around E_F and associated with a highly correlated electron gas.

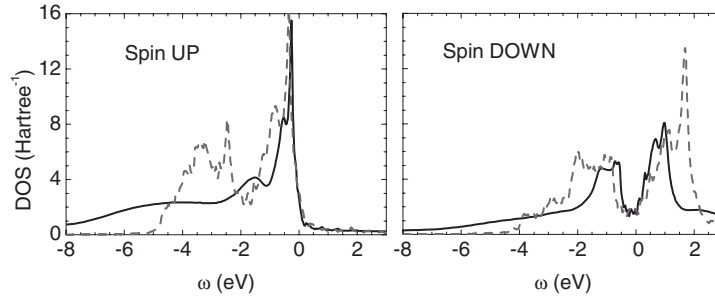


Figure 1. The total Fe spin DOS for the many-body solution with $U^{\text{eff}} = 4$ eV (continuous curve) and for the DFT-LDA solution (dashed curve). Notice the shift of the peaks towards E_F when correlation effects are introduced.

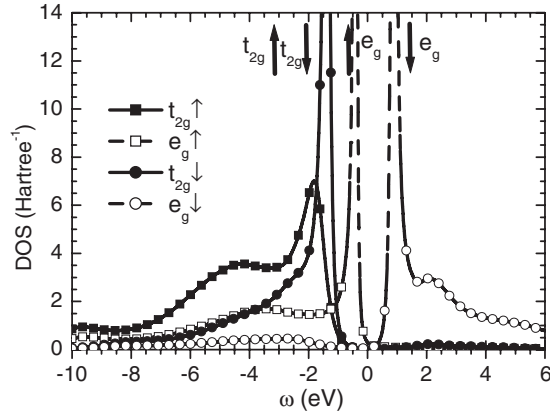


Figure 2. The spin DOS, split into the t_{2g} and e_g components, at the P point for Fe. The positions of the DFT-LDA eigenvalues are indicated by arrows. Notice that the t_{2g} (up) state (black squares) has lost its quasiparticle character.

On the other hand, we also find that the DOS structure at energies far away from E_F is strongly modified by the many-body solution; in particular, a new satellite structure appears around 5 eV below E_F . We analyse these many-body effects in more detail by considering the DOS for a particular \vec{k} -vector: we have chosen the P point, a point for which there are high-quality photoemission data taken along the (111) direction [12, 13].

Figure 2 shows the electron DOS for this \vec{k} -vector split into the t_{2g} and the e_g components, and the energy levels corresponding to the DFT-LDA solution for this \vec{k} -point. In this figure we also find the effects already discussed in relation to figure 1: the e_g (up) and t_{2g} (down) levels located 0.6 and 2.1 eV below E_F are shifted to around 0.4 and 1.4 eV, respectively. In both cases, we also find some satellites at higher binding energies due to many-body effects. The other t_{2g} (up) level located 3.1 eV below E_F is completely smeared out by the self-energy, giving rise to two features: one almost coincides in energy with the t_{2g} (down) peak; the other is a very broad peak located around 4.5 eV below E_F . For energies above E_F , we find the e_g (down) level, located 1.4 eV above E_F , shifted by many-body effects to 0.9 eV. In figure 3 we compare these results with photoemission data [12, 13], by considering the appropriate weight that each state has in the photoemitted electrons. This is done assuming the final state to be a plane wave; in this way we find that, for the P point, the t_{2g} levels are reduced in intensity

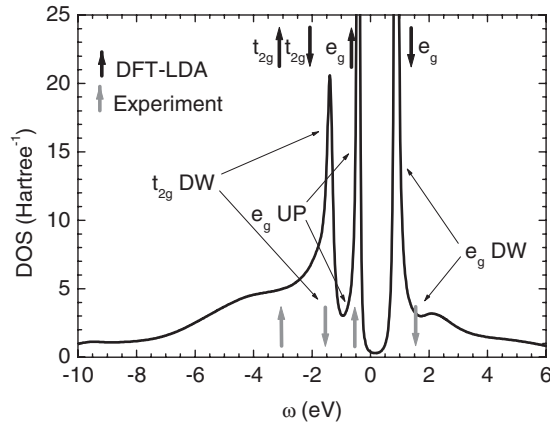


Figure 3. Quasiparticle spectra (considering the appropriate weight for each state; see the text) at the P point for Fe. Black arrows indicate the eigenstates of the DFT-LDA Hamiltonian. Experiments [12, 13] show three well-defined peaks close to E_F and a very broad feature around 3 eV below E_F traditionally interpreted as the t_{2g} (up) state (grey arrows).

by a factor of 3 w.r.t. the e_g levels. Comparing this DOS with the photoemitted spectra, we clearly see that the two peaks below E_F (at 0.4 and 1.4 eV) are related to the e_g (up) and t_{2g} (down) states calculated in the LD approach, while the peak above E_F (at 0.9 eV) corresponds to a e_g (down) level; these results are in reasonable agreement with the experimental data of [12, 13]. More importantly, we find that the very broad peak located around 3–4 eV below E_F cannot be related directly to the t_{2g} (up) states found in the LD approach around 3.1 eV below E_F [12]. On the contrary, our results clearly show that this peak is a satellite structure created by many-body effects and appearing as a result of combining the tail intensities of e_g and t_{2g} states (see figure 2, and remember the factor $1/3$ we have to introduce in the weight of the t_{2g} states).

This analysis clarifies several contradictory points regarding the magnetism of iron. Our results show that we can find a reasonable agreement between theory and photoemission data for U^{eff} as large as 4 eV. The reason that a value of $U^{\text{eff}} \simeq 2$ eV has been used in the interpretation of these data is the tendency to identify the broad satellite peak, located around 3 eV below E_F , at the P point, with the quasiparticle level that in DFT-LDA appears around 3.1 eV below E_F . Our results show, however, that this quasiparticle level has lost its identity due to correlation effects and that it has been modified into a smeared DOS; this new DOS tends to create a satellite structure that should be reinterpreted as due to many-body effects and not as a quasiparticle level reminiscent of the DFT-LDA level. This same effect is also responsible for the satellite peak that we find in the total DOS (see figure 1) around 5 eV below E_F .

In conclusion, we have studied the electronic properties of ferromagnetic Fe using a first-principles LCAO scheme to analyse in detail the role of electron correlations. We find that the correlation potential strongly screens the magnetic effects commonly associated with a local Hubbard interaction: magnetism in Fe is an effect associated with the first atomic Hund's rule. Moreover, we also find important correlation effects in the spin-polarized DOS. In particular, our analysis shows that the t_{2g} (up) levels located 3.1 eV below E_F have lost their quasiparticle identity, due to many-body effects, and tend to create a satellite structure that has been observed experimentally.

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