Comment on "Magnetism and local order: *Ab initio* tight-binding theory"

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In a recent paper entitled "Magnetism and local order: *Ab initio* tight-binding theory," Feng Liu *et al.* [Phys. Rev. B **39**, 6914 (1989)] presented a model for the determination of the electronic structure of finite systems with reduced symmetry. The various matrix elements appearing in the tight-binding formulation are determined from the self-consistent treatment of the dimer. A simple method based upon the real space enables us to show that in the case of iron the intrasite matrix elements of the tight-binding calculation are not transferable to bulk and slabs without caution. Actually, the non-self-consistent calculation leads to a charge transfer that is at least an order of magnitude greater than that found in the present self-consistent one.

In a recent paper by Feng Liu *et al.*, the effects of the local environment on the magnetic moment of the Fe, Co, and Ni have been studied extensively.[1] Their method is based on the moment approach,[2] whereas the overlap-matrix elements $(dd\sigma, dd\pi, dd\delta, sd\sigma, ss\sigma)$ are determined through a molecular-cluster calculation based on the discrete-variation method[3] of the dimer. The determination of these spin-dependent overlap terms are performed within the Von Barth–Hedin approximation[4] to the local-spin-density functional for the exchange-correlation contribution. This model neglects the variation of the crystal-field integrals at the surface and the modification of the Coulomb term due to charge transfer.

Following Pastor *et al.*,[5] who uses a Hubbard Hamiltonian for "*d*" electrons for the description of small clusters, we derive the electronic structure for slabs of bcc α-Fe. In this model the hopping integrals are spin independent, whereas the spin-dependent diagonal term are given by[5]

$$\varepsilon_{i\sigma} = \varepsilon_d^0 + U\Delta N_i - \sigma \frac{J}{2}\mu_i , \qquad (1)$$

where i is the index of the atomic plane and σ the spin.

ε_d^0 is the d atomic level and can be chosen as zero. The exchange and effective direct intraatomic Coulomb integrals, denoted by J and U, respectively, are taken to be independent of the size of the slabs and of the position i; U is taken from Pastor *et al.*,[5] whereas J is adjusted to have, for bulk iron, the experimental $(2.21\mu_B)$ value.

The local magnetic moment μ_i is given by

$$\mu_i = N_{i\uparrow} - N_{i\downarrow} , \qquad (2)$$

whereas the numbers of electrons $N_{i\sigma}$ are determined by

$$N_{i\sigma} = \int^{E_F} n_{i\sigma}(E)dE . \qquad (3)$$

The spin-polarized local density of states (SPDOS) $n_{i\sigma}$ is calculated by using the recursion method[6] with ten levels of the continued fraction and hopping integrals of Pettifor.[7] We allow charge transfer ΔN_i between different atomic planes by requiring global charge neutrality for the N_L layer slab of Fe(001), i.e.,

$$\sum_{\sigma} \sum_{i=1}^{N_L} \int^{E_F} n_{i\sigma}(E)dE = N_L N_d , \qquad (4)$$

TABLE I. Magnetic moments per atom in 1-, 3-, 5-, 7-, 9-, and 11-layer slabs of Fe(001). ATB: Ref. 1; FLAPW: Ref. 8.

	1 layer			3 layers		5 layers		7 layers			9 layers		11 layers
	ATB	FLAPW	Present	ATB	Present	ATB	Present	ATB	FLAPW	Present	ATB	Present	Present
S	3.15	3.20	3.00	2.75	2.51	2.73	2.66	2.74	2.98	2.60	2.71	2.58	2.59
S-1				2.56	2.14	2.53	2.14	2.54	2.35	2.17	2.53	2.18	2.18
S-2						2.54	1.97	2.55	2.39	2.16	2.53	2.17	2.16
S-3								2.55	2.25	2.18	2.54	2.19	2.19
S-4											2.54	2.21	2.21
S-5													2.21

TABLE II. Magnetic moments μ and local charge transfer ΔN per atom in 1-, 3-, 5-, 7-, 9-, and 11-layer slabs of Fe(001). The hopping integrals are those of Feng Liu et al. (Ref. 1), whereas the splitting of the spin-up and spin-down has been adjusted in order to obtain the same bulk magnetic moment as Feng Liu et al. This calculation is non-self-consistent.

| | 1 layer | | 3 layers | | 5 layers | | 7 layers | | 9 layers | | 11 layers | |
	μ	ΔN	μ	ΔN	μ	ΔN	μ	ΔN	μ	ΔN	μ	ΔN
S	2.95	0.00	2.78	0.01	2.67	0.14	2.59	0.25	2.56	0.30	2.53	0.34
S-1			2.59	-0.02	2.53	-0.04	2.55	-0.00	2.57	0.03	2.57	0.05
S-2					2.53	-0.21	2.52	-0.17	2.53	-0.13	2.54	-0.11
S-3							2.45	-0.14	2.48	-0.12	2.48	-0.10
S-4									2.51	-0.15	2.51	-0.13
S-5											2.51	-0.11

where we have assumed $N_d = 7$ electrons per atom. ΔN_i is given by

$$\Delta N_i = \sum_{\sigma} (N_{i\sigma} - N_{\sigma}^0) , \qquad (5)$$

where N_{σ}^0 is the number of d electrons with spin σ of the bulk iron.

Due to the global charge-neutrality condition (4), the Fermi level has to be recalculated at each self-consistent step. Let us point out that our results display a very small local charge transfer (usually less than 0.03 electrons).

Our small charge transfer must probably be related to the Coulomb term U. We have investigated the magnetic moments per atom in 1-, 3-, 5-, 7-, 9-, and 11-layer slabs of Fe(001). It was necessary to perform the calculation up to 11 layers in order to recover the magnetic moment of the bulk. In Table I the comparison is made with the results of Feng Liu et al. and with the full-potential linearized augmented-plane-wave (FLAPW) method of Ohnishi et al.[8] It is difficult to compare these results because (i) the FLAPW has been performed only on 1- and 7-layer slabs and unfortunately the magnetic moment of the bulk has not been reached and (ii) the ab initio tight-binding (ATB) method has been performed up to 9-layer slabs but the magnetic moment of the bulk $(2.53\mu_B)$ is much higher than the experimental result $(2.21\mu_B)$. Feng Liu et al.[1] have taken into account s and d bands, whereas the present calculation is restricted to d orbitals. In fact, the polarization of the sp electrons for iron, obtained in a tight-binding framework, is less than $0.1\mu_B$, in opposition with d polarization.[9]

Nevertheless, what we can see is that the magnetic moment at the surface is much higher than that of the expected bulk. In the ATB method only the magnetic moment at the surface is different from the bulk, whereas in the FLAPW and in the present calculation there is some oscillation before reaching the bulk value.

We will now return to the problem of the local charge transfer. We have introduced in our slabs program the d parameters in Table II of Feng Liu et al. First a comment should be made relative to the value of the splitting of the d orbitals which is given by

$$\Delta\varepsilon_d = \varepsilon_d^{\uparrow} - \varepsilon_d^{\downarrow} = J\mu_b , \qquad (6)$$

where μ_b is the bulk magnetic moment. Pastor et al.,[5] using more levels for the continued fraction, have obtained a value of 0.73 eV, whereas our value is 0.82 eV. If we accept a bulk value of $2.53\mu_B$ and a value of $\Delta\varepsilon_d = 2.72$ eV (results obtained by Feng Liu et al.) then $J = 1.075$ eV. Also, due to the lack of the s-d hybridization which smoothes the d bands our calculation gives higher values, i.e., $2.81\mu_B$, for the bulk.

Because the results obtained with the parameters of Feng Liu et al. do not reproduce the bulk value, we have adjusted $\Delta\varepsilon_d$ such as to obtain the magnetic moment of the bulk given by Feng Liu et al., i.e., $\mu_b = 2.53\mu_B$; we obtained $\Delta\varepsilon_d = 2.217$ eV or $J = 0.876$ eV. The magnetic moment and the charge transfer are reported in Table II. We have performed a similar calculation with $\Delta\varepsilon_d = 1.60$ eV or $J = 0.72$ eV which gives $\mu_b = 2.21\mu_B$ (Table III).

We may conclude the following.

(1) We have shown that, in the case of iron, the param-

TABLE III. Magnetic moments μ and local charge transfer ΔN per atom in 1-, 3-, 5-, 7-, 9-, and 11-layer slabs of Fe(001). The hopping integrals are those of Feng Liu et al. (Ref. 1), whereas the splitting of the spin-up and spin-down has been adjusted in order to obtain the experimental value of the bulk magnetic moment. This calculation is non-self-consistent.

| | 1 layer | | 3 layers | | 5 layers | | 7 layers | | 9 layers | | 11 layers | |
	μ	ΔN	μ	ΔN	μ	ΔN	μ	ΔN	μ	ΔN	μ	ΔN
S	2.86	0.00	2.16	0.19	2.04	0.47	1.98	0.60	1.95	0.67	1.94	0.70
S-1			2.05	-0.39	2.08	-0.27	2.15	-0.19	2.19	-0.14	2.21	-0.10
S-2					2.09	-0.41	2.14	-0.30	2.15	-0.23	2.15	-0.19
S-3							2.06	-0.21	2.12	-0.18	2.13	-0.15
S-4									2.19	-0.23	2.19	-0.18
S-5											2.16	-0.17

eters obtained by Feng Liu *et al.* through a self-consistent treatment of the dimer are only partially transferable to bulk and slabs. The transferability is good for hopping integrals, but care should be taken in the intrasite matrix elements of the Hamiltonian.

(2) The non-self-consistent calculation leads to a charge transfer which is at least an order of magnitude bigger than that obtained in our self-consistent derivation. Therefore, charge neutrality was incorporated by Feng Liu *et al.*[1] by keeping each layer (in a slab calculation) neutral.

(3) In our opinion, based on self-consistent and non-self-consistent calculations, the only way to get reason-able results is to perform self-consistent calculations, starting from a coherent description of the bulk. (The exchange integral has to be adjusted in order to recover the bulk magnetic moment.)

We are currently extending our self-consistent derivation to the determination of the magnetism at the surface of iron.[10] Extension to interface with nonmagnetic material is also under present investigation.

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