Magnetic contribution to the vacancy-formation energy: An alternative method for the *ab initio* calculation of effective exchange parameters in ferromagnetic metals

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An alternative method is suggested for the *ab initio* calculation of effective exchange parameters in ferromagnetic metals from the magnetic contribution to the vacancy-formation energy. The advantage of the method is that it does not require a computer code that is able to rotate magnetic moments out of parallel alignment. Based on this approach, a linear-muffin-tin-orbital calculation in the atomic-sphere approximation yields a much larger effective exchange parameter than other approaches, and a likely reason for this discrepancy is discussed.

It is well known[1-5] that ferromagnetism in transition metals is based on the itinerant character of the electrons. The central quantity of the theory of metallic magnetism is therefore the Stoner exchange parameter I, which may be calculated in local spin-density approximation[6] (LSDA) or with a generalized Hubbard type of Hamiltonian.[1-4] Nevertheless, many (albeit of course not all) experimental results can be well explained at least qualitatively within the framework of the Heisenberg Hamiltonian. In this model the magnetic contribution to the total energy arises from pairwise interatomic exchange interactions (described by exchange parameters J_{ij}) between magnetic moments of fixed length at atomic sites i and j. The interaction energy depends on the cosine of the angle θ_{ij} between the considered moments.

To account for this observation the idea emerged[7-12] to try an approximate mapping of the itinerant system on a Heisenberg model by the following procedure. By additional constraints deviations from the ferromagnetic ground state are introduced, described by nonzero angles θ_{ij}, and the corresponding change ΔU of the total energy is calculated in LSDA or from the Hubbard Hamiltonian. If this energy change may be written for all configurations $\{\theta_{ij}\}$ as

$$\Delta U = \sum_{i,j} J_{ij}^{\text{eff}}(1-\cos\theta_{ij}) , \tag{1}$$

the quantities J_{ij}^{eff} may be conceived as effective exchange parameters for the mapping of the itinerant system on a Heisenberg Hamiltonian, being well aware of the fact that they do not have the meaning of interatomic exchange interactions in the original sense. Furthermore, for a reasonable mapping the size of the magnetic moments should be independent of $\{\theta_{ij}\}$.

The calculations reveal[3] that the pairwise decomposition of ΔU according to Eq. (1) is an adequate description at small angles θ_{ij}, for which the length of the moments depends only slightly on the magnetic configuration $\{\theta_{ij}\}$. Thereby the effective exchange parameters J_{ij}^{eff} are long ranged[3,7,8,11,12] (they have been determined for instance up to the sixth-neighbor shell[12]) and possibly oscillating in sign. Furthermore, the values of the individual J_{ij}^{eff} as obtained by different authors differ rather drastically, whereas the results for the quantity

$$J_0^{\text{eff}} = \sum_j J_{0j}^{\text{eff}} \tag{2}$$

agree rather well. This quantity may be conceived as an effective exchange parameter for the mapping on a nearest-neighbor Heisenberg model, and it may be related to the Curie temperature T_C. For larger angles, the size of the moments depends strongly[3,11,13] on $\{\theta_{ij}\}$, and there are possibly both deviations from the Heisenberg ($\cos\theta_{ij}$) form and multiatom effects,[3] i.e., the quantities J_{ij}^{eff} obtained by tentatively performing the pairwise decomposition of ΔU according to Eq. (1) depend on $\{\theta_{ij}\}$ and the mapping on the Heisenberg model breaks down. This is one reason why calculations of this type are restricted to small angles θ_{ij}, i.e., small changes of the effective interatomic exchange interactions. The other reason concerns the application of the LSDA which describes quite well only excitations of low energy close to the ground state $\{\theta_{ij}\}=0$.

In this Brief Report we outline an alternative method for the determination of the quantity J_0^{eff} without having to deal with nonlinear spin arrangements. Unlike the rival approaches discussed above, the method is only able to calculate the quantity J_0^{eff} rather than the individual J_{ij}^{eff}. It therefore cannot determine whether the energetics really maps onto a Heisenberg model, or the question of how long the range of the effective interactions is, etc. However, we think that the calculation of the global quantity J_0^{eff} is still useful because of two reasons. First, it may serve as a further check of the more complete analysis of the rival approaches. Second, it is rather common among people working in the field of classical

magnetism to describe at least the qualitative magnetic behavior of ferromagnetic metals within the framework of a nearest-neighbor Heisenberg model, and for this brute-force mapping the quantity J_0^{eff} is relevant. The basic quantity in this method is the magnetic contribution ΔE_V^F to the energy E_V^F of vacancy formation in a ferromagnetic system. Vacancy formation thereby requires in a first step the removal of a magnetic moment from a regular lattice site. Thereby q effective interatomic exchange interaction bonds with energy $2J_1^{\text{eff}}$, respectively, are broken within the framework of a nearest-neighbor Heisenberg model ($H=-\sum'_{ij} J_1^{\text{eff}} \mathbf{e}_i \cdot \mathbf{e}_j$, where $\mathbf{e}_i$ denotes the unit vector in the direction of the magnetic moment at site i; the summation over j runs over the q nearest-neighbor sites of site i). In a second step the atom is inserted at a typical surface site ("Halbkristall-Lage"), thereby regaining $q/2$ bonds. The whole process of vacancy formation therefore amounts to a change of the effective interatomic exchange energy of $\Delta E_V^F = qJ_1^{\text{eff}} = J_0^{\text{eff}}$, whereas the total number of magnetic moments is conserved. In contrast to the above discussed methods, we thus consider large changes of the effective interatomic exchange interactions. This does not constitute a problem as long as the values of the magnetic moments around a vacancy are close to the bulk values (Table I). Furthermore, whereas the rival methods consider constrained states close to the ground state, we deal from the very beginning with the ground state of the ferromagnetic system with vacancy.[14] Therefore, our method is not totally equivalent to a calculation which just rotates one single spin by 90° (which in a Heisenberg model would also "break" the exchange interactions to all other spins), because the so-obtained state would not correspond to the ground state.

As an example, we have calculated the vacancy formation energy E_V^F for bcc Fe by a supercell method according to Gillan,[15,16]

$$E_V^F = E(N-1,1,V') - \frac{N-1}{N} E(N,O,N\Omega_0) , \qquad (3)$$

where $E(N,n,V)$ denotes the total energy of a supercell with N atoms, n vacancies, and a volume V. The quantity $\Omega_0 = a^3/2$ is the volume of one atom in the perfect lattice (a=lattice constant), and for a we have used the theoretical value $a_f = 2.804$ Å for the lattice constant of the perfect ferromagnetic system as obtained by our calculations, or the experimental value $a_{f,\text{expt}} = 2.860$ Å. V' is the relaxed volume of the supercell with vacancy. To study the influence of relaxation, we have considered three different situations, $V' = N\Omega_0$ (no relaxation of supercell volume), $V' = V'_{\text{min}} = (N-1)\Omega_0$ (relaxation by one atomic volume), and $V' = V'_{\text{eq}}$, the theoretical equilibrium volume of the ferromagnetic supercell with vacancy (according to a lattice constant of $a'_{\text{eq}} = 2.794$ Å).

TABLE I. The magnetic moment m per Fe atom in successive neighbor shells of the distance d from the vacancy ($a = a_{f,\text{expt}}$, $V' = N\Omega_0$, $l_{\text{max}} = 2$). The corresponding value for the perfect lattice ($a_{f,\text{expt}}$) is 2.32 μ_B. The quantity a_{sc} denotes the lattice constant of the supercell.

d/a_{sc}	m (units of μ_B)
0.217	2.43
0.250	2.22
0.354	2.23
0.414	2.28
0.433	2.24
0.500	2.30

To obtain the magnetic contribution $\Delta E_V^F = E_V^F(\text{FM}) - E_V^F(\text{NM})$ we have determined E_V^F both for the ferromagnetic state [E_V^F(FM)] and for the artificial nonmagnetic state [E_V^F(NM)]. Because in a strict Heisenberg model the whole magnetic contribution to the energy is given by the interatomic exchange interaction whereas the structural properties (lattice constant a) do not depend on the magnetic state, we evaluate both quantities at the respective same values of Ω_0 and V'.

We have considered bcc Fe with superlattices up to 32 atoms. The calculations have been performed by the scalar-relativistic tight-binding linear-muffin-tin-orbital (LMTO) method in atomic-sphere approximation,[17,18] including combined correction terms. Both the LSDA (according to Barth and Hedin,[19] in the parametrization of Moruzzi *et al.*[20]) and the generalized-gradient approximation (GGA) according to Perdew and Wang[21] have been used. The basis set extended up to $l_{\text{max}} = 2$ or $l_{\text{max}} = 3$, and the results for the largest supercell were converged for 10 k points in the irreducible part of the first Brillouin zone.

Our results are listed in Table II. The calculated values for the vacancy formation energy E_V^F(FM) are on the average a factor of 2.5 larger than the experimental value[22] of $E_V^F(\text{FM}) = 1.73$ eV. Because we have tested for convergence with respect to the number of k points, the supercell size and l_{max}, and because we have performed the calculations both within LSDA and GGA, we guess that this big difference arises from the ASA. Indeed, it has been shown[23] for Cu by a Korringa-Kohn-Rostoker–

TABLE II. Results for the vacancy-formation energies and for J_0^{eff}, all in eV.

a	V'	l_{max}	LSDA GGA	E_V^F(FM)	E_V^F(NM)	$\Delta E_V^F = J_0^{\text{eff}}$
a_f	$N\Omega_0$	2	LSDA	4.21	3.45	0.76
$a_{f,\text{expt}}$	$N\Omega_0$	2	LSDA	4.39	3.64	0.75
$a_{f,\text{expt}}$	$N\Omega_0$	3	LSDA	4.70	3.91	0.79
$a_{f,\text{expt}}$	$N\Omega_0$	3	GGA	4.04	3.20	0.84
a_f	$(N-1)\Omega_0$	2	LSDA	4.29		
a_f	V'_{eq}	2	LSDA	4.19		

(KKR–)Green's-function method that the vacancy formation energy decreases by a factor of 2 and attains values close to the experimental one when releasing the atomic-sphere approximation. Similarly, an LMTO-ASA calculation of the vacancy formation energy in Li gives[24] a value which is a factor of about 2 larger than the one obtained by an *ab initio* pseudopotential calculation (which does not use a spherical approximation and which gives a value close to the experimental one). Finally, for Fe a KKR-ASA calculation yields[25] $E_V^F(\mathrm{FM})=4.8$ eV (for LSDA, $l_{\max}=3$, $a_f=2.788$ Å), which compares well to our corresponding value of 4.7 eV, whereas a full-potential KKR calculation[25] gives a value which is a factor of about 2 smaller. Obviously, all these calculations suggest that the vacancy-formation energy is strongly overestimated by the atomic-sphere approximation. Probably due to this fact, our values of 0.75 eV $\leq J_0^{\mathrm{eff}} \leq 0.84$ eV are much larger than those of Refs. 3, 11, and 12, which are in the range 0.1557 eV $\leq J_0^{\mathrm{eff}} \leq 0.204$ eV, and much larger than the effective exchange parameter of a nearest-neighbor Heisenberg model obtained experimentally by various methods[26] ($J_0^{\mathrm{eff}} \leq 0.170$ eV). Our guess is that a much better agreement is obtained if the nonspherical charge distribution is taken into account accurately. The question of whether both the magnetic and the nonmagnetic calculation will be corrected with sufficient accuracy that a good value of J_0^{eff} will be forthcoming in this way can be solved only by explicit calculations in this direction, which we hope to stimulate by this Brief Report.

To conclude, we have developed an alternative method which allows us to calculate the effective exchange interaction parameter J_0^{eff} without performing spin cantings. We believe that it is crucial to treat the nonspherical charge distributions accurately. By successively creating vacancies on crystallographically nonequivalent lattice sites, the method is also able to determine effective exchange interaction parameters for compounds.

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